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

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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.[4] 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 polyamides. On one hand, polyesteramides tend to strengthen the materials thanks to the polarity of amide groups and their ability to strong hydrogen bonding.
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.\[10\] 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 esteramide exchange reactions between preformed polyester and polyamide chains.\[10–12\] Interestingly, polyesteramides based on poly(\(\varepsilon\)-caprolactone) (PCLo) and PCLa have demonstrated their inherent ability to be readily tuned up 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 \(\text{H}_3\text{PO}_2\) 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-PCLA-co-CLo)-OH, composed of a polyester 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 \(^{13}\text{C}\) 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 \(\alpha\)-aminated polyester as a macrorinitiator. By contrast to the previously investigated PEO-OH macrorinitiator, this \(\alpha\)-aminated polyester 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 polyesters as macrorinitiators in ROP of CLa/CLo,\[14\] the use of \(\alpha\)-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 macrorinitiator 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 macrorinitiator 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 another extremity.

\[\text{Scheme 1. Aminolytic polymerization of CLa (1) and CLo (2).}\]
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).

Investigation of CLa Polymerization as Initiated by P(EO-co-PO)-NH₂

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)-NH₂, i.e., Jeffamine M1000. The $M$ symbol stands for Monoamine 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 polyamides as obtained by aminolytic polymerization of CLa initiated by Jeffamine M1000 ([CLa]/[P(EO-co-PO)-NH₂]₀ = 5) at 250 °C in the presence of 0.25 mol-% of H₃PO₂ (50 wt.-% in water) for different polymerization times.

Figure 1. $^1$H NMR spectrum of crude polyamide as obtained by aminolytic polymerization of CLa initiated by Jeffamine M1000 in the presence of 0.25 mol-% of H₃PO₂ at 250 °C for 7 h (entry 4, Table 2, solvent: TFA-d$_2$: 500.13 MHz).

**Table 1.** Molecular characteristics of P(EO-co-PO)-NH₂ Jeffamine M1000.

<table>
<thead>
<tr>
<th>Jeffamine</th>
<th>$M_{n, \text{NMR}}$ ³</th>
<th>$M_{n, \text{tet}}$ ³</th>
<th>PO/EO ³</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1000</td>
<td>1 400</td>
<td>1 200</td>
<td>1/16</td>
</tr>
</tbody>
</table>

³As determined by proton NMR; b) As determined by titration of the amine functions by an aqueous solution of oxalic acid.

Table 2. Monomer conversion and degree of polymerization of polyamides as obtained by aminolytic polymerization of CLa initiated by Jeffamine M1000 ([CLa]/[P(EO-co-PO)-NH₂]₀ = 5) at 250 °C in the presence of 0.25 mol-% of H₃PO₂ (50 wt.-% in water) for different polymerization times.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Time (h)</th>
<th>Conv$_{\text{CLA}}$ ³</th>
<th>$\overline{DP}_\text{exp}$ ³</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>29</td>
<td>2</td>
</tr>
<tr>
<td>2</td>
<td>3</td>
<td>53</td>
<td>3</td>
</tr>
<tr>
<td>3</td>
<td>5</td>
<td>65</td>
<td>3</td>
</tr>
<tr>
<td>4</td>
<td>7</td>
<td>68</td>
<td>3</td>
</tr>
<tr>
<td>5</td>
<td>9</td>
<td>69</td>
<td>3.5</td>
</tr>
</tbody>
</table>

³As determined by $^1$H NMR: Conv$_{\text{CLA}}$ = $I_{\text{PA2}}/(I_{\text{CLA2}} + I_{\text{PA2}}) \times 100$, $\overline{DP}_\text{exp} = I_{\text{PA2}}/I_{\text{AA3}}$ (see Figure 1).

The $\delta$ values range from 0.5 ppm to 9 ppm with an increment of 0.4 ppm.
Accordingly, the experimental degree of polymerization ($DP_{exp}$) 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$_3$PO$_2$ in bulk at 250 °C for 7 h. Again, an initial molar ratio [CLo]$_0$/[P(EO-co-PO)-NH$_2$]$_0$ of 5 was used (Table 3). For comparison, the results of the CLa polymerization obtained under identical conditions are also presented.

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

<table>
<thead>
<tr>
<th>Entry</th>
<th>Monomer</th>
<th>Conv</th>
<th>$DP_{exp}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CLo</td>
<td>&gt;99$^a$</td>
<td>5$^c$</td>
</tr>
<tr>
<td>2</td>
<td>CLa</td>
<td>68$^b$</td>
<td>3$^d$</td>
</tr>
</tbody>
</table>

$^a$As determined by $^1$H NMR: no residual signals for CLo; $^b$As determined by $^1$H NMR: $\text{Conv}_{CLa} = \frac{\text{I}_{PA2}}{\text{I}_{PA2} + \text{I}_{PA3}} \times 100$; $^c$As determined by $^1$H NMR: $DP_{exp} \text{CLo} = \frac{\text{I}_{PE3}}{\text{I}_{PE4}}$ (see Figure 2); $^d$As determined by $^1$H NMR: $DP_{exp} \text{CLa} = \frac{\text{I}_{PA2}}{\text{I}_{PA3}}$ (see Figure 1).

**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$_3$PO$_2$ at 250 °C for 7 h (entry 1, Table 3, solvent: TFA-; 500.13 MHz).
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 (\(DP_{\text{exp}}\)), 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)-NH₂**

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 \(\text{H}_2\text{PO}_2\) (50% in water), \(\text{p}-\text{toluenesulfonic acid (PTSA)}\), \(\text{tin(II) octanoate [Sn(Oct)₂]}\), \(\text{di-n-butyltin(IV) dilaurate (Bu}_2\text{SnLaurate)}\), and antimony(III) oxide (\(\text{Sb}_2\text{O}_3\)). 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 \([\text{CLa}]_0/\text{[CLo]}_0 = 1\) and \([\text{CLa} + \text{CLo}]_0/[\text{P(EO-co-PO)-NH₂}]_0 = 10\) (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 \(\text{P(EO-co-PO)-b-[P(\text{CLa-co-CLo})]}\) block copolymers end-capped by a hydroxyl function. As shown by the representative \(\text{^1H NMR} \) spectrum in Figure 3, the \(-\text{CH}_2-\text{OH} \) (PE4) end-group resonance at 4.05 ppm could be detected, the \(-\text{CH}_2-\text{NH}_2-\text{CH}-(\text{CH}_3)_2-\text{NH}_2\) protons, initially displayed from the polyether macroinitiator, being not observed anymore. Moreover, the ratio between the relative intensity ratio of the \(-\text{CH}_2-C(O)-O-\) (PE2) signal at 2.1 ppm and the \(-\text{CH}_2-O-C(O)-\) (PE3) one at 3.8 ppm is equal to unity.

In agreement with NMR analyses previously discussed in homopolymerizations of CLa and CLo as initiated by \(\text{P(EO-co-PO)-NH₂}\), CLo conversion appeared quantitative after 7 h at 250 °C, while CLa conversion is again lower as determined from the relative intensities of the \(-\text{CH}_2-C(O)-\) resonance (PA2) at 2.3 ppm and the residual CLa cyclic monomer resonance (CLA2), at 2.45 ppm. Among the catalysts investigated, \(\text{H}_2\text{PO}_2\) in aqueous solution proved the best 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. Based on such a mechanism, the slower rate of CLa conversion recorded in the CLo/CLa copolymerization reaction with respect to CLa homopolymerization (ConvCLa = 65% after 7 h), as initiated by \(\text{P(EO-co-PO)-NH₂}\), can be accounted for. Importantly, the involvement of transamidation and/or transesterification reactions cannot be excluded, especially when organometallic \(\text{n-Bu}_2\text{Sn(Laurate)}\), \(\text{Sn(Oct)}_2\), and \(\text{Sb}_2\text{O}_3\) catalysts are used. Accordingly, it has been chosen to focus only on \(\text{H}_2\text{PO}_2\) 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 \(\text{^13C NMR} \) 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. In the case of the polyesteramide based on CLa and CLo units, the carbon atom of the methylene group in \(\alpha\) position to the amide and ester functions, i.e., \(-\text{CH}_2-C(O)-\text{NH}-\) and \(-\text{CH}_2-C(O)-\text{O}-\), respectively, is monitored in terms of \(\text{^13C} \) dyads (AA, AB, BA, and BB where A and B represent the two co-monomer units), meaning that the \(\text{^13C} \) chemical shift is mainly determined by whether the adjacent repetitive unit originates from a CLa unit (AA and AB dyads) or a CLo one (BB and BA dyads; Figure 4), the small chemical shift difference within 1 ppm for each group of the

### Table 4. Monomer conversion and degree of polymerization in copolymerization of CLa and CLo as initiated by Jeffamine M1000 ([CLa]/[CLo] = 1, [CLa + CLo]/[P(EO-co-PO)-NH₂] = 10) at 250 °C for 7 h in the presence of 0.25 mol-% of the selected catalyst.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Conv**</th>
<th>(DP_{\text{exp}}^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>CLa</td>
</tr>
<tr>
<td>1</td>
<td>(\text{H}_2\text{PO}_2)</td>
<td>55</td>
<td>&gt;99</td>
</tr>
<tr>
<td>2</td>
<td>Sn(Oct)₂</td>
<td>30</td>
<td>&gt;99</td>
</tr>
<tr>
<td>3</td>
<td>(n-Bu_2\text{Sn(Laurate)})</td>
<td>41</td>
<td>&gt;99</td>
</tr>
<tr>
<td>4</td>
<td>(Sb_2\text{O}_3)</td>
<td>32</td>
<td>&gt;99</td>
</tr>
</tbody>
</table>

**As determined by \(\text{^1H NMR} \): ConvCLa = I_{PA2}/(I_{CLa2} + I_{PA2}) \times 100, ConvCLo quantitative, \(DP_{\text{exp}}^a\) determined based on \(I_{SS}:\) \(DP_{\text{exp}}^a = [(90I/I_{PA2})]_{\text{exp}}/2\), ConvCLa = [(90I/I_{PA2})]_{\text{exp}}/2\) see Figure 3.**
dyad resonance pairs being determined by whether the co-monomer raises from CLo (A) or CLa (B). The $^{13}$C NMR data of the isolated polyesteramide-based block copolymer were acquired from mixed CDCl$_3$/(CF$_3$CO)$_2$O/CF$_3$COOD (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 $\alpha$ position of amide and ester functions, the average length of PCLo ($L_{PCLo}$) and PCLa ($L_{PCLa}$) blocks were determined using Equations (1) and (2).

$$L_{PCLo} = \frac{I_{AA}}{I_{AB}} + 1$$  

$$L_{PCLa} = \frac{I_{BB}}{I_{BA}} + 1$$

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

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$_3$PO$_4$ (entry 1, Table 4, solvent: TFA-$d_7$, 500.13 MHz).
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\(_3\)PO\(_2\) 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 mechanism...
The polyester block. Moreover, the formation of an amide bond between the initiator and 2.30 ppm) protons. The presence of the latter is the result of copolymerization under identical conditions shows the spectrum of the crude product obtained after the CLa initiated by Jeffamine M1000 was performed for 24 h in the 250 mL glass reactor for different [CLa]/[CLo] and [CLa + CLo]/[P(EO-co-PO)-NH2]0 molar ratios. The 1H NMR spectrum reveals high conversions in both co-monomers after reaction completion under these conditions (Figure 5). Signal from –CH2 –OH (PE4: 4.05 ppm) end-groups are readily observed but signal from –CH2 –NH2 (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 13C 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 Tg, Tm, and E’ values, respectively (see Table 5, entries 3–5). Interestingly, the investigated copolymers display intermediate thermal transitions with respect to the corresponding PClas and PCLc homopolymers. Both Tg and Tm 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(Cl-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 azotropic distillations of toluene were performed and CLa was stored under N2. CLo (99%, Acros) was dried over calcium hydride at room temperature for 48 h and distilled under reduced pressure and stored under N2. Jeffamine M1000 (Jeff-NH2, Mntrix = 1,200 g·mol−1) from Hunst-
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 (H₃PO₂, 50 wt.-% in water, Aldrich), tin octanoate [Sn(Oct)₂, 95%, Sigma–Aldrich], di-n-butyl dilaurate tin (n-Bu₂SnLaurate₂, Aldrich), and antimony (III) oxide (Sb₂O₃, 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-NH₂]₀ = 5) and H₃PO₂ (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–N₂ 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 ¹H 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]/[P(EO-co-PO)-NH₂]₀ = 5), and H₃PO₂ (0.25 mol-% with respect to the ester functions) were added. After three vacuum–N₂ 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 ¹H NMR using TFA-d.

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*Figure 5. ¹H 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 H₃PO₂ at 250°C (entry 2, Table 7, solvent: TFA-d; 500.13 MHz).*
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]/[P(EO-co-PO)-NH₂]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–N₂ 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 ¹H 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 N₂ 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-skinned balloon preliminarily filled with N₂ was placed at the extremity of the condenser instead of using a continuous N₂ 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. 0.5% of H₃PO₂ (relative to the amide functions) was added and the reactor is kept under N₂ 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 ¹H 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. 0.5% of H₃PO₂ (relative to the ester functions) was added and the reactor is kept under N₂ 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 ¹H NMR using deuterated TFA-d.

Simultaneous Copolymerization of CLa and CLo Initiated by Jeffamine M1000 in Reactor for Different [CLA + CLo]/[P(EO-co-PO)-NH₂]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 and CLo copolymerization. In the first steps of the reaction and subsequently, the polymerization of CLa allows synthesizing original P(EO-co-PO)-NH₂, a block copolymer P(EO-co-PO)-b-PCLo-OH is quickly formed in the last step of the reaction.

Conclusion

The use of an α-aminated macroinitiator, P[EO-co-PO]-NH₂ like Jeffamine M1000, in ROP of CLa or CLo as catalyzed by H₃PO₂ 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-co-PO]-NH₂, 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 ¹³C NMR. This synthetic approach, promoted by a catalyst as simple as H₃PO₂ 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-
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.

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