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Structural characterization and hydrolytic degradation of solid copolymers of D,L-lactide-co-ε-caprolactone by Raman spectroscopy

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Abstract

A series of copolymers of DL-lactide and ε-caprolactone (PLA_XCL_Y: X, % L-lactyl and Y, % ε-caproyl units) were synthesized by ring-opening polymerization. Chemical composition, molecular weight, morphology and configuration were studied by Raman spectroscopy. Hydrolytic degradation was monitored comparatively by various techniques. Preferential degradation appeared in D,L-LA units in all the compounds. After 33 days, crystallinity increased in the degradation products of $PLA_{12.5}CL_{75}$ due to crystallization of the chain fragments enriched in CL-units, whereas $PLA_{25}CL_{50}$ and $PLA_{37.5}CL_{25}$ initially amorphous remained amorphous. The initially amorphous PLA_XCL_Y copolymers with $X \geq 40\%$ and $Y \leq 20\%$, i.e. having rather long PLA chain segments, yielded crystalline degradation products identified as composed of an oligomeric stereocomplex formed by L-LA, D-LA crystallizable fragments. From the viewpoint of degradation-induced morphology changes, PLA/CL behaved like PLA/GA copolymers but on a much longer time scale, PGA segments in PLA/GA copolymer playing the same role as the PLA ones in PLA/CL copolymers, i.e. being the more sensitive to hydrolysis. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: DL-Lactide; ε-Caprolactone; Copolymers

1. Introduction

In the family of polyesters used for many biomedical applications, poly(ε-caprolactone) or PCL and poly(lactide)s or PLA_X (X representing the percentage of L-lactic (L-LA) units in the monomer feed) have attracted considerable attention because of their biodegradability and miscibility with a variety of polymers [1]. PCL is biocompatible and permeable to many compounds. It is used as matrix for controlled drug release [2,3] and for agricultural purposes [4] as well. Semicrystalline poly(L-lactide) or PLA_{100} degrades slowly by simple hydrolysis in vivo, whereas poly(D,L-lactide) stereocopolymers or PLA_X degrade more rapidly. The homopolymer PCL itself is degraded very slowly when compared with poly(glycolide) and poly(lactide)s [5]. Slower degradation is preferable for long term delivery systems such as *Capronor*®, a 1-year release contraceptive device [6]. The degradation of PCL and PLA_{50} films in contact with enzymes (cell-tissues) had been reported as proceeding by non-enzymatic random hydrolytic scission of esters linkage [7,8]. Basically, degradability can be greatly enhanced if one deals with copolymers instead of homopolymers, as it was shown by many authors, especially for copolymers between lactide, glycolide or other lactones [9]. It as also been shown that degradation of hydrolytically degradable polyesters can lead to dramatic morphology changes with partial crystallization of degradation products [10,11].

Crystallinity is well known to play an important role in determining both permeability and biodegradability. PLA_X stereocopolymers are amorphous when the percentage X of L-LA units is lower than 90%. The crystallinity of PCL varies with its molecular mass and increases from 40 to 80% as the molecular weight decreases from high molar mass to 5000. Degradation-induced morphology changes are now considered as a major phenomenon in chemical degradation process because an initially amorphous polymeric material can lead to crystalline residues which can remain much longer in the body as a result of the well-known slower degradation of crystalline domains. In particular, the degradation of the amorphous stereocopolymers poly(D,L-lactide) or PLA_{50} [10] has been found to yield rather large amounts of crystalline degradation residues identified as composed of stereocomplex formed by L-LA, D-LA crystallizable oligomeric fragments [11]. The formation of such a stereocomplex PLA_{stereo} was correlated to the

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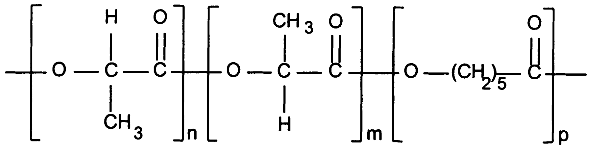
fact that the D,L-lactide ring opening polymerization leads to polymer chains containing rather long poly(L-LA) and poly(D-LA) sequences which become crystallizable once they are set free by degradation [11].

The characterization, structure and mechanical properties of PCL and its copolymers with lactide have been studied in recent years by size-exclusion chromatography, differential scanning calorimetry, X-ray diffractometry, nuclear magnetic resonance spectrometry and stress–strain testing [12,13]. However, vibrational spectroscopies, Raman scattering in particular, has never been used, although they appeared as powerful tools for the study of polymer structures [14,15]. Raman spectrometry is a remarkable technique to investigate: (i) the presence and the extent of conformational and configurational isomerisms from band frequency assignments; (ii) the degree and nature of crystalline and non-crystalline microdomains from the intensities of the assigned bands, their bandwidth and/or position; (iii) the nature of chain folding from mixed IR and Raman studies of crystals. Moreover, a great advantage of Raman technique over other techniques is that monitoring of Raman scattering does not require specific preparation and does not affect the morphological history of the sample. This method has already been used to study polyglycolide [16], polylactides [17,18] and their copolymers [19]. It was shown suitable to distinguish polylactides of same racemic composition in L- and D-lactyl units and different units distribution such those existing in poly(D,L-lactide), poly(mesolactide) and polylactide stereocomplex [17].

The aim of the present work was to synthesize poly(ε-caprolactone-co-D,L-lactide) copolymers of different compositions and to compare the influence of this ratio on their structural properties and on their biodegradability. For the sake of clarity, the various PLA/CL copolymers were currently named by the acronym $\mathrm{PLA}_X\mathrm{CL}_Y$ where X is the percentage $n/(n + m + p)$ of L-LA units present in the monomer feed and Y is the percentage $p/(n + m + p)$ of CL-units, the percentage in D-LA units being $100 - (n + p)$.



$$\left[\mathrm{O}-\overset{\mathrm{H}}{\underset{\mathrm{CH_3}}{\mathrm{C}}}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\right]_n\left[\mathrm{O}-\overset{\mathrm{CH_3}}{\underset{\mathrm{H}}{\mathrm{C}}}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\right]_m\left[\mathrm{O}-(\mathrm{CH_2})_5-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\right]_p$$

Characteristic vibrational bands of solid state Raman spectra of PCL homopolymer and its various $\mathrm{PLA}_X\mathrm{CL}_Y$ copolymers with D,L-lactide were discussed in comparison with the results of previous vibrational studies on poly(glycolide) [16], poly(L-lactide) homopolymer and its stereocopolymers [17] and on their copolymers $\mathrm{PLA}_X\mathrm{GA}_Y$ [19]. Correlation was made with morphology and configuration. Assignments and band variations were used to monitor the degradation process of the copolymers, the crystallinity and the compositional changes, as well.

2. Experimental

2.1. Materials

D,L-lactide was purchased from Purac (The Netherlands). Before use, it was recrystallized from acetone and vacuum dried at room temperature under reduced pressure. ε-caprolactone and PCL were supplied by Aldrich (France) and were used as received. Poly(D,L-lactide) was synthesized by ring-opening bulk polymerization of D,L-lactide by using Zn metal in the melt at 145°C [19]. The $\mathrm{PLA}_X\mathrm{CL}_Y$ copolymers were synthesized by ring opening polymerization of D,L-lactide and ε-caprolactone, according to a slightly modified procedure [20]. The two monomers (1/1 in mol) were introduced into a round-bottomed flask with 0.01% zinc lactate as initiator instead of zinc metal. After degassing, the flask was sealed under vacuum and allowed to stir 145°C for 8 days. The resulting crude polymers were purified by the dissolution/precipitation method using acetone as solvent and methanol as non-solvent. Circular plates (75 mm diameter and 2 mm thickness) were processed by compression moulding copolymer chips at 120°C with a pressure of 100 bars. From these circular plates, parallel-sided specimens ($10 \times 10 \times 2\ \mathrm{mm}^3$) were machine cut.

2.2. Hydrolytic degradation

For each copolymer, specimens were placed into small flasks filled with 25 ml of 0.13 M isoosmolar phosphate buffer ($\mathrm{pH} = 7.4$) containing 0.02% $\mathrm{NaN_3}$ to prevent bacteria development. The flasks were allowed to stand in a thermostated oven at 50°C for 33 days. At each degradation time, two specimens were withdrawn and washed with distilled water. Data were the average of the measurements for two specimens.

2.3. Methods

2.3.1. NMR spectra

^{1}H nuclear magnetic resonance (NMR) spectra were carried out on a Brucker AMX360 spectrometer operating at 100, 250 and 400 MHz. The spectra were obtained from 1%(w/w) solutions in DMSO-$\mathrm{d_6}$. Chemical shifts (δ) were expressed in ppm, the DMSO resonance at 249 ppm with respect to TMS being used as internal reference. All the spectra were recorded at room temperature.

2.3.2. X-ray diffraction

X-ray diffraction spectra were recorded on a diffractometer equipped with a CuKα ($\lambda = 0.155$ nm) source, a monochromator and a CGR goniometric plate.

2.3.3. Raman spectra

Raman spectra were obtained with a Jobin-Yvon HG2S spectrometer. The 514.5 nm line of the Spectra Physics 2017 argon ion laser was used as excitation source. Laser

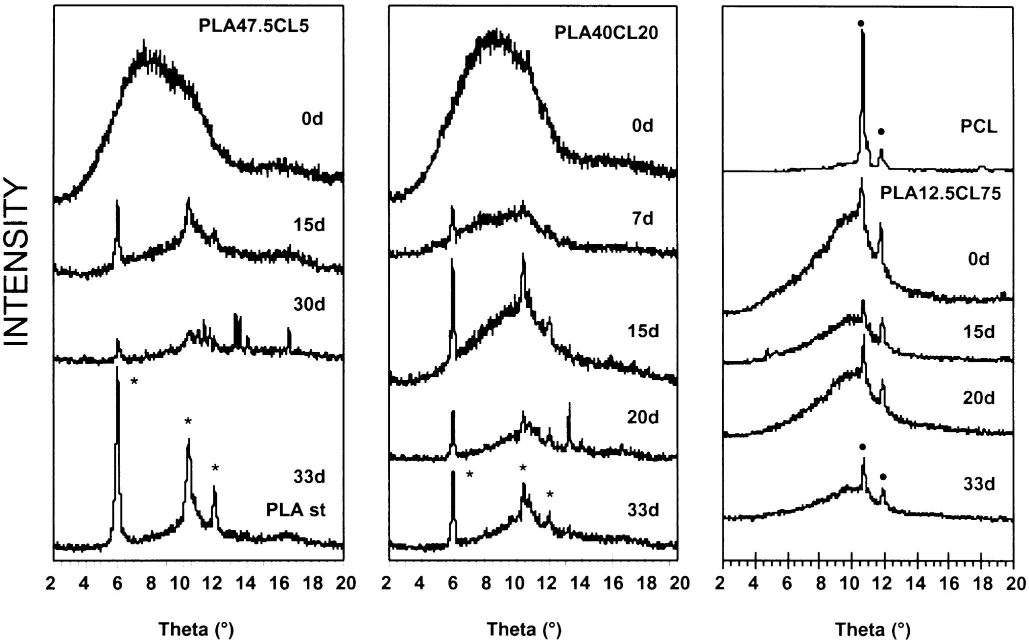


Fig. 1. X-ray diffractograms of PCL, $PLA_{stereocomplex}$, $PLA_{47.5}CL_5$, $PLA_{40}CL_{20}$ and $PLA_{12.5}CL_{75}$ during the first 33 days of hydrolytic degradation. (st: $PLA_{stereocomplex}$, ★: crystalline PLA_{st}, ●: crystalline PCL.)

power was 100 mW. The scanning operations and data processing were under the control of a Spectralink board and an IBM PC computer. The integration time was 1 s with a scanning increment of 1 cm^{-1} and a bandwidth of 2 cm^{-1}. Homopolymers and copolymers were analyzed under the form of small fragments cut from the round plates (dried for degraded samples) without any other specific preparation. Spectra were recorded at room temperature after the exposure time necessary to decay the fluorescence.

3. Results and discussion

The spectral analysis of the different PLA_XCL_Y copolymers was based on previous results obtained for PLA_{100} homopolymer and ‘preferentially isotactic’ PLA_{50} derived from D,L-lactide polymerization [16,17]. The PCL homopolymer was studied in the semicrystalline solid form and in the melt only because amorphous solid form cannot be obtained.

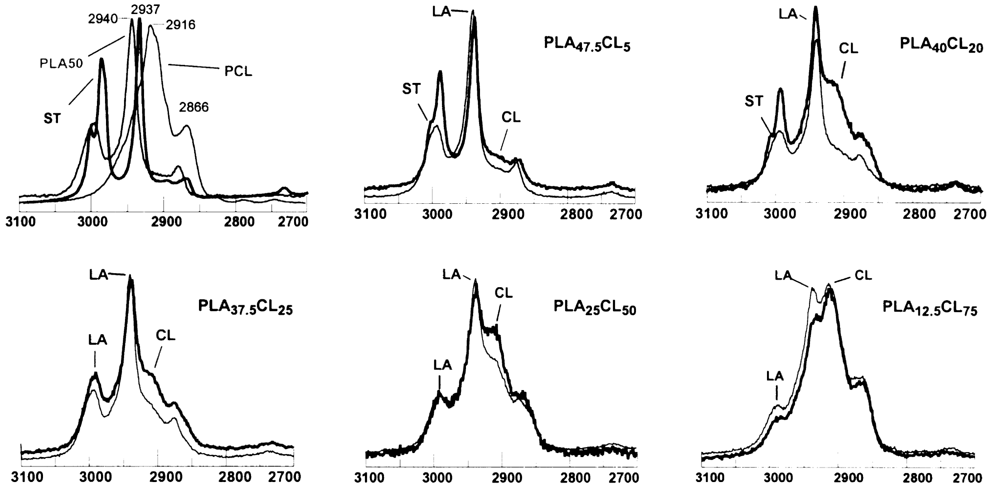


Fig. 2. Raman spectra of polymers and PLA_XCL_Y copolymers after 0 and 33 days of hydrolytic degradation in the CH stretching region. (Bold line: after 33 days of hydrolytic degradation.)

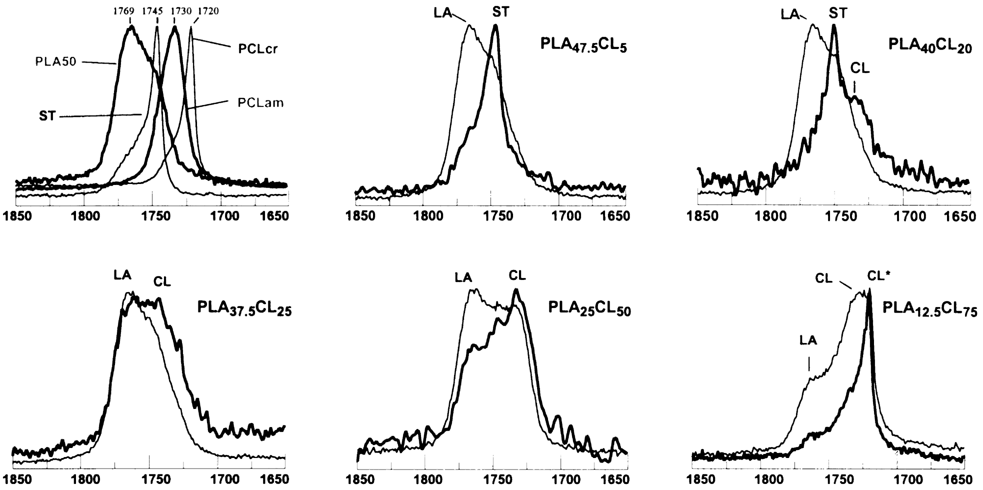


Fig. 3. Raman spectra of polymers and PLA_XCL_Y copolymers after 0 and 33 days of hydrolytic degradation in the C=O stretching region. (Bold line: after 33 days of hydrolytic degradation.)

3.1. Poly(ε-caprolactone)

PCL is a semicrystalline polymer with an orthorhombic unit cell compatible with an extended planar chain conformation involving two monomer residues related by a twofold screw axis in the chain direction [21]. The $P2_12_12_1$ space group indicates that the unit cell contains two chains with opposite orientation. The X-ray diffraction spectrum of regular PCL showed three peaks located at 10.7, 11.0 and 11.9° (Fig. 1). The factor group is D_2^4 isomorphous with the D_2 point group. All the vibrational modes are authorized in the infrared and Raman spectra [13]. The CH stretching region (3100–2800 cm^{-1}) is shown in Fig. 2. Two Raman peaks presenting shoulders were observed, centered respectively, at 2916 and 2866 cm^{-1}. Figs. 3 and 4 present the Raman spectra of semicrystalline and molten PCL (90°C) in the 1850–100 cm^{-1} region. A narrow line was observed at 1720 cm^{-1} which was assigned to νC=O stretching mode. Several further narrow peaks at 1470–1415 (δCH_2), 1303–1281 (wCH_2), 1107–1033 (skeletal stretching) and 912 (νC–COO) (cm^{-1}) reflected crystalline domains. These vibrational modes were found at similar frequencies in the IR spectrum. The lines observed in the Raman spectrum of molten PCL, assumed to be similar to those of amorphous compound, were broader with no splittings. They presented small shifts in frequency, as referred to crystalline compound. In particular, the νC=O stretching was shifted to 1730 cm^{-1}. Moreover, the presence of the broad band at 868 cm^{-1} and the absence of the 1107 and 912 cm^{-1} narrow peaks were also discriminant to characterize the amorphous part of PCL.

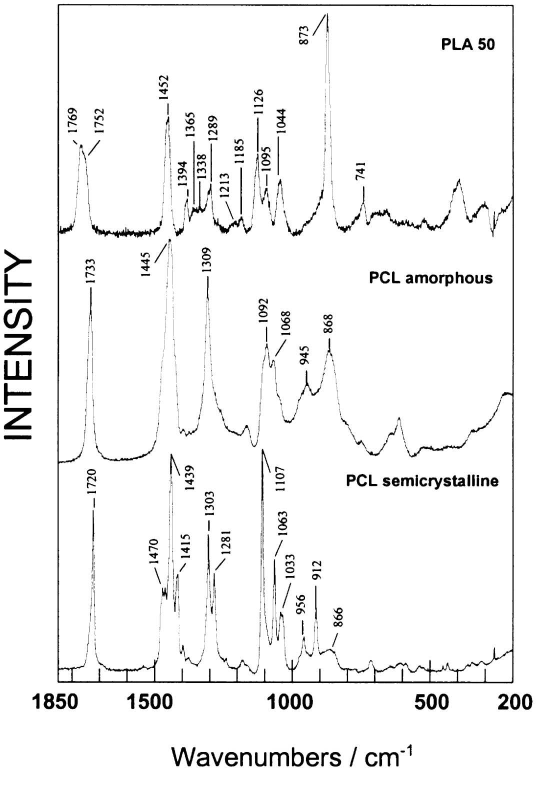


Fig. 4. Raman spectra of PLA_{50}, $PCL_{amorphous}$ and $PCL_{semicrystalline}$.

3.2. Poly(D,L-lactide)

PLA_{50} obtained from a feed composed of 50/50 w/w of L- and D-lactide is an amorphous 'preferentially isotactic' polymer characterized by the predominance of *iso* dyads (L,L or D,D pairs) over L,D or D,L *hetero* dyads [22]. Fig. 2 shows the CH and CH_3 stretching region (3100–2800 cm^{-1}) where three Raman lines at 2993, 2940 and 2874 cm^{-1} are observed. In Fig. 3, the carbonyl region showed the disymmetric band at 1769–1752 cm^{-1} which is typical of the particular chiral unit enchainments generated by the pair addition mechanism. The presence of a large band covering the 1300–1360 cm^{-1} zone and including the band at 1338 cm^{-1} due to the presence of D-LA units is typical of

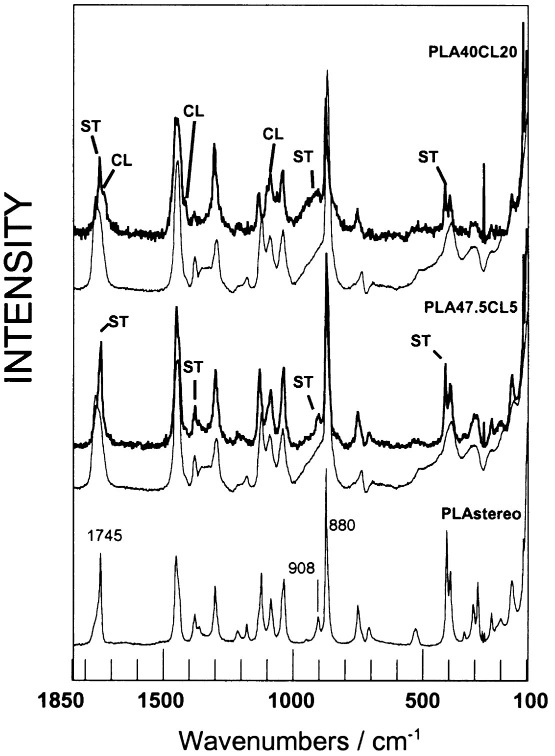


Fig. 5. Raman spectra of $PLA_{stereocomplex}$ and PLA_XCL_Y ($X \geq 40\%$) after 0 (bottom) and 33 (top) days of hydrolytic degradation in the 200–1850 cm^{-1} region: CL: ε-caproyl unit ST: $PLA_{stereocomplex}$. (Bold line: after 33 days of hydrolytic degradation.)

the 'preferentially isotactic' PLA_{50} [17]. This band is attributed to δCH and δCH_3 bending modes. The most intense line located at 873 cm^{-1} was identified as the νC–COO stretching mode (Fig. 4).

3.3. Poly(lactide) stereocomplex

PLA_{stereo} is a stereocomplex which is formed between two isomeric $PLA_{100} + PLA_0$ chains. It is a semicrystalline compound with a triclinic unit cell involving both the poly(L-lactide) and poly(D-lactide) chains were left-handed 3_1 helical PLA_{100} chain and right-handed 3_1 helical PLA_0 chains are side by side alternatively [23]. In contrast, PLA_{100} homopolymer crystallizes within a 10_3 helical conformation [17]. The X-ray diffraction spectrum of stereocomplex showed three peaks located at 5.96, 10.3 and 12.0° (Fig. 1). The νCH and νCH_3 stretching region (Fig. 2) showed medium to strong splitted lines as doublets at 2871–2890, 2937 and 2990–3007 cm^{-1}.

In Figs. 3–5, the Raman spectrum of PLA_{stereo} differed from PLA_{100} by the presence of narrow lines shifted in frequency, especially from 1773–1763–1749 [17] to 1745 cm^{-1} (νC=O) and from 873 to 880 cm^{-1} (νC–COO). A doublet was also detected at 398–411 cm^{-1} (deformation modes). The 908 cm^{-1} line was characteristic of the skeletal stretching mode of the 3_1 helix, whereas the 920 cm^{-1} peak was observed in PLA_{100} of 10_3 helical conformation [17].

3.4. Poly(D,L-lactide-co-ε-caprolactone)

$PLA_{47.5}CL_5$, $PLA_{40}CL_{20}$, $PLA_{37.5}CL_{25}$, $PLA_{25}CL_{50}$, $PLA_{20}CL_{60}$ and $PLA_{12.5}CL_{75}$ were studied. Copolymer compositions were determined by ^{1}H-NMR, and the physical characteristics, molecular weights (by SEC), thermal properties (by DSC) are presented in Table 1.

3.4.1. Morphology

The X-ray diffraction spectra shown in Fig. 1 revealed that only $PLA_{12.5}CL_{75}$ was crystalline with two weak peaks at 10.7° and 11.9° characteristic of crystalline CL-units, according to a rather low crystallinity. Figs. 5 and 6 present the Raman spectra in the 100–1850 cm^{-1} region. In all the compounds with $Y \leq 60\%$, no crystalline peak was observed in agreement with the amorphous character shown by X-ray studies. After subtracting the PLA_{50} spectrum [17] from the PLA_XCL_Y ones, the obtained spectrum was comparable that of molten PCLs with CL-unit bands typical of assigned to disordered domains. Only the $PLA_{12.5}CL_{75}$ spectrum showed the peaks characteristic of slightly crystalline PCL domains at 1720, 1107 and 912 cm^{-1}. In particular, the component analysis of the stretching carbonyl region (Fig. 7) revealed four bands at 1769–1750 (D,L-LA amorphous band), 1733

Table 1
Characterization of PLA_XCL_Y copolymers

		$PLA_{47.5}CL_5$	$PLA_{40}CL_{20}$	$PLA_{37.5}CL_{25}$	$PLA_{25}CL_{50}$	$PLA_{12.5}CL_{75}$
SEC	$\bar{M}_n$	14 000	11 400	26 000	34 000	33 000
	$\bar{M}_w$	26 000	22 000	49 000	70 000	67 000
DSC	T_v(°C)	43	18	16	−18	−37
	T_f(°C)	—	—	—	—	44
^{1}H NMR						
	L-units %	95	40	37.5	25	12.5
	CL-units %	5	20	25	50	75
	$\bar{L}_c$[a]	4.75	2.8	2	2.8	4.75
Morphology		Amorphous	Amorphous	Amorphous	Amorphous	Semi crystalline

[a] Average lengths of ε-oxycaproyl sequences.

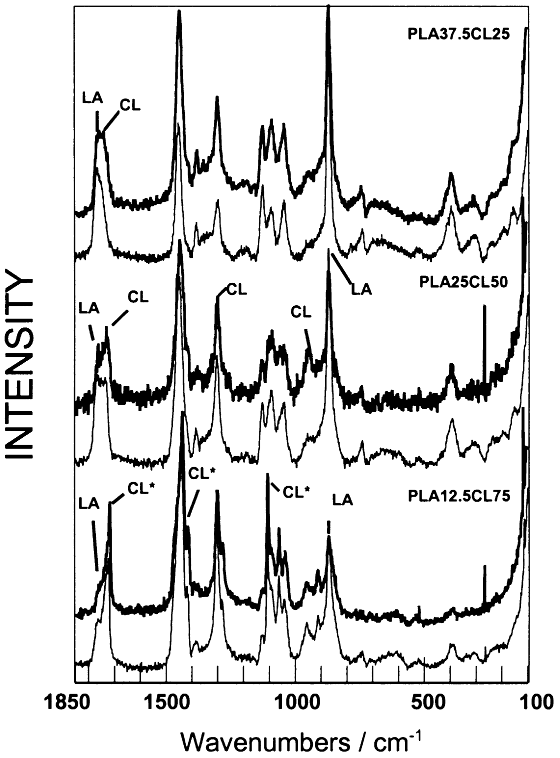


Fig. 6. Raman spectra of PLA_XCL_Y ($X < 40\%$) after 0 (bottom) and 33 (top) days of hydrolytic degradation in the 200–1850 cm^{-1} region: CL: ε-caproyl unit CL*: crystalline ε-caproyl unit LA: lactyl unit. (Bold line: after 33 days of hydrolytic degradation.)

(CL-amorphous band) and 1720 cm^{-1} (CL-crystalline band).

3.4.2. Configuration

The stereostructures were studied by comparing the spectra of PLA_XCL_Y copolymers and of PLA_{50} in the 1300–1360 cm^{-1} region corresponding to $\delta_S(CH_3)$ and $\delta(CH)$ bending modes (Figs. 5 and 6). When the percentage Y of ε-oxycaproyl units was $\leqslant 60\%$, the copolymers spectra exhibited a large band lying from 1300 to 1360 cm^{-1} which was shown as typical of the presence of PLA_{50} lactyl units. Moreover, by subtracting the amorphous and semi-crystalline PCL spectra from those of $PLA_{37.5}CL_{25}$, $PLA_{25}CL_{50}$ and $PLA_{12.5}CL_{75}$, the PLA_{50} spectrum was obtained. This finding indicated that the rather long sequences of D,L-LA units with predominant *iso*-dyads (LL, or DD pairs) were present in copolymer macromolecular chain, forming rather long blocks of L- or D-lactic units [17].

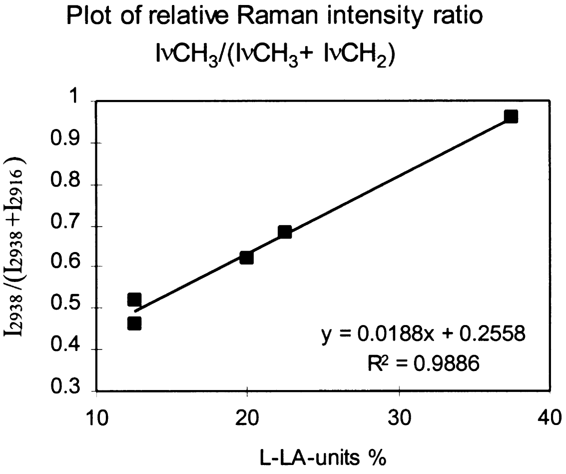


Fig. 8. Plot of Raman relative intensity ratio $I_{\nu(CH_3)}/(I_{\nu(CH_3)} + I_{\nu(CH_2)})$ versus % L-LA units content.

3.4.3. Copolymer composition

Differentiation of copolymers with different compositions in CL units was possible considering the νCH and νC=O stretching regions of Raman spectra, as exemplified for a series of samples (Figs. 2 and 3).

Fig. 2 presents the spectra of five copolymers in the 2700–3100 cm^{-1} region. The component analysis realized on $PLA_{12.5}CL_{75}$ (Fig. 7) showed the presence of five bands at 2995, 2938, 2916, 2875 and 2866 cm^{-1}. The three Raman lines at 2995, 2938 and 2875 cm^{-1} (νCH and νCH_3 stretching modes) were assigned to D,L-LA units according to

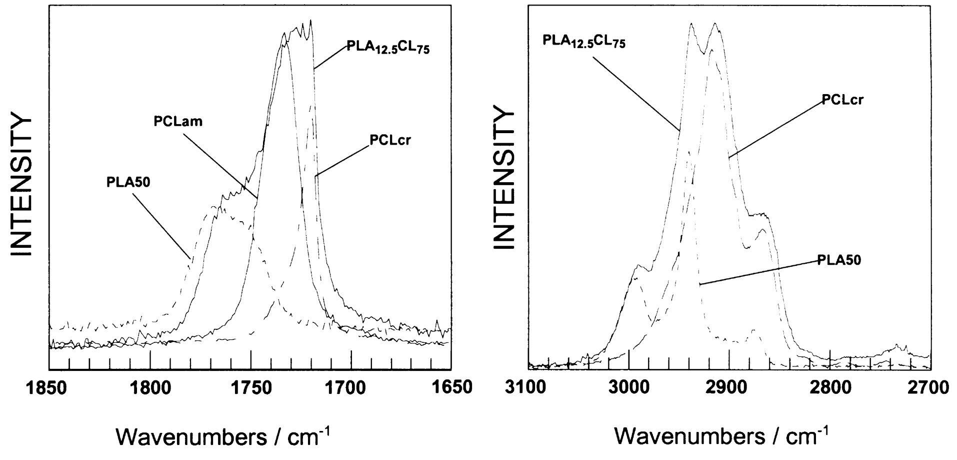


Fig. 7. Component analysis of $PLA_{12.5}CL_{75}$ copolymer by Raman spectroscopy in the νC=O and νCH regions.

Table 2
Compositional and morphological changes of PLA$_X$CL$_Y$ copolymers after 33 days of hydrolytic degradation

0 day			33days	
PLA$_{12.5}$CL$_{75}$	Semicrystalline (CL-units)	→	PLA$_{10}$CL$_{80}$	Semicrystalline (CL-units)
PLA$_{25}$CL$_{50}$	Amorphous	→	PLA$_{20}$CL$_{60}$	Amorphous
PLA$_{37.5}$CL$_{25}$	Amorphous	→	PLA$_{25}$CL$_{50}$	Amorphous
PLA$_{40}$CL$_{20}$	Amorphous	→	PLA$_{stereo}$CL$_{am}$	Semicrystalline (LA$_{stereo}$-units)
PLA$_{45}$CL$_{10}$	Amorphous	→	PLA$_{stereo}$	Semicrystalline (LA$_{stereo}$-units)

PLA$_{50}$ spectrum, whereas the two 2916 and 2866 cm^{-1} peaks (νCH$_2$ stretching) were assigned to CL-units according to PCL spectrum. The evaluation of the intensity ratio of the most intense bands, as $I^{LA}_{2938}/(I^{LA}_{2938} + I^{CL}_{2916})$, was reported as a function of content in L-LA units. A significant linear regression (R^2 determination coefficient = 0.989) was obtained (Fig. 8). Fig. 3 shows the spectra of the different PLA$_X$CL$_Y$ in the 1700–1800 cm^{-1} carbonyl region. The component analysis realized on PLA$_{12.5}$CL$_{75}$ (Fig. 7) can present four bands at 1720 cm^{-1} (PCL crystalline band), 1730 cm^{-1} (PCL amorphous band), 1752–1769 cm^{-1} (PLA$_{50}$ band).

3.5. Hydrolytic degradation

Five PLA$_X$CL$_Y$ copolymers were studied, namely PLA$_{42.5}$CL$_5$, PLA$_{40}$CL$_{20}$, PLA$_{37.5}$CL$_{25}$, PLA$_{25}$CL$_{50}$ and PLA$_{12.5}$CL$_{75}$. Figs. 2–6 present the Raman spectra of the solid samples obtained after 33 days of hydrolytic degradation at 50°C. Structural and composition changes were analyzed through the crystalline bands characteristic of PCL, PLA$_{100}$ and PLA$_{stereo}$ stereocomplex [16], and through the intensity ratios of the νCH and νC=O stretching mode Raman lines.

3.5.1. Crystallinity changes

After 33 days of hydrolysis at 50°C, the PLA$_{12.5}$CL$_{75}$ spectrum showed that the intensity of the CL-crystalline bands at 1107 cm^{-1} (skeletal stretching) and at 1720 cm^{-1} (νC=O) increased, reflecting an increase in crystallinity of PCL segments, as found by X-ray analysis (Fig. 1). Crystalline peaks did not appear in the spectra of degraded PLA$_{25}$CL$_{50}$ and PLA$_{37.5}$CL$_{25}$ confirming the amorphous character of the remnants (Fig. 5). Concerning the PLA$_X$CL$_Y$ with a high percentage of D,L-lactyl units ($X \geq 40\%$ and $Y \leq 20\%$), many changes were observed after the first 15 days. Spectra were modified and many bands appeared in the PLA$_{47.5}$CL$_5$ and PLA$_{40}$CL$_{20}$ spectra. The νC=O stretching region presented a narrow line at 1745 cm^{-1}, whereas the disymmetric band at 1769–1752 cm^{-1} (νC=O in PLA$_{50}$) disappeared. The δ(CCO) bending appeared as a doublet at 410–430 cm^{-1}. The 873 cm^{-1} band characteristic of PLA$_{50}$ 'preferentially isotactic' segments shifted at 880 cm^{-1}. In fact, these new bands were typical of the crystalline poly(lactide) stereocomplex or PLA$_{stereo}$ formed by the two PLA$_{100}$ and PLA$_0$ chains [17]. These results were confirmed by X-ray studies where the apparition of the diffraction peaks at 10.3 and 12.0° characterized the stereocomplex PLA$_{stereo}$ (Fig. 1). Thus, as found by Li [11] in PLA$_{62.5}$ and in PLA$_{50}$ stereocopolymers, the hydrolytic degradation of PLA$_X$CL$_Y$ with $X \geq 40\%$ induced morphology changes, the initially amorphous copolymers presenting partially crystalline degradation residues typical of stereocomplexation of L-LA and D-LA oligomers.

3.5.2. Compositional changes

The νCH and νC=O stretching regions reflected composition changes. After 33 days, the intensity of the 2938 cm^{-1} band (νCH + νCH$_3$) and of the shoulder at 1769 cm^{-1} (νC=O), characteristic of LA units in the PLA$_{12.5}$CL$_{75}$ semi-crystalline copolymer spectrum, diminished reflecting the preferential hydrolytic attack of amorphous PLA segments. Moreover, the large band at 1730 cm^{-1}, which was assigned to amorphous CL-units, was turned into a shoulder of a new narrow peak located at 1720 cm^{-1} typical of crystalline CL-domains. The hydrolysis of amorphous PLA$_{25}$CL$_{50}$ and PLA$_{37.5}$CL$_{25}$ copolymers bring out an increasing of the intensity of the νCH$_2$ band at 2916 cm^{-1} (CL-units) relatively to that of the νCH$_3$ line at 2938 cm^{-1} representing the LA-units (Fig. 2). On the same way, the νC=O characteristic of the amorphous oxycaproyl units at 1730 cm^{-1} increased in intensity, whereas the νC=O disymmetric band of the lactyl units at 1769–1752 cm^{-1} diminished (Fig. 3). The intensity ratios evaluated from the νCH and νC=O stretching bands showed that degradation affected preferentially the amorphous D,L-LA units sequences. Thus, after 33 days of hydrolysis, the PLA$_{25}$CL$_{50}$ and PLA$_{37.5}$CL$_{25}$ spectra became identical to that of PLA$_{20}$CL$_{60}$ and PLA$_{25}$CL$_{50}$ respectively. In PLA$_{40}$CL$_{20}$, the hydrolysis led to a richness in amorphous CL-units because of the stronger intensity of the 1730 cm^{-1} peak and the amorphous D,L-LA long sequences are replaced by long sequences of PLA$_{stereo}$ according to the presence of the new peaks at 1745 cm^{-1} (νC=O) and 2995–3000 cm^{-1} (νCH$_3$) lines, as shown in the precedent paragraph. The PLA$_{47.5}$CL$_5$ spectrum was close to the spectrum of PLA$_{stereo}$. The results are presented in Table 2.

4. Conclusion

PLA$_X$CL$_Y$ copolymers of D,L-lactide/ε-caprolactone were synthesized with the different 12.5/75, 25/50, 37.5/25, 40/20 and 47.5/5 compositions (*X* represents the percentage of L-LA units, *Y* the percentage of CL-units in the monomer feed) using Zn–lactate as the initiator. Vibrational spectroscopy was used to discuss the solid state morphology, conformation, configuration and composition of the copolymers in the solid state. Raman spectroscopy appeared to be a suitable method for the identification of PLA_XCL_Y samples directly from solid devices without any special preparation. Only $PLA_{12.5}CL_{75}$ was a semicrystalline compound. The hydrolytic degradation of all the compounds led to crystallinity and composition changes which were discussed from the identification and the intensity of the crystalline peaks of CL-units and of L-LA or D-LA units of the PLA stereocomplex in the one hand, and of the amorphous bands of CL- and D,L-LA units in the other hand. Preferential degradation appeared in amorphous D,L-LA rich domains for all the compounds. After 33 days hydrolysis, crystallinity increased in the degradation products of $PLA_{12.5}CL_{75}$ with crystalline sequences of CL-units, whereas $PLA_{25}CL_{50}$ and $PLA_{37.5}CL_{25}$ initially amorphous stayed amorphous and transformed themselves into $PLA_{20}CL_{60}$ and $PLA_{25}CL_{50}$ respectively. PLA_XCL_Y copolymers with $X \geq 40\%$ and $Y \leq 20\%$, initially amorphous, yielded crystalline degradation products identified as composed of an oligomeric stereocomplex formed by L-LA, D-LA crystallizable fragments.

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