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Thermogravimetric analysis of poly(ε-caprolactam) and poly[(ε-caprolactam)-*co*-(ε-caprolactone)] polymers

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Abstract

The thermal degradation of poly(ε-caprolactam) and its copolymers with ε-caprolactone has been studied by high-resolution thermogravimetric analysis (TGA), followed by the analysis of evolved gas via a simultaneous coupling to Fourier transform infrared spectrometry (FTIR) and mass spectrometry (MS). Poly(ε-caprolactam) and poly(ε-caprolactone) polymers are, respectively, degraded at different temperatures, rendering this study to be particularly useful in determining the structure of their copolymers, i.e. random or blocky-like copolymers. The poly[(ε-caprolactam)-*co*-(ε-caprolactone)] polymers have been synthesized in bulk by anionic ring-opening copolymerization promoted by ε-caprolactammagnesium bromide in a temperature range from 120 to 180°C. A multi-step degradation was observed by TGA, and characterization of the evolved gas by FTIR and MS gives credit to some blocky-like enchainment of the comonomers. This assignation has been further confirmed by TGA directly performed on blends of poly(ε-caprolactam) and poly(ε-caprolactone) as obtained by solvent casting. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Aliphatic polyesters such as poly(ε-caprolactone) (PCLO) are an important class of biodegradable synthetic polymers. The biodegradation of these polymers is of considerable interest to environmentalists and industrialists, as well as academicians and researchers [1,2]. On the other hand, aliphatic polyamides such as poly(ε-caprolactam) (PCLA) are known as non-biodegradable polymers. The large concentration of hydrogen bonds and the high regularity of the polyamide structure (high crystallinity) are the evoked reasons for the inertness of these nylons to biodegradation. Interestingly enough, poly[(ε-caprolactam)-*co*-(ε-caprolactone)] polymers have been reported to be biodegradable and could be considered as a new class of biodegradable commodity polymers [3–8] whose properties vary from plastic to elastomer depending on the amount of lactone monomer present in the starting polymerization composition. Next to their relative composition, it is also important to determine how the lactone units are distributed all along the copolymer backbone.

In order to determine the actual structure of the poly[(ε-caprolactam)-*co*-(ε-caprolactone)] polymers, thermogravimetric analysis (TGA) has been investigated. Indeed PCLO and PCLA are, respectively, degraded at very different temperatures: mainly below 400°C for PCLO and above 400°C for PCLA (for a heating rate of 20°C min^{-1} under inert atmosphere). Therefore, if the copolymers have a blocky structure the degradation steps relative to the two (homopolymers or at least enriched sequences) should be detected in their TGA thermograms.

The thermal degradation of P(CLA-*co*-CLO) has been studied by both high resolution TGA and conventional TGA coupled with a Fourier transform infrared spectrometer (FTIR) and a mass spectrometer (MS) for evolved gas analysis (TGA-*co*-FTIR/MS). Hi-Res™ TGA is a method, which is able to reduce the heating rate when the thermobalance undergoes some weight loss. This technique increases, therefore, the resolution between two consecutive degradation steps. However, Hi-Res™ TGA cannot be used when the evolved gases are analyzed on line by FTIR and MS since the heating rate decrease leads to a very high dilution of the evolved gases preventing their detection with enough accuracy.

The degradation of PCLO has already been studied by TGA-*co*-FTIR/MS in a previous work [9] and has pointed

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Table 1
Anionic ring-opening copolymerization of CLA and CLO (15 wt% CLO) promoted by ε-caprolactammagnesium bromide (CLAMgBr) in bulk at a temperature T_p

Code	CLAMgBr (mol%)	T_p (°C)	Polymer yield (%)[a]
AK21E	0.5	130	97
AK20E	0.5	140	97
AK2E	0.5	150	97
AK17E	0.5	160	96
D1E	1.0	120	96
D2E	1.0	130	96
D3E	1.0	140	95
D4E	1.0	150	96
D5E	1.0	160	94
D6E	1.0	170	94
D7E	1.0	180	96

[a] As determined after hot water extraction of residual initiators, monomers and water-extractable oligomers.

out the presence of two main degradation steps, respectively, at 300–360°C and 360–420°C (depending on the polyester molecular weight) as measured with a heating rate of 20°C $\min^{-1}$ under helium purge gas. The analysis of the evolved gases by MS and FTIR has allowed us to determine that during the first step, the degradation of PCLO proceeds through ester pyrolysis. When ester pyrolysis involves two consecutive ester functions in the polyester chain, 5-hexenoic acid is evolved. Next to the formation of 5-hexenoic acid, water and CO_2 are also evolved as a result of condensation and decarboxylation reactions occurring at this high temperature range. The second step results from an unzipping depolymerization leading to the production of ε-caprolactone cyclic monomer.

In this work, the thermal degradations of PCLA and P(CLA-*co*-CLO) copolymers as synthesized by anionic (co)polymerization have been studied first by TGA-*co*-MS/FTIR. The evolved gases have been then analyzed in order to assign the different degradation steps. Then Hi-Res™ TGA have been investigated to characterize the comonomer distribution along the P(CLA-*co*-CLO) copolymers.

2. Experimental

2.1. Preparation of PCLA and P(CLA-co-CLO) samples

A poly(ε-caprolactam) sample (PCLA, code AK39A) was first synthesized by anionic ring-opening polymerization of ε-caprolactam (CLA) in bulk at 150°C in the presence of 0.5 mol% ε-caprolactammagnesium bromide (CLAMgBr) as initiator and 0.5 mol% *N*-benzoyl-ε-caprolactam as activator in analogy to Refs. [10–12]. In the melt of ε-caprolactam at 80°C the activator was dissolved first in glass flask under inert atmosphere. Later, the solid concentrate of CLAMgBr in CLA was dosed and after dissolution (max. 3 min), the polymerization mixture was transferred to polymerization aluminum mold heated to 110°C and immediately transferred to an oil polymerization bath at a given temperature. The polymerization was conducted for 30 min. The crude polymer was disintegrated by special rasp and purified by extraction with hot water to remove unreacted CLA monomer, water-extractable oligomers and residual initiator. The polymer yield as determined after hot water extraction was equal to 97 wt%.

The copolymer samples were synthesized by anionic ring-opening copolymerization of CLO and CLA at a temperature ranging from 120 to 180°C in the presence of 0.5 (or 1.0) mol% ε-caprolactammagnesium bromide (CLAMgBr) similar to the CLA homopolymerization by hand casting in Al mold with 4 mm × 140 mm × 160 mm internal dimensions and 4 mm wall thickness [6,11,12]. In a glass flask, the mixture of CLA and CLO was homogenized under dry argon at 80°C, concentrate of CLMgBr was dissolved and immediately transferred to the Al mold heated to the polymerization temperature. The mold was heated again for 30 min and slowly cooled down at room temperature. After demolding and disintegration of copolymer plaques, the copolymers were extracted by hot water. The specific experimental conditions used in all the investigated copolymerizations are reported in Table 1.

2.2. Characterization

The thermogravimetric analyses were performed on a Hi-Res™ TGA 2950CE from TA Instruments, using helium as purge gas. High resolution analyses were performed with a heating ramp of 30°C $\min^{-1}$ and by using a resolution parameter of 5, which means that a continuously variable heating rate is applied in response to changes in the sample decomposition rate. This resolution parameter can be tuned within an eight-step scale to maximize weight loss resolution. A ±1°C precision over the degradation temperature has been estimated from the derivative of the temperature dependant weight loss curves (DTGA curves). The analysis of gas evolved all along the thermal degradation was carried out with a Bio-Rad Excalibur FTIR spectrometer with a 0.2 cm^{-1} resolution. Spectra were recorded (from 4000 to 400 cm^{-1}) owing to a gas cell heated at 225°C and an MCT detector cooled down by liquid nitrogen. On the other side, the evolved gases were also analyzed by mass spectrometry on a Thermostar quadrupolar apparatus from Balzers Instruments covering a mass range from 0 to 300 amu. Evolved gas was ionized by electron impact (70 eV). The simultaneous analysis of evolved gases by FTIR and MS spectrometers were made possible by a double coupling device set up by our laboratory in close collaboration with TA Instruments. It consists of a Teflon-coated stainless steel 'T' connection, which was heated at 225°C for avoiding any condensation of evolved gas. To this connection are contacted, on one hand, the mass spectrometer via a

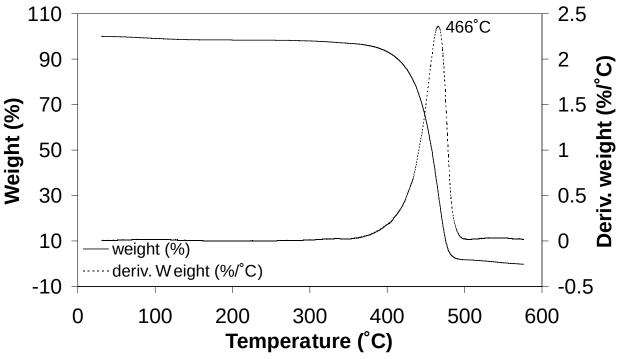


Fig. 1. TGA thermogram of PCLA AK39E (see Section 2). Heating rate: 20°C min^{-1} under He as purge gas.

one-meter long quartz capillary (inner diameter = 150 μm) heated at 200°C, and on the other hand, the gas cell of FTIR spectrometer through a one-meter long stainless steel tube (inner diameter = 2 mm) heated at 225°C.

3. Results and discussion

3.1. Thermal degradation of poly(ε-caprolactam)

3.1.1. TGA/MS-FTIR measurements

First, the degradation of PCLA derived from residual monomer and initiator (sample PCLA AK 39 E, see Section 2) has been studied by TGA-*co*-MS/FTIR. One single degradation step is observed at 466°C (Fig. 1). The FTIR spectrum of the evolved gases (Fig. 2) shows the production of water (absorption bands at 3800–3200 and 1800–1200 cm^{-1}), carbon dioxide (2355–2310 cm^{-1}) and an olefinic compound (928, 966 and 1508 cm^{-1} and between 3100 and 3000 cm^{-1}). Absorption bands are also observed at 1653, 1772 and 3331 cm^{-1} and are assigned to amide, carboxylic acid (in gas phase), and hydroxyl functional groups, respectively. The absorption at 1653 cm^{-1} does not correspond to the amide function of PCLA oligomers (known to absorb at 1638 cm^{-1}) but rather to ε-caprolactam monomer in agreement with published data [13].

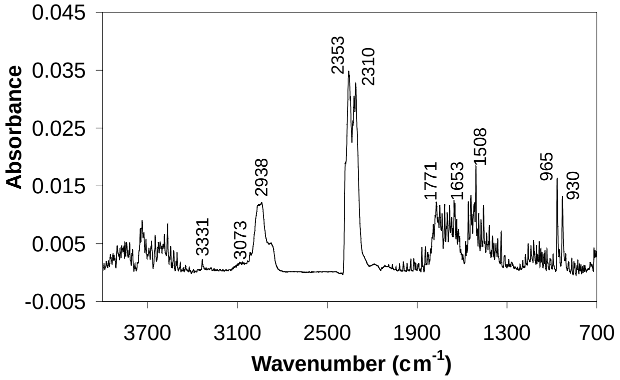
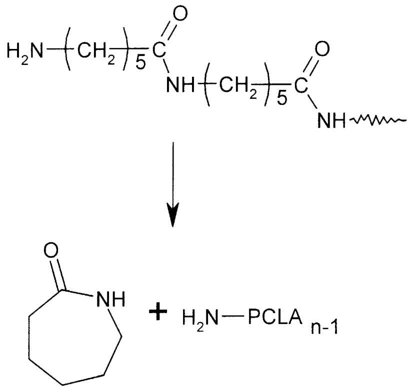


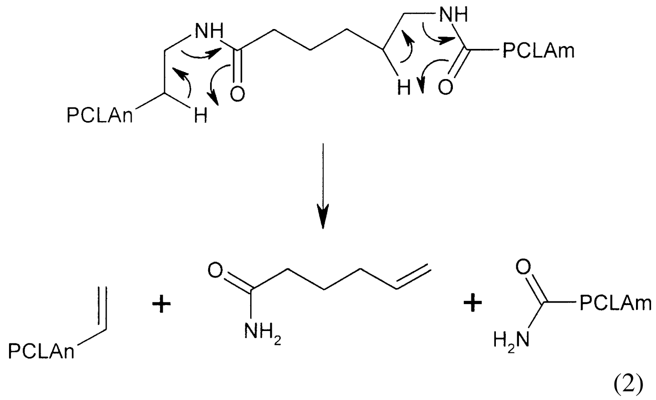
Fig. 2. FTIR spectrum of gas evolved from the degradation step of PCLA AK39E at 465°C (see Fig. 1).

These observations suggest that PCLA more likely degrades via a process involving both a mechanism of 'unzipping' depolymerization leading to the evolution of ε-CLA cyclic monomer (Eq. (1)), and random chain cleavage through amide pyrolysis (Eq. (2)). When this pyrolysis reaction involves adjacent amide functions, 5-hexenamide is formed. This molecule might be responsible for the absorption bands at 1653 (amide function), and 1508, 967, 928 cm^{-1} (alkene function). The amide function can also react at high temperature with water, e.g. trapped within the polymer, and therefore produce volatile carboxylic acid compounds detected in FTIR at 1772 cm^{-1}. The decarboxylation reaction of this acid leads to CO_2 emission (absorption at 2310–2355 cm^{-1}). The alkene function of 5-hexenamide can react with water too and produce alcohol that can be responsible for the absorption band at 3331 cm^{-1}.

This mechanism was confirmed by MS. Indeed the ion currents relative to *m/z* ratios equal to 96, 113 and 114, whose attribution is given in Table 2, reach their maximum values at the temperature corresponding to the main degradation of PCLA at 466°C (Fig. 3).



(1)



(2)

3.1.2. Hi-Res™ TGA measurements

Hi-Res™ TGA has been studied in order to resolve the two degradation mechanisms discussed here. Similar to the PCLO thermal degradation investigated by Hi-Res™ TGA [9], two main degradation steps are detected for PCLA (Fig. 4), especially on the Hi-Res™ DTGA curve, with

Table 2
Assignment of the main ion currents (*m*/*z*) detected by MS at the temperature corresponding to the most important degradation step of PCLA, i.e. at 465°C by TGA (see Fig. 1)

Ion current (*m*/*z*)	Attribution
96	5-hexenoic acid–H_2O
113	ε-caprolactam and 5-hexenamide
114	ε-caprolactone and 5-hexenoic acid

two maxima at 377 (86.2% weight loss) and 431°C (8.3%). A small weight loss of 1.8% is also observed at 328°C. Furthermore, this limited weight loss is preceded by a continuous evolution of volatile products starting at ca. 70°C, which has been assigned to the evolution of H_2O molecules more likely trapped within the highly hygroscopic PCLA sample.

As aforementioned, the degradation of PCLA would proceed through a mechanism yielding the production of CLA (cyclic monomer) and random chain scission via amide pyrolysis. The pyrolysis reaction of PCLA more likely occurs at higher temperatures compared to the depolymerization reaction (unzipping process), which should therefore represent the main first degradation step (Eq. (1)). Thus the amide pyrolysis reaction should be responsible for the other degradation at higher temperature (Eq. (2)).

The very limited degradation observed at ca. 328°C has been attributed to the degradation of some remaining traces of initiator, unreacted monomer, and/or activator residues. Indeed the extent of this degradation step is much more pronounced when the PCLA sample has not been previously derived from these residues by hot water extraction, with a weight loss of 4.1% (to be compared to 1.8% for extracted sample).

3.2. Thermal degradation of poly[(ε-caprolactam)-co-(ε-caprolactone)] polymers

Let us first note that for the degradation study of the P(CLA-*co*-CLO) polymers the results obtained by TGA/FTIR has not been considered since the gases evolved during the degradation of PCLO or PCLA chains have very similar FTIR spectra. Therefore, no distinction of the different sequences could be performed. Moreover, water and carbon dioxide are produced during both degradation processes, which impede an accurate detection of species such as carboxylic acid functions.

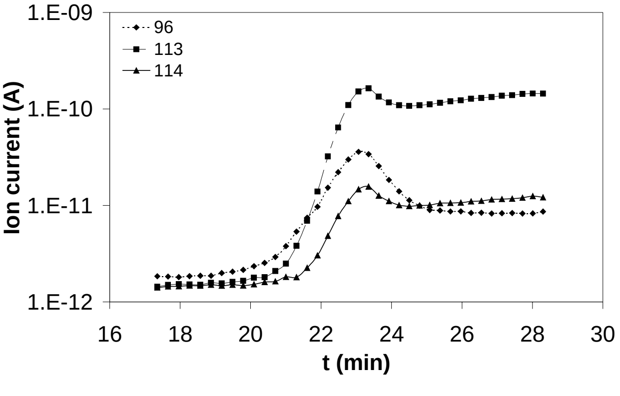


Fig. 3. Evolution of the ion currents *m*/*z* equal to 96, 113 and 114 during the heating of PCLA AK39E from 20 to 600°C under He as purge gas. A 23 min time corresponds to a temperature of 465°C in TGA (see Fig. 1).

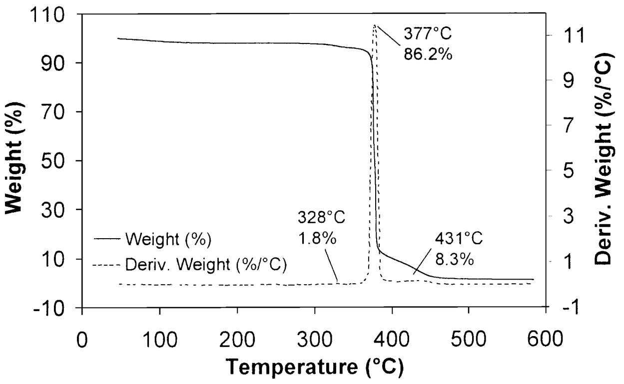


Fig. 4. Hi-Res. TGA thermogram of PCLA AK39E. Heating rate: 30°C min^{-1} (resolution parameter = 5) under He as purge gas.

3.2.1. Attribution of the degradation steps

3.2.1.1. Study by TGA/MS. The result obtained by TGA/MS on the copolymer D1E, thus containing 15 wt% CLO units (Table 1), is illustrated in Fig. 5. The degradation steps are detected at ca. 340 (6.7% weight loss), 430 (45.3%) and 453°C (47.3%). This suggests that the structure of the copolymer could be partially blocky. Indeed, the degradation of PCLO proceeds at a temperature lower than that of PCLA, the peak around 340°C could be mainly due to the degradation of PCLO blocks while the last degradation should be essentially due to that of PCLA sequences. This proposition is supported by the analysis of the evolved gases detected by MS. Indeed, the MS spectrum of the gases evolved around 340°C (Fig. 6a) exhibits a high ion current

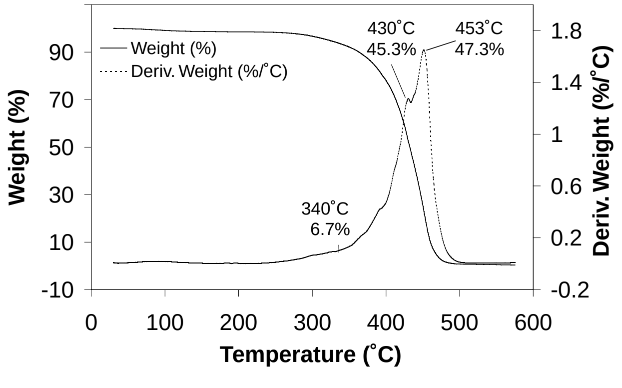


Fig. 5. TGA thermogram of the copolymer D1E (see Table 1). Heating rate: 20°C min^{-1} under He as purge gas.

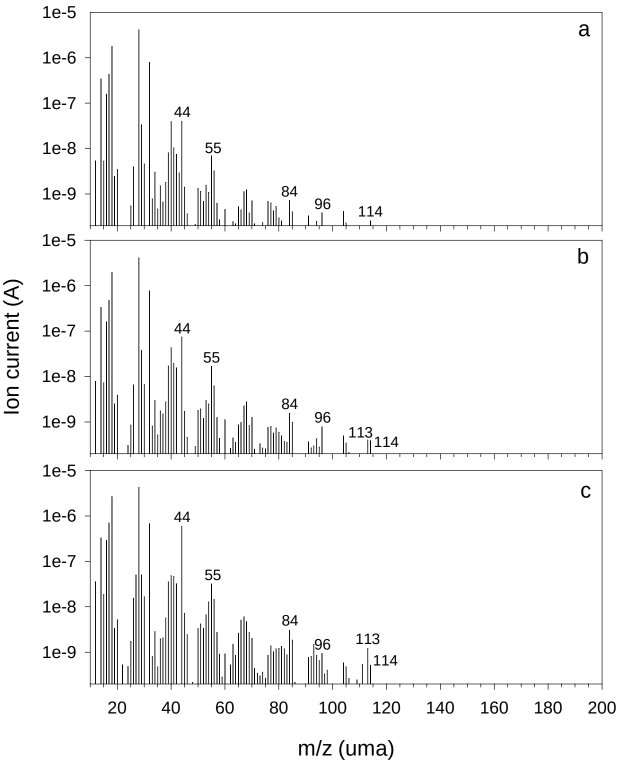


Fig. 6. Mass spectra of the gases evolved during the thermal degradation of copolymer D1E (see Fig. 5): at (a) 340, (b) 430, and (c) 453°C.

at *m*/*z* 114 while no current is detected at *m*/*z* 113. This can be assigned to PCLO degradation with the evolution of ε-caprolactone (CLO) and/or 5-hexenoic acid (molecular ions at *m*/*z* 114). This is also confirmed by the molecular fragments present at *m*/*z* 84, 55 and 42. The detection of CLO, i.e. the cyclic monomer, during the degradation of the copolymer is interesting since it means that the polymer more likely displays a blocky structure. Indeed CLO can only be generated by unzipping depolymerization of PCLO blocks.

MS spectra of the gases evolved around 430 and 453°C (Fig. 6b and c) interestingly exhibit an increasing ion current at *m*/*z* 113 indicating an increased production of 5-hexenamide and/or CLA cyclic monomer, while CLO evolution still occurs as indicated by currents at *m*/*z* 96 and 114. Therefore, the step at 430°C could be due to the degradation of CLA/CLO heterosequences while the process at 453°C could result from the degradation of enriched PCLA blocks.

3.2.1.2. *Hi-Res™ TGA measurements.*

The blocky structure is further confirmed by Hi-Res™ TGA carried out on D1E sample (Fig. 7). Indeed four main degradation steps are observed at ca. 340 (60.9%), 379 (12.1%), 395 (7.1%) and 420°C (12.3%) and are assigned as follows: the first step should be due to the PCLO blocks, the last one to the degradation of PCLA blocks. The attribution of the two intermediate peaks is more difficult since they can be due to the degradation of CLA/CLO heterosequences or to another degradation step of the respective homosequences. Indeed the degradations of the PCLO and PCLA homopolymers are known to proceed in two main steps.

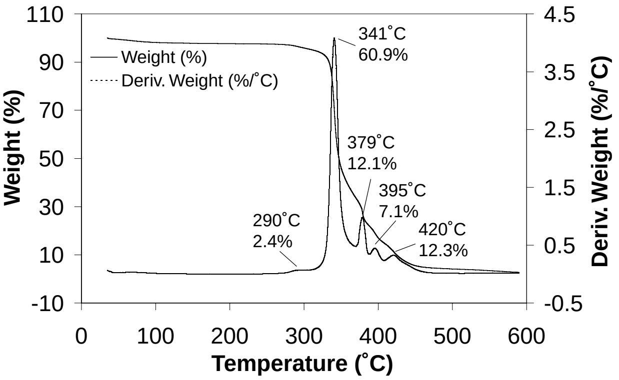


Fig. 7. Hi-Res™ TGA thermogram of copolymer D1E. Heating rate: 30°C min^{-1} (resolution parameter = 5) under He as purge gas.

3.2.2. *Influence of the polymerization temperature*

The results obtained by TGA/MS on the copolymers synthesized with 15 wt% CLO and 1 mol% CLAMgBr at different polymerization temperatures are collected in Table 3.

Neither the temperature of the different degradation steps nor the weight loss observed at every step are significantly influenced by the copolymerization temperature suggesting that the structure of these copolymers should be the same. Furthermore, very similar MS spectra are recorded whatever the copolymer studied. This is very interesting because the materials differ distinctly in mechanical properties, e.g. toughness [11].

3.2.3. *Influence of the initial content of initiator*

3.2.3.1. *Study by TGA/MS.*

The results obtained by TGA/MS on the copolymers prepared with 15 wt% CLO but promoted by a lower content in CLAMgBr (0.5 mol%) at either 150 or 160°C are shown in Table 4.

First and in agreement with Table 3, Table 4 shows that the characteristic temperatures of the different steps of degradation are not significantly influenced by the polymerization temperature. Compared to samples D4E and D5E, both prepared with 1 mol% CLAMgBr (Table 3), samples studied in Table 4 (with 0.5%mol CLAMgBr, all other conditions kept unchanged) undergo a two-stage degradation with maxima centered on ca. 440 and 460°C. No degradation at lower temperature is actually observed, such degradation would have been assigned to PCLO blocks. The presence of two main degradation processes instead of three for the samples prepared with 1 mol% CLAMgBr might suggest that the copolymers AK, i.e. copolymerized with 0.5 mol% CLAMgBr, might not display very well defined blocky structure. The degradation of PCLA occurring at higher temperatures than that of

Table 3
Temperatures at maximum of DTGA peaks and weight loss at every degradation step as recorded by TGA/MS for the degradation of P(CLA-*co*-CLO) synthesized at different polymerization temperatures T_p with 15 wt% CLO in the presence of 1 mol% CLAMgBr (see Table 1)

Samples	T_p (°C)	First step	Second step	Third step
D1E	120	305°C	430°C	453°C
		6.7%	45.3%	47.3%
D2E	130	303°C	430°C	447°C
		5.2%	50.4%	43.9%
D3E	140	295°C	424°C	453°C
		3.8%	58.3%	36.1%
D4E	150	304°C	427°C	446°C
		11.1%	51.3%	38.1%
D5E	160	313°C	436°C	459°C
		6.8%	57.9%	33.2%
D6E	170	307°C	421°C	438°C
		14.7%	36.1%	16.9%
D7E	180	309°C	444°C	461°C
		8.7%	59.9%	31.0%

PCLO, the step at ca. 460°C should be due to the degradation of PCLA blocks while the process at 440°C should be relative to the CLA/CLO heterosequences. Therefore, an increase of the relative content in CLAMgBr seems to favor the synthesis of more blocky copolymers.

3.2.3.2. Hi-Res™ TGA measurements. The presence of four and even five degradation steps in Hi-Res™ TGA thermograms of the copolymers prepared with 0.5 mol% of CLAMgBr (Table 5) support the hypothesis of a blocky structure since the first step is likely due to the degradation of the (enriched) PCLO blocks while the degradations above 400°C may result from that of the (enriched) PCLA sequences. The assignment of the intermediate steps is not staightforward but it can be anticipated that the process close to 400°C should result from the CLA/CLO heterosequences while the degradation at 380°C should be due to PCLO blocks containing a non-negligible quantity of CLA units.

Moreover, the temperature at which the first degradation step takes place, i.e. at 360°C, is systematically higher compared to D1E sample (340°C, see Table 5). Again, this could be explained by the higher CLA content in PCLO blocks for copolymers prepared with 0.5 mol% rather than with 1 mol% CLAMgBr. Therefore, this supports a blocky structure somehow less well defined in copolymers prepared with 0.5 mol% CLAMgBr, as already pointed out from TGA/MS investigations.

Table 4
Temperatures at maximum of DTGA peaks and weight loss at every step as recorded by TGA/MS for the degradation of P(CLA-*co*-CLO) synthesized at 150 and 160°C with 15 wt% CLO in the presence of 0.5 mol% CLAMgBr

Samples	T_p (°C)	First step	Second step
AK2E	150	445°C	460°C
		74.0%	24.7%
AK17E	160	440°C	466°C
		70.5%	29.5%

It is worth noting that again the copolymerization temperature does not have a significant effect on the thermal behavior and therefore, on the structure of the copolymers.

However, it is surprising to observe that in each case the weight loss (from 30 to 60%) relative to the PCLO blocks degradation steps that are systematically much higher than the initial quantity of CLO used in copolymerization (15 wt% CLO). This is also observed by comparing the degradation behavior of P(CLA-*co*-CLO) copolymers prepared with different relative contents in CLO units (Table 6). More degradation steps are actually observed in Hi-Res™ TGA thermograms of copolymers enriched in CLO units (ZK30E and ZK40E). Such a thermal behavior can only be explained by a sequential distribution of the comonomers along the copolymers. The first two degradations at ca. 320 and 350°C more likely result from the degradation of (enriched) PCLO blocks. Compared to data gathered in Table 5, increasing the CLO content from 15 to 40 wt% induces an increase of both weight loss and degradation temperature relative to the PCLO sequences. However, there is again no direct correlation between the weight loss triggered by the PCLO blocks degradation step(s) and the initial quantity of CLO comonomer.

In order to shed some light on this apparent discrepancy, experiments by Hi-Res™ TGA have been carried out on PCLO/PCLA polymers blends.

3.3. Thermal degradation of PCLA/PCLO blends

Blends with different compositions have been studied by Hi-Res™ TGA. The temperature at maximum of DTGA peaks as well as the weight loss relative to each step are summarized in Table 7. For the sake of comparison, Hi-Res™ TGA of PCLO has been recorded under the same experimental conditions, i.e. with a heating ramp of 30°C min^{-1} and a resolution parameter of 5 under He as purge gas. Two resolved degradations are detected at ca. 310 and 335°C.

For blends with high PCLO contents (30 and 40 wt%), a DTGA peak or simply a shoulder around 350°C is observed, which should be due to the degradation of PCLO chains. Therefore, the second step above 350°C should be attributed to the degradation of PCLO sequences containing some CLA units. Such sequences would result from fast transacylation reactions occurring between the PCLA and PCLO polymers at high temperature. This hypothesis is supported by the fact that the increase of the PCLO content in the blend induces both a decrease of the temperature corresponding to this degradation step and an increase of the respective weight loss (valid for all partial degradation steps, see Table 7).

The last two steps should result from the degradation of PCLA chains. Very similarly to PCLO degradation steps,

Table 5
Hi-Res™ TGA of P(CLA-*co*-CLO) copolymers synthesized with 15 wt% CLO in the presence of 0.5 mol% CLAMgBr at a given temperature T_p. Temperatures at maximum of DTGA peaks and weight loss at every degradation step

Samples	T_p (°C)	First step	Second step	Third step	Fourth step	Fifth step
AK21E	130	360°C	379°C	393°C	407°C	420°C
		48.6%	10.0%	14.6%	10.5%	12.2%
AK20E	140	360°C	378°C	398°C	410°C	427°C
		42.8%	11.2%	19.2%	10.8%	10.2%
AK2E	150	361°C		399°C	Shoulder	428°C
		46.9%		37.3%		11.8%
AK17E	160	360°C	Shoulder	398°C	409.8°C	424°C
		51.9%		22.2%	10.1%	10.1%
D1E	120[a]	341°C	379°C	397°C	–	423°C
		61.2%	11.7%	6.7%	–	11.3%

[a] In the presence of 1.0 mol% CLAMgBr.

the temperature of the degradation around 400°C decreases with the increase in PCLO amount. Therefore this DTGA peak should be relative to PCLA chains containing a non-negligible amount of CLO units. Consequently the shoulder or the peak around 370–385°C should correspond to the degradation of some CLA/CLO heterosequences.

Whatever the blend, the weight loss relative to the PCLO degradation is never proportional to the PCLO contents in the blend. It means that the degradation steps previously attributed for the copolymers remains correct but unfortunately it also means that no quantification of the blocky structure in the copolymers can be made. Indeed, an explanation for the lack of proportionality between the weight loss relative to a given sequence and its content in the copolymer could be due to exchange reactions (‘scrambling’ reactions) occurring during the heating step of the samples. The thermal treatments above PCLA and PCLO melting temperatures should increase the chain mobility and favor transacylation reactions between PCLO and PCLA. This leads to the formation of heterosequences and the incorporation of CLO units in PCLA blocks and the opposite. This is confirmed by the presence of a DTGA peak around 370°C relative to the intermediate sequence whose extent increases with the PCLO content in the blends. Hence, CLA units incorporated in the PCLO blocks are likely evolved during the main degradation of PCLO blocks as previously evidenced by TGA/MS.

Another way to support the existence of such scrambling reactions upon heating has been achieved by heating at 185°C for 30 min a given copolymer (D1E sample, see Table 1) right above its highest melting temperature. Then, a TGA was recorded from 20 to 600°C under helium as purge gas with a heating ramp of 20°C min^{-1}. TGA thermogram displays three degradation steps, respectively, at 424, 436 and 459°C. Compared to the TGA thermogram recorded on the same sample but without any previous thermal treatment (see D1E sample in Table 3), the first degradation initially observed at 305°C totally disappeared and a new degradation step appears at a much higher temperature (at 424°C). The other two high temperature degradations still take place in the same temperature range. Such a thermal behavior can be explained by the occurrence of intermolecular transacylation reactions, which convert the PCLO blocks into CLA/CLO heterosequences known to degrade at 424 and 435°C depending on their comonomer composition.

4. Conclusion

TGA-*co*-MS/FTIR and Hi-Res™ TGA measurements have pointed out that the mechanism of degradation of the PCLA involves both an unzipping depolymerization leading to the production of ε-caprolactam and random chain cleavage through amide pyrolysis. TGA experiments have been carried out also on P(CLA-*co*-CLO) polymers with 15 wt% ε-caprolactone as copolymerized in bulk in the presence of ε-caprolactammagnesium bromide (0.5 or

Table 6
Hi-Res™ TGA of P(CLA-*co*-CLO) copolymers with different CLO relative contents synthesized in bulk at 150°C in the presence of 0.5 mol% CLAMgBr. Temperatures at maximum of DTGA peaks and weight loss at every degradation step

Samples	CLO (wt%)	First step	Second step	Third step	Fourth step	Fifth step
AK2E	15	–	–	361°C	399°C	428°C
		–	–	46.9%	37.3%	11.8%
ZK30E	30	321°C	350°C	375°C	393°C	418°C
		3.9%	63.6%	7.3%	8.6%	11.6%
ZK40E	40	316°C	347°C	360°C	377°C	422°C
		2.1%	61.9%	14.7%	4.9%	9.6%

Table 7
Hi-Res™ TGA of PCLA/CLO blends with different compositions. Temperatures at maximum of DTGA peaks and weight loss at every degradation step

Blends PCLO/PCLA					
PCLO (wt%)	Successive steps				
10		370°C	385°C	402°C	434°C
		27.4%	9.4%	46.3%	8.2%
20		364°C	385°C	400°C	443°C
		38.7%	9.3%	38.8%	8.7%
30	351.3°C	360°C	366°C	390°C	422°C
	4.5%	46.9%	15.8%	9.1%	8.8%
40	Shoulder	355°C	369°C	383°C	Shoulder
		59.6%	12.4%	7.4%	

1 mol%). As PCLO and PCLA blocks are degraded at well separated temperature ranges, the presence in the thermograms of degradation steps in the close vicinity of their respective degradation temperatures gives credit to the existence of at least enriched PCLO and PCLA blocks in the copolymers. This has been confirmed by the TGA/MS measurements that show the formation of ε-caprolactone cyclic monomer at the low degradation temperature range. The evolution of ε-caprolactone confirms the blocky structure of the copolymers since it can only be produced by a mechanism of unzipping depolymerization of (enriched) PCLO blocks. Moreover, at higher temperatures 5-hexenamide were detected by MS indicating the degradation of PCLA blocks. Degradations occurring at intermediate temperatures were attributed to the CLA/CLO heterosequences.

The copolymerization temperature (from 120 to 180°C) does not significantly influence the thermal behavior of the copolymers, implying that their structure is quite similar at a given composition. On the contrary, the relative content of ε-caprolactammagnesium bromide (CLAMgBr) used as an anionic promoter for the copolymerization have proven to be essential for the sequential distribution of the comonomers. Indeed a higher content in CLAMgBr provides copolymers with a more blocky structure.

However, the attribution of the degradation steps has been questioned since the weight loss relative to the degradation step(s) of PCLO blocks is not proportional to the CLO content. This apparent discrepancy can be explained by the existence of exchange reactions (transacylation reactions) occurring before the weight loss of the sample. The thermal treatment of copolymers or PCLA and PCLO blends above their melting temperature leads to the incorporation of CLO units in PCLA and the opposite, which explains the aforementioned non-proportionality. Such exchange reactions have also been evidenced by TGA performed on a copolymer previously heated at high temperature for a few minutes. This experiment revealed the complete disappearance of the degradation step initially detected for the PCLO blocks, these being converted in CLO/CLA heterosequences. Thus, one can conclude that anionic copolymerization of CLO and CLA promoted by ε-caprolactammagnesium bromide yields copolyester/amides with a rather blocky-like structure, with enriched PCLO and PCLA sequences. The reported results determine the efficiency of TGA-*co*-MS/FTIR and Hi-Res™ TGA analyses in (co)polymer characterization. However, in the specific study of P(CLA-*co*-CLO) copolymers, quantitative analysis cannot be performed due to exchange (scrambling) reactions taking place at high temperature.

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