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Novel polyesteramide-based di- and triblock copolymers: From thermo-mechanical properties to hydrolytic degradation

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ABSTRACT

Two types of biodegradable poly(ε-caprolactone (CLo))-*co*-poly(ε-caprolactam (CLa)) copolymers were prepared by catalyzed hydrolytic ring-opening polymerization. For the first type of materials, the respective cyclic comonomers were added simultaneously in the reaction medium leading to the formation of copolymers having a random distribution of co-units within the polyesteramide sequence, as evidenced by ^{1}H and ^{13}C NMR. For the second type of copolymers, the cyclic comonomers were added sequentially in the reaction medium yielding diblock polyesteramides, again evidenced by NMR. The thermal and thermo-mechanical properties of the copolymers were investigated by DSC and DMA and correlated with the copolymer topology and composition. The copolymers were characterized by a storage modulus and α transition temperature intermediate to the modulus and T_g of the corresponding homopolymers. The chemical composition and molecular weight of the copolymers proved to have only a limited effect on the thermo-mechanical properties of the materials. The hydrolytic degradation of random copolymers was studied in a phosphate buffer at 60 °C and discussed in terms of chemical composition and molecular weight of the copolymers.

1. Introduction

In recent years, extensive research has been devoted to the synthesis of biodegradable polymers for biomedical, pharmaceutical, agricultural and environmental applications [1]. Aliphatic polyesters are the most widely reported biodegradable polymers [1]. However, low thermal, mechanical, and processing performances severely restrict the practical use of these materials. Improvement in the mechanical properties can be achieved by introducing some chemical moieties differing from ester functions, such as amide bonds, in the main chain.

Aliphatic polyesteramides (PEA) represent a new type of degradable materials, known for years but having found recently renewed interest and developments [2]. Due to the polar nature of the amide groups in the polyamide segments, these polyamides segments may form intra- as well as inter-molecular hydrogen bonds strengthening the resulting materials. On the other hand, the hydrolytically degradable ester bonds in the main chain impart good degradability to the copolymers and reduce the extent of crystallinity of the resulting polyesteramides. These copolyesteramides are further known for their remarkable thermal and thermo-mechanical properties even at relatively low molecular weight.

Poly(ε-caprolactone-*co*-ε-caprolactam) copolymers (PCLo-*co*-PCLa) can be considered as representing one of the most promising class of biodegradable polymeric materials.

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These PCLo-*co*-PCLa copolymers have been synthesized through anionic polymerization, interfacial polymerization, polycondensation, ring-opening polymerization (ROP) and by chain transfer reaction in the melt [3–13].

Goodman and Vachon [12,13] obtained random copolymers (PCLo-*ran*-PCLa) by anionic copolymerization of a mixture of ε-caprolactone (CLo) and ε-caprolactam (CLa). As expected for random copolymers, both the glass transition temperature (T_g) and the melting point (T_m) were function of the relative copolymer composition. The dependence of T_m and T_g on the composition of PCLo-*ran*-PCLa random copolymers obtained by anionic ring-opening copolymerization was also observed by Chromcová et al. [6,7]. Gonsalves et al. [4] prepared PCLo-*co*-PCLa copolymers using similar anionic ROP and investigated their random microstructure by ^{1}H NMR. Again, they highlighted the dependence of T_m values on the polyesteramide composition. Furthermore, they investigated the enzymatic (employing *fusarium moniliforme*) and hydrolytic degradation of the PCLo-*ran*-PCLa copolymers and concluded that a faster degradation was obtained by enzymatic means [4]. Later, the same authors performed a detailed study of the degradation products and as expected, the results showed that the degradation process occurs by attack of the ester groups spread all along the copolymer backbone [14].

In a previous research, several block copolymers based on an ω-amino-terminated polyether, Jeffamine® M1000 (JeffM1, Fig. 1), covalently bound to a polyesteramide sequence were synthesized in bulk (in the absence of solvent) at 250 °C, in the presence of aqueous H_3PO_2 [5]. Two sets of experiments were performed. A detailed study revealed that when the simultaneous copolymerization of CLa and CLo was performed in the presence of JeffM1 as macro-initiator (P(EO-*co*-PO)-NH_2, with M_n = 1200 g/mol and PO/EO molar ratio = 1/16), a block copolymer P(EO-*co*-PO)-*b*-PCLo-OH is quickly formed in the first step of the reaction and subsequently, the polymerization of CLa followed a hydrolytic reaction mechanism, with the major involvement of hydrolytic cleavage of the lactam ring with condensation/amination reactions between the resulting amine and the ester functions of the PCLo growing block [5]. Since the condensation/amination reactions occurred statistically, random polyesteramide sequences were formed and covalently bound to the JeffM1 macro-initiator as confirmed by ^{13}C NMR.

When the cyclic comonomers were added sequentially in the reaction medium, block copolymers are obtained. More precisely, the CLa was first polymerized in the presence of the same ω-aminated polyether macro-initiator, leading to the formation of a diblock copolymer P(EO-*co*-PO)-b-PCLa-NH_2. Subsequently, the aminolytic ring-opening polymerization of CLo was initiated by the terminal amine function of the previously synthesized polyamide block (P(EO-*co*-PO)-*b*-PCLa-*b*-PCLo-OH). The NMR results evidenced the formation of new types of block copolymers.

On the basis of previously reported data exploring ω-amino-terminated polyether as macro-initiator in ROP of CLa/CLo, the use of a α,ω-diamino polyether macro-initiator was investigated, Jeffamine® ED2003 (JeffED, with M_n = 2400 g/mol and PO/EO molar ratio = 1/11, Fig. 1). In comparison with the mono-aminated polyether used in our previous research, Jeffamine® ED2003, a difunctionalized macro-initiator, is able to initiate the ROP of CLa and CLo on both ends, leading to higher molecular weight copolymers characterized by a triblock macromolecular structure. By varying the initial composition of the reaction

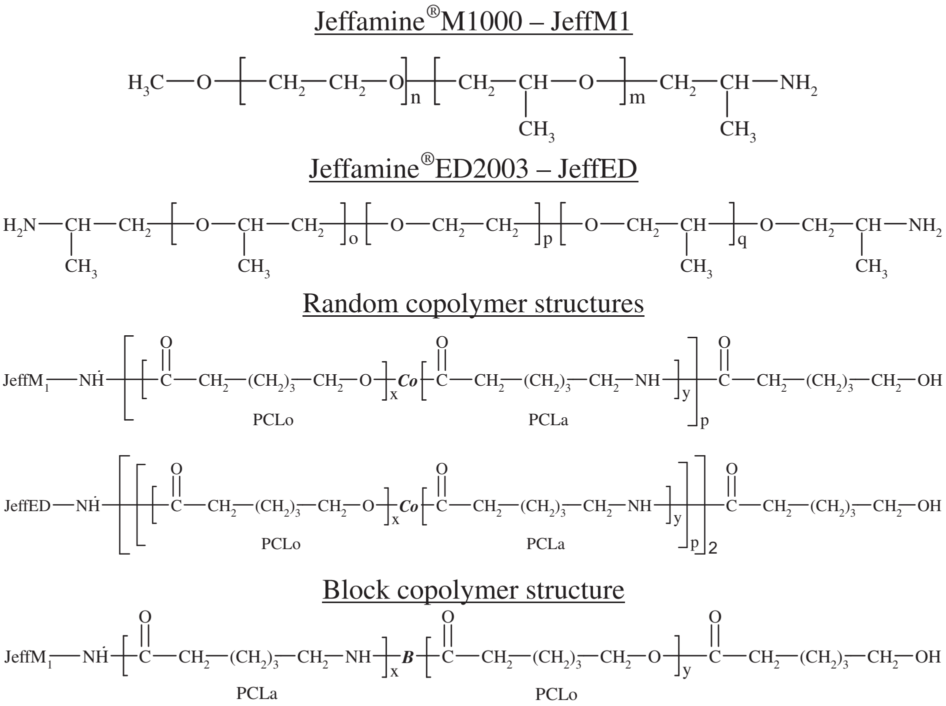

Fig. 1. Molecular structures of the macro-initiators employed and the formed random and (di- and tri-)block copolymers.

medium ($[CLa]_0/[CLo]_0$), the comonomer distribution in the polyesteramide sequence and the resulting material properties can be tuned.

Depending on the type and quantity of ester and amide units but also on the comonomer distribution along the chain, the polyesteramides are likely to present intermediate thermal and mechanical properties with respect to the corresponding homopolymers [15]. Interestingly, the enzymatic degradation of these diblock and triblock copolymers have been recently studied in composted soil and showed a synergistic behavior where much faster degradation was obtained for random copolymers with CLo content larger than 30% than for neat homo-PCLo [16].

The purpose of the present study is to investigate by DSC and DMA the thermo-mechanical properties of these polyesteramide-based di- and triblock copolymers. Particular attention is paid to the loss modulus (G') of the materials. Large variations in the loss modulus can be indicative of phase changes occurring at the glass transition temperature (T_g) or the melting temperature (T_m) of the copolymers. We also studied the hydrolytic degradation behavior of some of the polyesteramides, i.e. the random copolymers, in a phosphate buffer at 60 °C, since they recently proved faster enzymatic degradation in composted soil than the homo-PCLo (*vide supra*). Such a study should enable one to get a better insight into such findings and into the discrimination between enzymatic and hydrolytic degradation occurring in polyesteramide chain cleavage. Indeed, PCLo is known for undergoing readily enzymatic degradation while displaying rather good resistance to hydrolysis as a result of its pronounced hydrophobic character. If faster degradation of semi-crystalline polyesteramides occurs in compost, it can be assumed that it is due to faster hydrolytic cleavage within the esteramide 'hetero-link' spread along the chain.

2. Experimental

2.1. Materials

ε-Caprolactam (CLa, 99%, Acros), ε-caprolactone (CLo, 99%, Acros), Jeffamine® M1000 (JeffM1, $M_{n\ titr}$ = 1200 g/mol, EO/PO molar ratio = 1/16 from Hunstman), Jeffamine® ED2003 (JeffED, $M_{n\ titr}$ = 2400 g/mol, EO/PO molar ratio = 1/11 from Hunstman) and hypophosphorous acid (H_3PO_2, 50 wt% in water, Aldrich), as well as commercial Polyamide 6 (PA6, Rhodia, M_n = 18,500 g/mol) and the Poly(ε-caprolactone) (PCLo, CAPA 6500, Solvay Interox UK, M_n = 50,000 g/mol) were used as received.

2.2. Synthesis of polyesteramide-based copolymers

The copolymerization reactions were carried out in a 250 ml glass reactor 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 through 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.

2.3. Simultaneous copolymerization of CLa and CLo initiated by Jeffamine® for different $[CLa + CLo]_0/[Jeff]_0$ and $[CLa]_0/[CLo]_0$ molar ratios

The following example aims at illustrating the conditions for the simultaneous copolymerization of CLa and CLo initiated by Jeffamine® ED2003 within the following conditions: $[CLa + CLo]_0/[JeffED]_0 = 600$ and $[CLa]_0/[CLo]_0 = 2$.

CLa (115.6 g, 1 mol), CLo (58.3 g, 0.5 mol) and Jeffamine® ED2003 (6.1 g, 3 mmol) were introduced successively into the reactor. The reactor was placed in a heating mantle preliminarily heated to 100 °C. 0.50 mol% of H_3PO_2 (relative to the amide functions) was added in the reactor kept under N_2 with 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 ^1H NMR using TFA-*d*.

2.4. Sequential copolymerization of CLa and CLo initiated by Jeffamine® M1000 for different $[CLa + CLo]_0/[JeffM1]_0$ and $[CLa]_0/[CLo]_0$ molar ratios

The following example aims at illustrating the conditions for the sequential copolymerization of CLa and CLo initiated by Jeffamine® M1000 within the following conditions: $[CLa]_0/[JeffM1]_0 = 200$ and $[CLo]_0/[JeffM1]_0 = 25$.

CLa (170.8 g, 1.5 mol) and Jeffamine® M1000 (7.7 g, 8 mmol) were introduced successively into the reactor. The reactor was placed in a heating mantle preliminarily heated to 100 °C. 0.50 mol% of H_3PO_2 (relative to the amide functions) was added in the reactor kept under N_2 with a balloon. The temperature was raised to 250 °C. After 24 h, a sample aliquot was collected and characterized by ^1H NMR using TFA-*d.* The heating and stirring are stopped and the reaction mixture is maintained under inert atmosphere overnight. The CLo (21.5 g, 0.19 mol) is then added to the medium heated up at 250 °C and the polymerization takes place during 4 h. The product was transferred into a rectangular aluminum mold. The crude product was analyzed by ^1H NMR using TFA-*d*.

2.5. Hydrolytic degradation tests

Samples (3 cm × 1 cm × 0.5 mm) were submerged in a phosphate buffer (NaH_2PO_4/Na_2HPO_4, 0.1 M, pH 7.4) at 60 °C for a time ranging from 15 to 90 days. At predetermined times, the samples are taken out of the buffer, dried under reduced pressure at 40 °C overnight, weighed and characterized by ^1H NMR and DSC.

2.5.1. NMR spectroscopy

The ^1H and ^{13}C NMR spectra were recorded on a Bruker AMX500 instrument operating respectively at 500.13 MHz using hexamethyldisiloxane as internal reference. For ^1H 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).

2.5.2. GPC-MALLS-RI

Samples were eluted through 2 Phenomenex 60 cm linear columns (5 μm) at 1 ml/min in DMAC containing 2w% LiCl. The injected volume is 100 μl. The GPC-MALLS coupling (Rayleigh, multiangles) enables the determination of the absolute molecular mass distribution and of the polymer concentration at each elution volume. The calculation is done by taking into account the amount of polymer injected and the (dn/dc) term which represents the difference of the refractive index between the polymer and the solvent by concentration unit (slope of $n-n_0$ versus concentration). The (dn/dc) term is determined by refractometry or obtained from literature.

2.5.3. Differential scanning calorimetry (DSC)

Differential scanning calorimetry (DSC) measurements were performed on a TA Instrument Q200 apparatus under N_2 atmosphere at a heating rate of 10 K/min from −120 to 280 °C. The first scan was recorded.

2.5.4. Dynamic mechanical analysis (DMA)

Dynamic mechanical analysis (DMA) was carried out with a TA Instrument 2980 apparatus operating in the dual cantilever mode. A frequency of 1 Hz, amplitude of 20 μm and heating rate of 2 °C/min from −100 to 150 °C were used. The elastic modulus values gathered in Table 5 were recorded at 25 °C.

3. Results and discussion

The copolymers studied in this work were obtained by ring-opening copolymerization of CLa and CLo according to an efficient hydrolytic reaction mechanism initiated from the amine function of a commercially available ω-aminated polyether (Jeffamine® M1000, P(EO-*co*-PO)-NH_2, with M_n = 1200 g/mol and PO/EO molar ratio = 1/16) [5,17]. Two kinds of copolymers were produced. On one hand, (P(EO-*co*-PO)-*b*-(PCLa-*ran*-PCLo)-OH) copolymers were synthesized with the random polyesteramide sequence resulting from the simultaneous copolymerization of CLa and CLo (see Introduction). On the other hand, (P(EO-*co*-PO)-*b*-PCLa-*b*-PCLo-OH), triblock copolymers were formed by sequential polymerization of CLa and CLo. Interestingly, the use of a short macro-initiator such as Jeffamine® M1000 proved very efficient for determining the overall copolymer composition and molecular weight [5,8]. Therefore, we will refer to the copolymers obtained by the first method as random copolyesteramides: PCLo-*ran*-PCLa, and to those obtained by the second method as block copolyesteramides: PCLa-*b*-PCLo for the sake of clearly differentiating them (Fig. 1).

3.1. Random copolyesteramides: thermo-mechanical properties

Dynamic mechanical analyses (DMA) (Table 1) are useful to determine precisely the thermal transitions and the mechanical properties of a material. The heating rate used was set to 2 °C/min, the amplitude was 20 μm and the frequency 1 Hz. It is worth mentioning that the range of temperature used in DMA depends on the sample melting temperature. In other terms, DSC analyses were performed on each copolymer prior to DMA in order to determine their respective melting temperature.

Table 1 shows the molecular and thermal characteristics of the copolymers analyzed by DMA (Table 1), copolymers obtained by simultaneous copolymerization of CLa and CLo.

Table 1 reveals that at similar composition, the melting temperature (T_m) of the copolymers is more or less independent of the molecular weight and the macro-initiator used.

Commercially available polyamide 6 (PA6, Rhodia, M_n GPC = 18,500 g/mol) and poly(ε-caprolactone) (PCLo, CAPA 6500, Solvay, M_n = 50,000 g/mol) were characterized by

Table 1
Molecular and thermal characteristics of the copolymers obtained by simultaneous copolymerization of CLa and CLo characterized by DMA (a sketch of their structure is presented for clarity: Jeffamineis shown as a black line while CLo and CLa units are represented in open dots and dark dots, respectively).

Code	Initiator	Structure	DP_{CLa}/DP_{CLo} [a]	M_n (g/mol)	T_m (°C) [b]	L_{PCLa} [c]	L_{PCLo} [c]
PEA-1	JeffM1		44/25	7800	151	3.4	1.6
PEA-2	JeffM1		150/10	18,000	213	–	–
PEA-3	JeffM1		170/50	25,000	183	3.3	1.2
PEA-4	JeffM1		180/100	32,000	152	2.6	1.6
PEA-5	JeffED		230/20	28,000	211	–	–
PEA-6	JeffED		350/200	62,000	157	2.7	1.5

[a] Mean degree of polymerization of CLa and CLo sequences as determined by ^{1}H NMR.

[b] Melting temperature as determined by DSC: first heating run, 10 °C/min, from −120 to 280 °C.

[c] Average length of PCLo (L_{PCLo}) and PCLa (L_{PCLa}) sequencesas determined by ^{13}C NMR.

DMA under identical conditions and were chosen as references in this study (Table 2).

The graphs of the storage modulus (G') and tan δ (G''/G') versus the temperature of polyamide 6 (PA6) and poly(ε-caprolactone) (PCLo), as obtained by DMA, and used below as references, are presented in Figs. 1-SI and 2-SI.

At low temperature, e.g., −100 °C, the storage moduli (G') of both polymers are equivalent. However, G'_{PCLo} drops at −60 °C to reach 360 MPa at 25 °C, G'_{PA6} being equal to 1900 MPa at the same temperature.

Fig. 2-SI shows that tan δ versus temperature of PA6 displays two maxima. The first maximum corresponds to the α transition, generally associated to the glass transition temperature (T_g), and is centered at *ca.* 70 °C for the PA6 and at *ca.* −40 °C for the PCLo. The second one, of lower intensity, is assigned to the β transition, well known for polyamides, corresponding to an increase in mobility between amide bonds [15]. This maximum is centered at ca. −55 °C for PA6 while it is not present in the case of PCLo.

Table 3 shows the thermal and thermo-mechanical properties of PEA-1, polyesteramide obtained by simultaneous copolymerization of CLa and CLo (see Table 1 for molecular characteristics). It is obvious that PEA-1, characterized by a molecular weight lower than 10,000 g/mol, has poor thermo-mechanical properties. Both the storage modulus at 25 °C and the T_g are lower than for neat PCLo. Such a behavior is more likely explained by a length of polyesteramide chains lower than the critical molecular weight of entanglement.

Figs. 2 and 3 represent the storage modulus (Fig. 2) and tan δ (Fig. 3) versus temperature for PEA-1 compared to PA6 and PCLo. Note that a β transition is noticeable in the PEA-1 curve, which is characteristic for an increase of the amide bond mobility.

Table 2
Thermal and thermo-mechanical characteristics of commercially available polyamide 6 (PA6) and poly(ε-caprolactone) (PCLo).

Entry	DP_{CLa}/DP_{CLo}	T_g (°C)[a]	T_m (°C)[b]	Storage modulus (G') at 25 °C (MPa)[a]
PCLo	–/438	−40	60	366
PA6	163/–	70	225	1900

[a] Transition temperature as determined by DMA: dual cantilever, 2 °C/min, from −100 to 150 °C, 1 Hz, 20 μm.

[b] Melting temperature as determined by DSC: first heating run, 10 °C/min, from −120 to 250 °C.

When the polyesteramide molar masses are increased and range from 18,000 to 32,000 g/mol, the copolymers are characterized by significantly higher thermo-mechanical properties. Indeed, higher G' values are recorded lying in between those of neat PA6 and neat PCLo (Table 4).

As far as the melting temperatures (T_m) are concerned, DSC thermograms show that the higher the polyesteramide sequence is rich in ester functions, the lower the T_m value becomes. This behavior has already been demonstrated by Frunze et al. and Goodman et al.; in the case of polyesteramides based on PCLo and PCLa, they showed that a decrease in the melting temperature is observed when the amount of ester units increases in the polyesteramide sequence [18,10].

Fig. 4 shows the storage modulus versus temperature for PEA-2 to PEA-4, which were obtained by simultaneous polymerization of CLa and CLo initiated by Jeffamine® M1000 and are characterized by different $[CLa]_0/[CLo]_0$ ratios.

Fig. 4 shows that, at low temperatures (below −20 °C), G' of PEA-2 to PEA-4 is higher than G' of both PA6 and PCLo. It is worth mentioning that, up to now, we cannot provide any explanation regarding that phenomenon. Fig. 4 also shows that the increase in G' is more pronounced for copolymers with lower DP in CLo units. At room temperature, the G' value of the polyesteramides is in between the values of PA6 and PCLo references. Concerning the copolymer containing the highest studied ester content (PEA-4, Table 4), its G' value recorded at room temperature is in the same order than G' of neat PCLo (399 MPa). The evolution of tan δ versus temperature for PEA-2 to PEA-4 is shown in Fig. 5.

Whatever the investigated composition, the β transition remains visible. The transition is shifting towards lower temperatures when the amount of ester units is increased, while its intensity decreases. Therefore, we can assume that the ester links being present along the polyesteramide sequences disturb the regularity of the PA6 chains and allow the occurrence of amide bond motions at lower temperature. The α transition (~T_g) appears between those of PA6 and PCLo and shifts to higher temperatures upon increase of the content of amide units and the molecular weight of the copolymers.

Interestingly, initiating the simultaneous copolymerization of CLa and CLo by Jeffamine® ED2003, an α,ω-diamino polyether macro-initiator, leads to a two-fold increase of the polyesteramide molecular weight without changing

Table 3
Thermal and thermo-mechanical characteristics of PEA-1 as obtained by simultaneous polymerization of CLa and CLo initiated by Jeffamine® M1000 for $[CLa]_0/[CLo]_0 = 2$ and $[CLa + CLo]_0/[JeffM1]_0 = 75$.

Code	DP_{CLa}/DP_{CLo}	T_g (°C)[a]	T_m (°C)[b]	Storage modulus (G') at 25 °C (MPa)[a]	L_{PCLa}[c]	L_{PCLo}[c]
PEA-1	44/25	−8	151	236	3.4	1.6
PCLo	–/438	−40	60	366	–	–
PA6	163/–	70	225	1900	–	–

[a] As determined DMA: dual cantilever, 2 °C/min, from −100 to 150 °C, 1 Hz.

[b] As determined DSC: first heating run, 10 °C/min, from −120 to 250 °C.

[c] As determined by ^{13}C NMR.

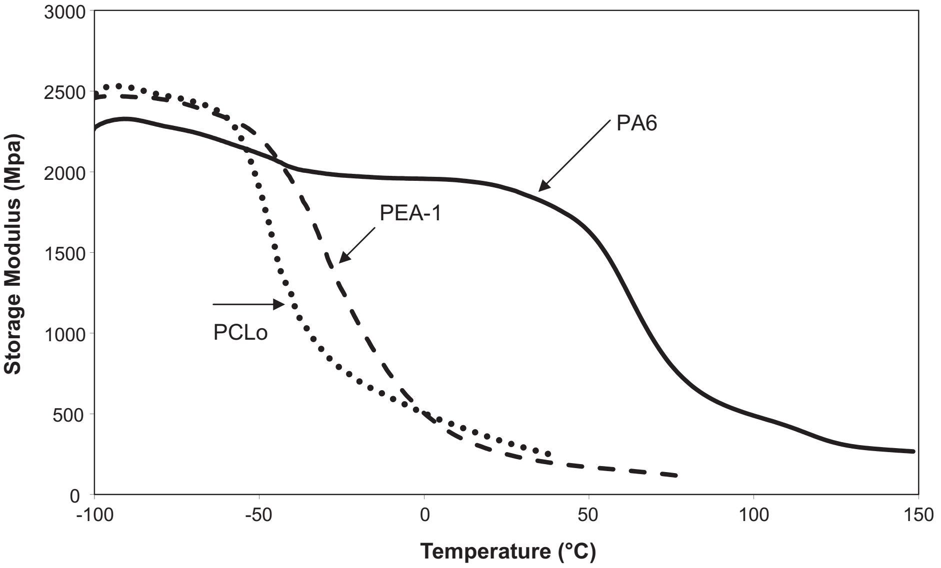

Fig. 2. Graph of PEA-1 storage modulus (MPa) as a function of temperature (dual cantilever mode, 3 °C/min, from −100 °C to 150 °C, 1 Hz).

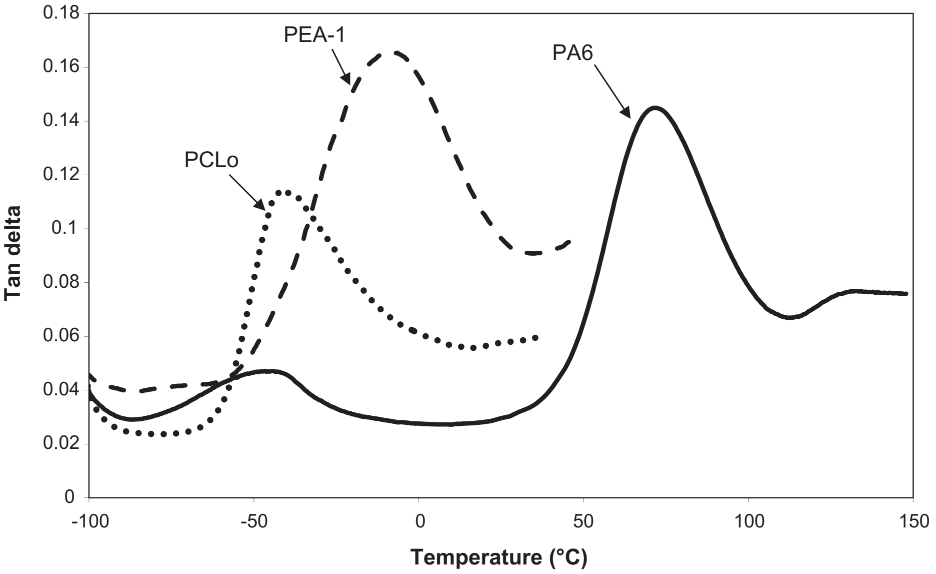

Fig. 3. Graph of PEA-1 tan (δ) as a function of temperature (dual cantilever mode, 3 °C/min, from −100 °C to 150 °C, 1 Hz).

Table 4
Effect of $[CLa]_0/[CLo]_0$ and $[CLa + CLo]_0/[JeffM1]_0$ molar ratios on the thermo-mechanical properties of copolymers obtained by simultaneous copolymerization initiated by Jeffamine® M1000.

Code	DP_{CLa}/DP_{CLo}	T_g (°C)[a]	T_m (°C)[b]	Storage modulus (G') at 25 °C (MPa)[a]	L_{PCLa}[c]	L_{PCLo}[c]
PEA-2	150/10	59	213	1600	–	–
PEA-3	170/50	9	183	771	3.3	1.2
PEA-4	180/100	−6	152	399	2.6	1.6
PCLo	–/438	−40	60	366	–	–
PA6	163/–	70	225	1900	–	–

[a] As determined DMA: dual cantilever, 2 °C/min, from −100 to 150 °C, 1 Hz.
[b] As determined DSC: first heating run, 10 °C/min, from −120 to 250 °C.
[c] As determined by ^{13}C NMR.

the composition and the distribution of the comonomers in the polyesteramide blocks.

In comparison with PEA-2 (M_n ~18,000 g/mol, Table 4), the storage modulus at room temperature of PEA-5 (M_n

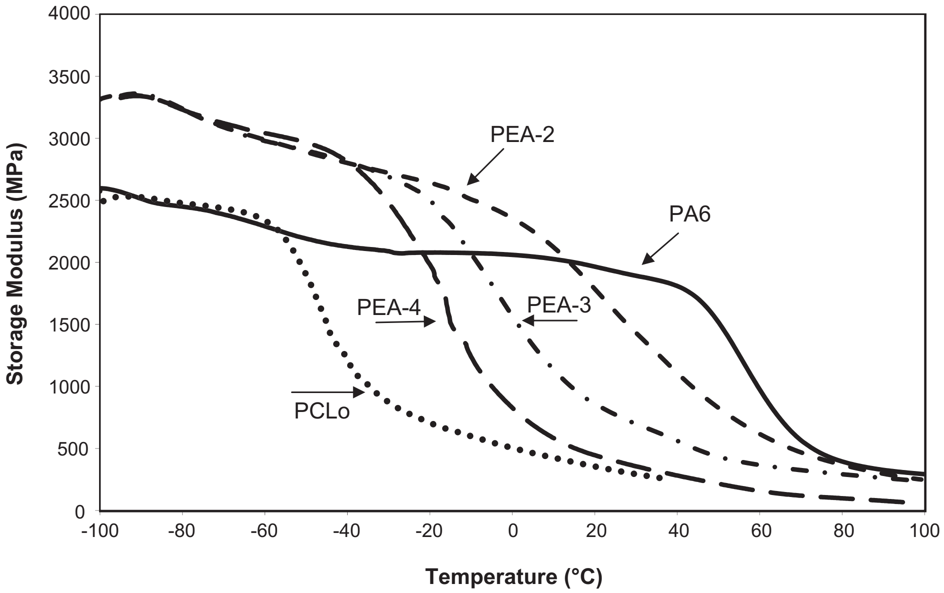

Fig. 4. Graph of PEA-2 to PEA-4 storage modulus (MPa) as a function of temperature for copolymers obtained by simultaneous polymerization of CLa and CLo initiated by Jeffamine® M1000 with different $[CLa]_0/[CLo]_0$ molar ratios (dual cantilever mode, 2 °C/min, from −100 °C to 100 °C, 20 μm, 1 Hz).

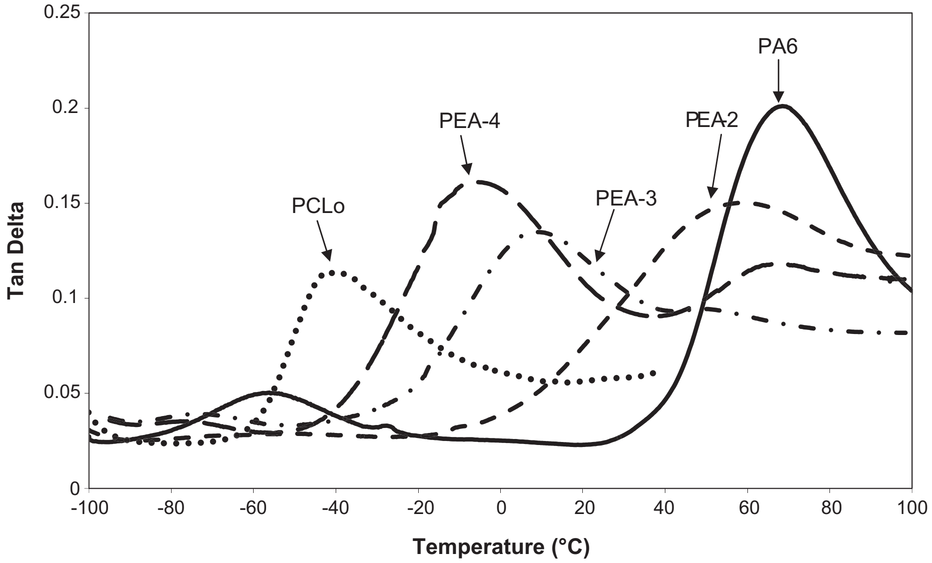

Fig. 5. Graph of tan δ as a function of temperature for PEA-2 to PEA-4 as obtained by simultaneous polymerization of CLa and CLo initiated by Jeffamine® M1000 for different $[CLa]_0/[CLo]_0$ molar ratios (dual cantilever mode, 2 °C/min, from −100 °C to 100 °C, 20 μm, 1 Hz).

~28,000 g/mol) is noticeably higher, 1944 MPa for PEA-5 compared to 1600 MPa for PEA-2 (Table 5). In the same respect, even if PEA-6 (M_n ~62,000 g/mol) has a molecular weight twice as high as PEA-4 (M_n ~32,000 g/mol, Table 4), those copolymers are characterized by a similar value of G' at room temperature. For that specific composition in ester links, the thermo-mechanical properties are barely influenced by the higher molecular weight, meaning that the molecular weight of PEA-4 might already be higher than the limit molecular weight of entanglement (Table 5). Furthermore, one cannot exclude the concomitant formation of intramolecular interactions between the polyesteramides blocks of the triblock copolymers. Figs. 6 and 7 represent the effect of temperature on the storage modulus (Fig. 6) and tan δ (Fig. 7) for PEA-5 and PEA-6 copolymers obtained by simultaneous copolymerization of CLa and CLo as initiated by Jeffamine® ED2003.

3.2. Block copolyesteramides: thermo-mechanical properties

Sequential copolymerization of CLa and CLo was also investigated. By adding first the CLa into the reaction medium, in the presence of Jeffamine® M1000, a diblock copolymer Jeff-NH-*b*-PCLa-NH_2 is obtained. Subsequently, the CLo is introduced into the reaction medium, and its polymerization is initiated by the terminal amine function of the previously synthesized block. A Jeff-NH-*b*-PCLa-*b*-PCLo-OH triblock copolymer is formed, its properties being expected to differ more significantly than those of random copolymers. Since such triblock copolymers have never

Table 5
Effect of $[CLa]_0/[CLo]_0$ and $[CLa + CLo]_0/[JeffED]_0$ molar ratios on the thermo-mechanical properties of copolymers obtained by simultaneous copolymerization initiated by Jeffamine® ED2003.

Code	DP_{CLa}/DP_{CLo}	T_g (°C)[a]	T_m (°C)[b]	Storage modulus (G') at 25 °C (MPa)[a]	L_{PCLa}[c]	L_{PCLo}[c]
PEA-5	300/20	60	211	1944	–	–
PEA-6	350/200	−6	157	336	2.7	1.5
PCLo	–/438	−40	60	366	–	–
PA6	163/–	70	225	1900	–	–

[a] As determined DMA: dual cantilever, 2 °C/min, from −100 to 150 °C, 1 Hz.
[b] As determined DSC: first heating run, 10 °C/min, from −120 to 250 °C.
[c] As determined by ^{13}C NMR.

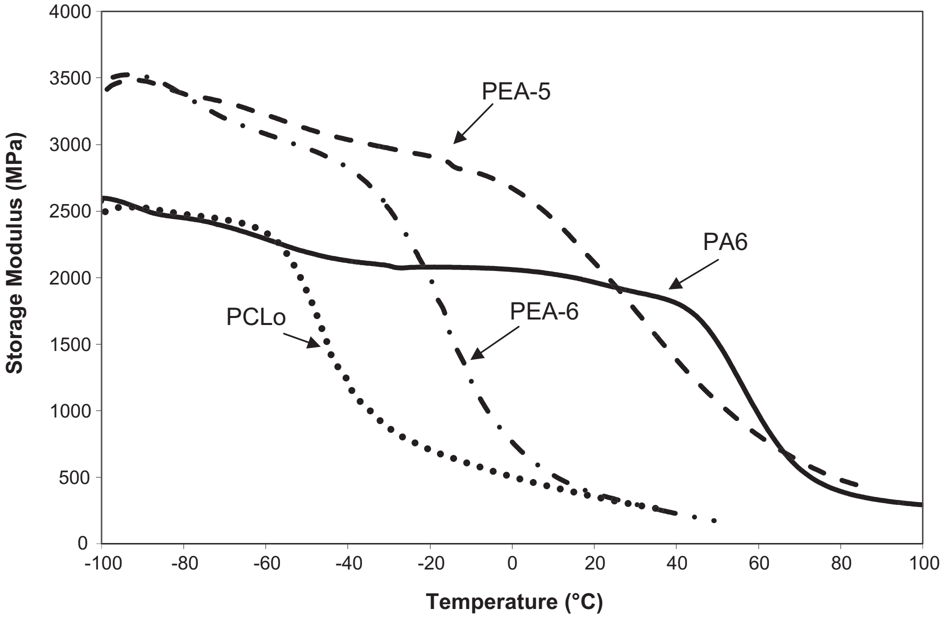

Fig. 6. Graph of storage modulus (MPa) as a function of temperature of PEA-5 and PEA-6 as obtained by simultaneous copolymerization of CLa and CLo initiated by Jeffamine® ED2003 (dual cantilever mode, 2 °C/min, from −100 °C to 100 °C, 20 μm, 1 Hz).

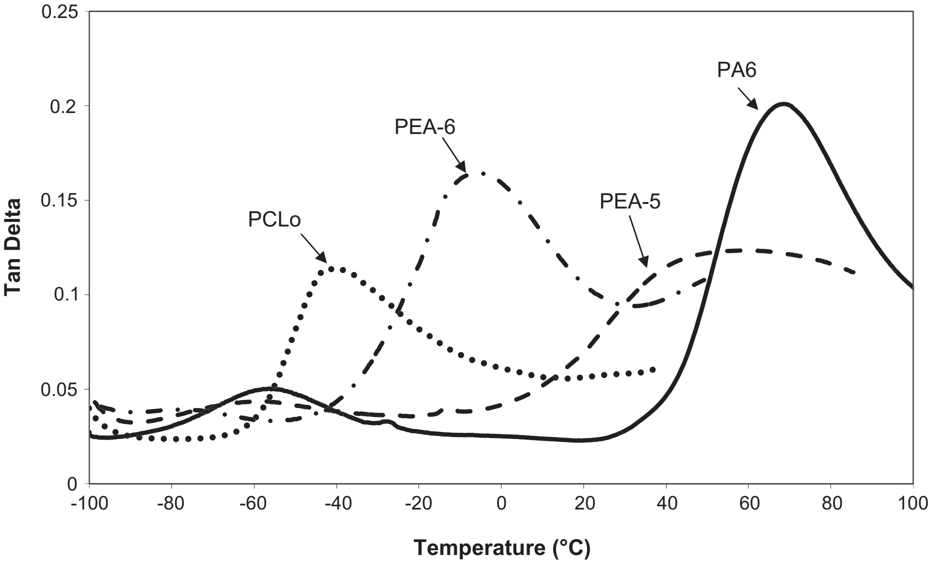

Fig. 7. Graph of tan δ as a function of temperature of PEA-5 and PEA-6 as obtained by simultaneous copolymerization od CLa and CLo initiated by Jeffamine® ED2003 (dual cantilever mode, 2 °C/min, from −100 °C to 100 °C, 20 μm, 1 Hz).

been reported so far, to the best of our knowledge, a detailed description of their synthesis is described hereafter.

First of all, the aminolytic polymerization of CLa is initiated by Jeffamine® M1000 in the presence of 0.50 mol% of H_3PO_2 (compared to the amide functions present in the medium) at 250 °C ($[CLa]_0/[JeffM1]_0 = 25$). After 7 h, heating and stirring are stopped and the reaction mixture is maintained under inert atmosphere overnight. The CLo is then added to the mixture, heated up at 250 °C, and the polymerization takes place during 4 h ($[CLa]_0/[CLo]_0 = 1$, Table 6).

For the first step of this synthesis (CLa polymerization), the ^1H NMR spectrum shows the formation of polyamide (not shown here). After 7 h, the conversion, as determined from the relative integrated areas of the resonances of the methylene protons in α position of the carbonyl amide of the polymer, at 2.3 ppm, and the monomer, at 2.45 ppm, reaches 88%. The presence of the signal characteristic of terminal methylene amine functions at 2.85 ppm suggests that the CLa polymerized predominantly through an aminolytic mechanism leading to the formation of a diblock copolymer Jeff-*b*-PCLa-NH_2. The absence of a signal assignable to carboxylic acid functions further supports this observation. During the second step, a quantitative conversion of the CLo is obtained since no characteristic signals from CLo are visible any more in the ^1H NMR spectrum of the final product. Only terminal hydroxyl functions are present, as confirmed by the signal of $–C\underline{H_2}–OH$ protons (PE4: 4.05 ppm); no terminal amine functions could be evidenced, neither by ^1H NMR spectrum nor by titration. These observations indicate that the terminal amine functions of the diblock copolymer Jeff-*b*-PCLa-NH_2 have initiated, quantitatively, the CLo polymerization (Fig. 8).

The chromatogram of the final product, as obtained by GPC-MALLS-RI (Fig. 3-SI) reveals that the molecular mass distribution is monomodal and shifts towards lower retention volume compared to the chromatogram of the macroinitiator, Jeffamine® M1000 (Fig. 3-SI, $M_n = 5700$ g/mol, $M_w/M_n = 1.7$).

In order to obtain block copolymers with molecular masses sufficiently high in terms of thermo-mechanical properties, the CLa polymerization was initiated by Jeffamine® M1000 in the presence of 0.50 mol% of H_3PO_2 for a $[CLa]_0/[JeffM1]_0$ molar ratio of 200 during 24 h, followed by the CLo polymerization for a $[CLo]_0/[JeffM1]_0$ molar ratio of 25 during 4 h.

Conversions of 90% in CLa and 100% in CLo were determined from the ^1H NMR spectrum of the crude product (not shown here). This copolymer was also characterized by DSC and DMA. The thermo-mechanical properties of the triblock copolymer (PEA-7) are shown in Table 7.

Figs. 4-SI and 5-SI show the effect of temperature on the storage modulus and tan δ of PEA-7, as compared to the neat PA6 and PCLo used as references. Despite the sequential structure of PEA-7, no cumulative properties of both sequences are observed. Rather intermediate thermo-mechanical properties are recorded. Between the formation of the 2 blocks during the sequential copolymerization, the residual CLa monomer is not extracted from the reaction medium. Therefore, we can assume that during the CLo polymerization, the residual CLa can be inserted within the third PCLo block [5], leading to the formation of a Jeff-*b*-PCLa-*b*-P(CLo-*co*-CLa)-OH like triblock copolymer. Such a topology and composition could account for the intermediate thermal and thermo-mechanical properties observed for PEA-7. Actually, PEA-7 properties are very close to those of random polyesteramide PEA-2 (Jeff-NH-*b*-P[CLa-*co*-CLo]-OH, $DP_{CLa} = 150$ and $DP_{CLo} = 10$, Table 4), suggesting that the PCLo sequence (M_n ~2900 g/mol) is disturbing the organization of the PA6 chains (M_n ~20,000 g/mol), decreasing both T_g and G' (as measured at room temperature).

3.3. Random copolyesteramides: hydrolytic degradation

PCLo is a well-known biodegradable polymer. It can be degraded in compost by a combination of hydrolytic and enzymatic degradation [19]. On the other hand, PA6 (PCLa) is not biodegradable. However, the random copolymers prepared here are expected to be biodegradable through the PCLo units present along the chains [4,10].

Indeed, the (bio)degradation of various polyesteramides based on PCLa and PCLo was investigated by either hydrolytic degradation (at 60 °C), composting (from 65 °C, in the beginning of the test, to 20 °C at the end) or fungus treatment (at 37 °C) [6]. Hydrolytic degradation by immersion of the samples at 60 °C in a phosphate buffer for 8 weeks implied a drop of the molar masses, while the films became fragile.

The main objective of this study was to evaluate the sensitivity of the random copolyesteramides towards hydrolytic chain cleavage. Samples of dimensions 3 cm by 1 cm by 0.5 mm were immersed into a phosphate buffer (NaH_2PO_4/Na_2HPO_4, 0.1 M, pH 7.4) at 60 °C for a period of time ranging from 15 to 90 days according to conditions previously reported by Gonsalves et al. [4]. The hydrolytic

Table 6
Molecular characteristics of the copolymers obtained by sequential copolymerization of CLa, followed by CLo, initiated by Jeffamine® M1000 in the presence of 0.50 mol% of H_3PO_2 during 7 h and 4 h, respectively at 250 °C ($[CLa]_0/[CLo]_0 = 1$ at $[CLa + CLo]_0/[JeffM1]_0 = 50$).

Entry	Time (h)	Conv[a] (%)		R-NH_2[b] (meq/kg)	$M_{n\ RMN}$[c]	$M_{n\ GPC}$[d]	M_w/M_n[d]
		CLa	CLo				
1	7	88	–	ND	3700	–	–
2	11 (7 + 4)	92	>99	<15	6700	5800	1.7

[a] As determined by ^1H NMR proton: $conv_{CLa} = I_{PA2}/(I_{CLa2} + I_{PA2}) \times 100$, $conv_{CLo}$ quantitative.

[b] As determined by titration of the amine functions with HCl 0.05 M in trifluoroethanol based solution (limit of detection = 15 meq/kg); ND, not determined.

[c] As determined by ^1H NMR: $M_{n\ RMN} = (DP_{CLa}eff \times M_{w\ CLA}) + (DP_{CLo}eff \times M_{w\ CLo}) + M_{n\ R\text{-}NH2}$ with $M_{w\ CLa} = 11{,}316$ g/mol and $M_{w\ CLo} = 11{,}414$ g/mol.

[d] As determined by GPC-MALLS-RI.

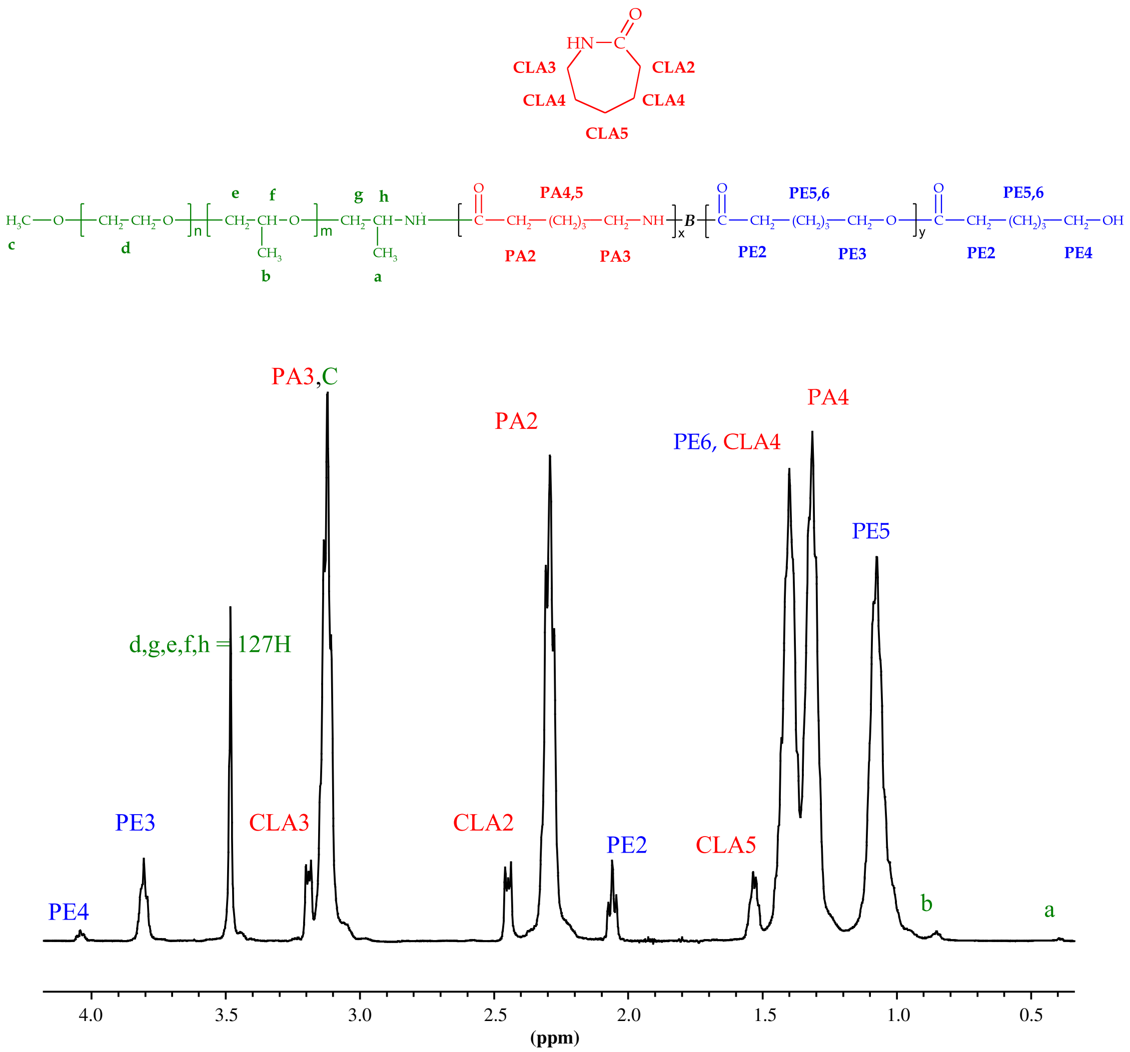

Fig. 8. ^{1}H NMR spectrum of the crude product obtained by sequential copolymerization of CLa and CLo initiated by Jeffamine® M1000 in the presence of 0.50 mol% of H_3PO_2 during, respectively 7 h and 4 h, at 250 °C (solvent: TFA-*d*, Table 6).

Table 7
Thermal and thermo-mechanical characteristics of the triblock copolymer PEA-7 obtained by sequential copolymerization of CLa and CLo initiated by Jeffamine® M1000.

Entry	DP_{CLa}/DP_{CLo}	T_g (°C)[a]	T_m (°C)[b]	Storage modulus at 25 °C (MPa)[a]
PEA-7	180/25	40	205	1239
PCLo	–/438	−40	60	366
PA6	163/–	70	225	1900

[a] As determined by DMA: dual cantilever, 2 °C/min, from −100 to 150 °C, 1 Hz, 20 µm.
[b] As determined by DSC: first heating run, 10 °C/min, from −120 to 250 °C.

degradation was followed at predetermined time periods by weight loss measurements (gravimetric measurements) and by DSC analyses. ^{1}H NMR was used to determine the copolymer composition as a function of immersion time. Table 8 shows the molecular characteristics of the polyesteramides after hydrolytic degradation.

As shown in Fig. 9, the opacity of the samples is already changing after 15 days of immersion in the phosphate buffer. The copolymer containing the highest content of CLa units are affected first (sample 1, Fig. 9). The samples become brittle and some of them are even broken. This behavior can be explained by predominant hydrolysis at the ester links on one hand and at the amorphous regions on the other; this leads to an increase of sample crystallinity [20,21].

The hydrolytic degradation of each sample was characterized by weight loss measurements with immersion (see Table 1-SI). Each sample was picked out of the buffer at

Table 8
Molecular characteristics of the random copolyesteramides studied by hydrolytic dation in phosphate buffer at 60 °C.

Entry	Initiator	Structure	DP[a]		Weight Fraction[a] (%)			T_m (°C)[b]	ΔH_m (J/g)[b]
			CLa	CLo	CLa	CLo	Ether		
1	JeffM1		170	50	68	24	8	183	42
2			180	100	60	35	5	152	27
3			176	150	50	46	4	104	29
4	JeffED		350	200	61	33	6	157	23

[a] As determined by ^{1}H NMR.
[b] As determined by DSC: first heating run, 10 °C/min, from −120 to 280 °C.

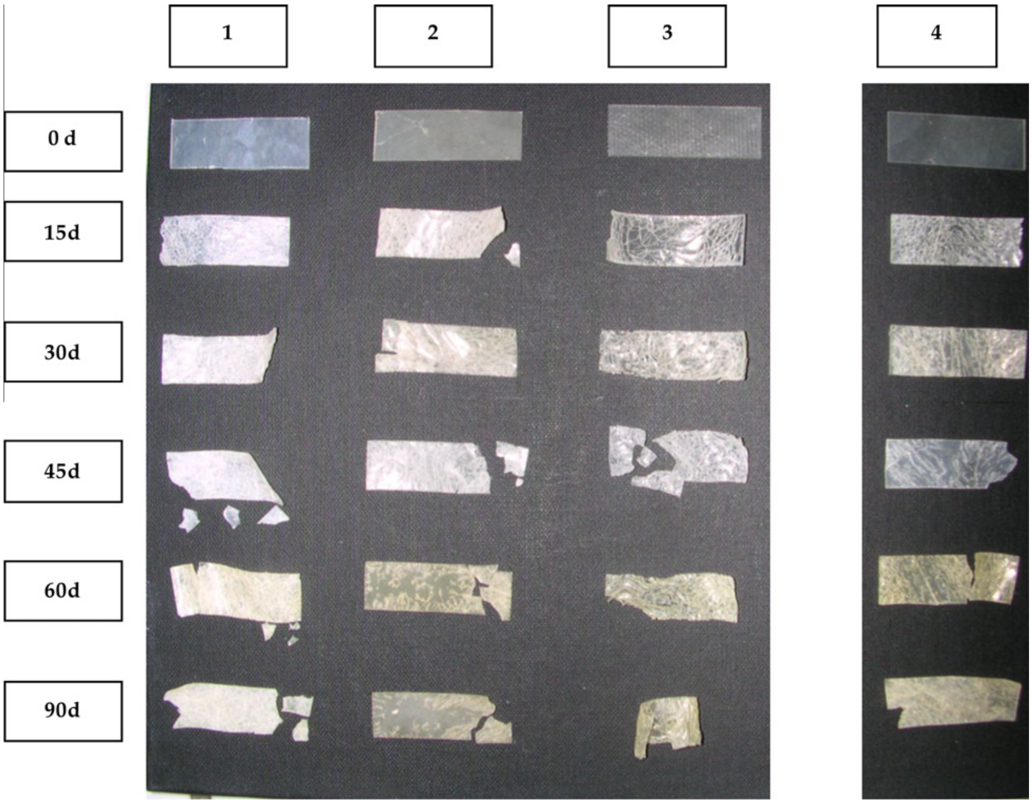

Fig. 9. Immersion time effect on samples aspect and opacity (see Table 8 sample codes and molecular characteristic features).

predetermined time, dried under vacuum at 40 °C, and then weighed. A graph of the loss weight *versus* the immersion is shown in Fig. 6-SI.

Polyamides being known for their stability against hydrolysis [22], it is expected that, for copolymers rich in amide content, the degradation is slow. For the polyesteramides obtained by simultaneous copolymerization of CLa and CLo initiated by Jeffamine® M1000, the major weight loss is obtained for the copolymer containing the largest amount of ester functions (Fig. 6-SI, 3, 50% weight in CLa). ^{1}H NMR spectra of the solid residues after 90 days of immersion show the selective hydrolysis of ester bonds. This observation is based on the ratio of the relative intensity of the methylene protons in α position to the carbonyl ester (PE3: 3.8 ppm) and the methylene hydroxyl end-group (PE4: 4.05 ppm), which decreases as a function of the immersion time, evidencing the increase of the relative amount of hydroxyl functions (Fig. 10). Accordingly, the proton NMR spectrum reveals the appearance of a triplet at 2.1 ppm, characteristic for the $-CH_2-COOH$ methylene protons; the ratio of the integrated areas of the $-CH_2-C(O)-O-$ and $-CH_2-O-C(O)-$ resonances is not equal to the unity anymore.

Fig. 6-SI further evidences that the copolymer containing the highest content of ester units (entry 3, see Table 1-SI) is characterized by a regular weight loss as a function of the immersion time, the three other copolymers displaying a bimodal behavior. Indeed, their weight loss is fast till *ca.* 20 wt%, subsequently a plateau is observed prior to an additional decrease in weight. Such a behavior was previ-

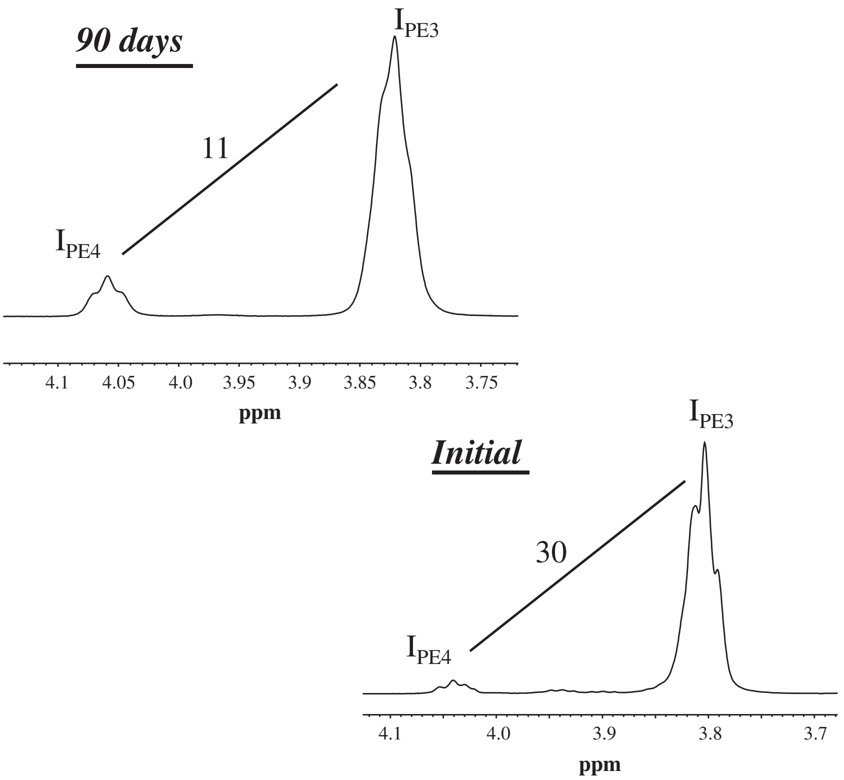

Fig. 10. Evolution of the ratio of the relative intensities I_{PE3}/I_{PE4} during the hydrolytic degradation of polyesteramide 3: JeffM1, 176/150 (solvent ^{1}H NMR: TFA-*d*, entry 3 Table 1-SI).

ously observed by Chromcová et al. who studied the hydrolytic degradation of random polyesteramides based on CLa and CLo [6]. They explained this behavior by fast hydrolysis of the ester bonds with solubilization of the resulting low molecular weight oligomers in the aqueous solution. It is obvious that, if the distribution of CLa and CLo units is completely random, the proportion of the oligomers which are soluble in water will increase with the proportion of CLo units. As evidenced by ^{13}C NMR, the length of the CLo sequence is increased upon decreasing the $[CLa]_0/[CLo]_0$ molar ratio [17]. Therefore, the higher the content in CLo units in the polyesteramide sequence, the more random the comonomer distribution will be. It is then not surprising that the amount of soluble oligomers is higher for the copolymer characterized by a CLa/CLo molar ratio of 176/150, as shown by its monotonous curve of weight loss as a function of the immersion time (curve 3, see Fig. 6-SI).

For a similar composition in CLa and CLo units (~60% weight of CLa units), using Jeffamine® ED2003 instead of Jeffamine® M1000 as an initiator does not have a major effect on the weight loss during hydrolytic degradation in the phosphate buffer (compare entries 2 and 4, see Table 1-SI). This observation can be explained by a similar distribution of the co-units along the polyesteramide chains, and also by a similar organization of the chains whether the initiator is di- or mono-functionalized. This is further confirmed by the sequence length obtained by ^{13}C NMR (JeffM1: $L_{PCLa} = 2.6$, $L_{PCLo} = 1.6$ and JeffED: $L_{PCLa} = 2.7$, $L_{PCLo} = 1.5$) and the similar melting temperatures (JeffM1: 152 °C and JeffED: 157 °C).

4. Conclusions

Block copolymers based on poly(ε-caprolactone (CLo))-*co*-poly(ε-caprolactam (CLa)) polyesteramide were synthesized by catalyzed hydrolytic ring-opening polymerization. Either random or block polyesteramide sequences were covalently linked to Jeffamine®, i.e. ω- and α,ω-aminated polyether blocks. Their thermal and thermo-mechanical properties were investigated by DSC and DMA and compared to commercially available polyamide 6 (PA6) and poly(ε-caprolactone) (PCLo) used as references. In general, the polyesteramide-based copolymers have storage modulus (G') and α transition ($\sim T_g$) properties intermediate to those of the references used. Increasing the molecular weight by using a α,ω-difunctionalized polyether macroinitiator has only a slight effect on the thermo-mechanical properties of the copolymers, especially at high CLo ester content. Increasing the CLa content in the polyesteramide blocks enhances the storage modulus of the block copolymers, leading to the best ever recorded molecular weights, being higher than 38,000 g/mol. Interestingly, all studied copolymers display significantly increased storage moduli, at least at low temperature, with respect to the reference commercial homopolymers.

The hydrolytic degradation of random copolymers was studied in a phosphate buffer at 60 °C. While the hydrolytic degradation appears slightly influenced by the chemical composition and molecular weight of the copolymers, it comes out that the degradation process occurs by polyesteramide chain cleavage at the level of the ester linkages. Compared to homo-PCLo, the presence of more hydrophilic

CLa units along the chain favors the hydrolysis reaction of the nearby ester bonds increasing the overall hydrolytic degradation rate. Enzymatic degradation of random copolyesteramides in composted soil occurred also much faster, at least for a CLo content larger than 30%), than for neat homo-PCLo [16].

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.eurpolymj.2010.07.005.

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