Research Article

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Microwave-assisted synthesis of the lipase-catalyzed ring-opening copolymerization of ε-caprolactone and ω-pentadecanolactone: Thermal and FTIR characterization

Abstract: Microwave-assisted synthesis of the lipase-catalyzed ring opening polymerization of ε-caprolactone (ε-CL) and ω-pentadecanolactone (ω-PDL) monomers was studied. A series of P(CL-co-PDL), with different molar feed ratios, including (ε-CL/ω-PDL) 100/0, 75/25, 50/50, 25/75, and 0/100, were synthesized. The resulting polyesters were characterized by Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA). The microwave-assisted polymerization of the monomers reached high conversions (91–95%) within 60 min. FTIR spectra showed the typical absorption bands of these polyesters. A very intense band in the carbonyl region, which was shifted from $1,720\,cm^{-1}$ for PCL to $1,732\,cm^{-1}$ for PPDL homopolymer, as well as peaks owing to methylene groups in the $2,990–2,850\,cm^{-1}$ range. DSC results revealed that all polyester samples were semi-crystalline. Interestingly, the copolymers exhibited only one melting peak (T_m), and their T_m values linearly increased from 57°C to 95°C as PPDL concentration was increased. Thermal stability of polyesters also depended on PDL content; an increase in PDL concentration increases polymer degradation temperature (T_d).

Keywords: microwave-assisted synthesis, lipase-catalyzed ring-opening polymerization, copolyesters, ε-caprolactone, ω-pentadecanolactone

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1 Introduction

Enzymatic polymerizations offer unique advantages such as reaction selectivity, and they prevent the use of toxic metal catalysts and they use mild reaction conditions. However, these processes are not still commercially available, probably due to the high enzyme cost. In this regard, the lipase-catalyzed ring opening polymerization (ROP) of ε-caprolactone (ε-CL) and ω-pentadecanolactone (ω-PDL) monomers have been investigated by several groups (1–4), as both poly(caprolactone) and poly(pentadecanolactone) have attracted recently a lot of attention due to their multiple biomedical applications. For instance, these homopolymers have been employed as absorbable bone plates, artificial skin, tissue scaffolds, and carriers of drugs for controlled release systems (5–9). However, the lipase-catalyzed ROP of these lactones requires long time that can range from hours to days (10,11). Therefore, shortening the reaction time would lead to an important advantage in this type of polymerization.

One approach to overcome this drawback is by combination of microwave (MW) irradiation with lipase-catalyzed ROP of the lactones. This new approach offers a potentially alternative green chemistry synthetic route for enhancement of reaction rates and therefore reduction of reaction time. Also, the possibility of enzyme recycling could make these biotransformation more cost effective (12–14).

Microwave (MW) heating is a green method for chemical and enzymatic synthesis. This method not only provides a safe, clean, and convenient way to heat reactions to elevated temperatures but also accelerates many reactions providing a selective activation and allowing faster optimized reactions. It also offers high efficiency and homogeneous heating (12–17).

There are few reports in the literature concerning microwave-assisted lipase-catalyzed ROP of ε-CL (18,19) and only one report on the polymerization of ω-PDL (20). In this regard, Kerep and Ritter (19) reported for the first time the combination of MW irradiation with enzymatic

catalyzed ROP to synthesize PCL from ε-CL and Novosyme 435 and compared their results with those obtained for the reaction performed with conventional heating. They concluded that MW-assisted enzymatic polymerizations could impart an accelerating effect depending on the kind of solvent used during the reaction (19). Matos et al. investigated the effect of some MW process parameters such as power, intensity, time, and temperature on ε-CL lipase-catalyzed polymerizations (18). Conversely, Mahapatro and Matos reported the polymerization of ω-PDL using the synergistic effects of lipase and microwave technology (20).

It is important to mention that to our knowledge there are no reports in the literature on the synthesis of copolymers of (ε-CL) and ω-PDL by means of MW-assisted lipase-catalyzed ROP even though these copolymers have been prepared by conventional heating of lipase-catalyzed ROP (10,11,21). Therefore, the aim of this study is to synthesize copolyesters from ε-CL and ω-PDL by MW-assisted lipase-catalyzed ROP and to characterize the polymers and copolymers obtained by using FTIR, DSC, and TGA. These aliphatic polyesters have received an increasing attention due to their physical properties, biocompatibility, and biodegradability, which makes them suitable for biomedical and pharmaceutical applications (22).

2 Experimental

2.1 Materials

ε-CL (97%) and ω-PDL (98%) monomers, as well as chloroform (98%) and methanol (98%), were used as received without further purification; in contrast, toluene (99%) was dried over molecular sieve (3 Å) before its use. All these reagents were purchased from Sigma-Aldrich. Novozyme 435 (immobilized *Candida antarctica* lipase B supported on acrylic resin) was also obtained from Sigma-Aldrich Inc. and was used as received.

2.2 MW-assisted synthesis of the polymers

Microspheres of Novozyme 435 (dried at 50°C overnight), monomer(s), molecular sieve (3 Å), and a stir bar were

placed in a microwave reaction vial (G30), and then, it was sealed under nitrogen atmosphere with a snap caps and silicone septum. For all reactions, an enzyme-to-monomer(s) ratio of 1/10 wt/wt% was used. In the next step, 5 mL of toluene was added to it using a syringe. MW-assisted polymerization was performed on a monomode microwave reactor (Monowave 400, Anton Paar Co.) at a preset temperature (85°C), time (1 h), and power (240 W) settings. These parameters were established based on previous experiments performed in our laboratory. Reaction media was stirred at 300 rpm through the MW-assisted polymerization process. The reactions were terminated by adding an excess of cold chloroform to the reaction media and separating the insoluble enzyme by filtration. The excess chloroform was removed by rotary evaporation and the polymer precipitated in cold methanol. The precipitated polymer or copolymer was purified by redissolving it in chloroform and precipitating again with methanol at least three times. The polymers obtained were dried at 60°C for 24 h in a vacuum oven and then characterized. The corresponding amounts of ε-PCL and ω-PDL were selected and added to the reaction to obtain (co)-polyesters with different molar feed ratios as reported in Table 1. The copolymerization reaction is illustrated in Figure 1, whereas the reaction mechanism is displayed in Figure 2.
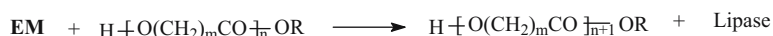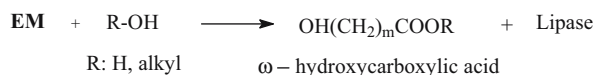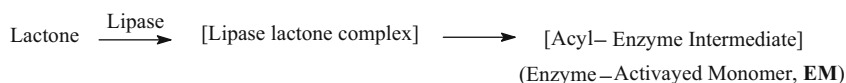
The reaction mechanism for the lipase-catalyzed ROP has been reported previously (23,24). The catalytic site of lipase is the serine-residues $-CH_2OH$ group in the triad Ser–His–Asp. In the first step, the lactone ring-opening and enzyme–lactone complex is accomplished to obtain the acyl-enzyme intermediate (enzyme-activated monomer, EM). Then, in the initiation step, the ω-hydroxycarboxylic acid can be obtained through the nucleophilic attack at the acyl carbon of the intermediate, and the shortest propagating chain is created. Next is the propagating process to form a long polymer chain. In this process, the terminal hydroxyl groups of the propagating chain end attacks EM nucleophilically (24).

Table 1: Monomer ratio composition for the polymers synthesized in this work

Sample PCL-co-PDL	ε-CL (% mol)	ω-PDL (% mol)
100/0	100	0
75/25	75	25
50/50	50	50
25/75	25	75
0/100	0	100
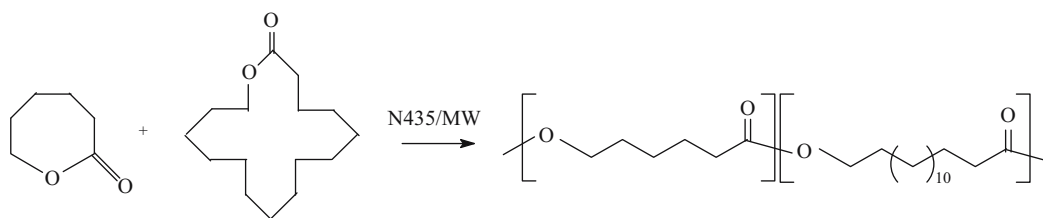
Figure 1: MW-assisted ring-opening copolymerization of ε-CL and ω-PDL catalyzed by novozyme 435 (N435) and microwave.

Figure 2: Reaction mechanism of the lipase-catalyzed ROP (23,24).

2.3 Polymer and copolymer characterization

The conversion percentage (%) was defined as the amount of monomer(s) that has been polymerized, and it was determined by the gravimetric analysis (the solvent and monomer were evaporated at 60°C in vacuo until the constant weight was reached). Synthesized polymers were analyzed by FTIR. This analysis was conducted with a Nicolet FTIR 8700 spectrometer (Thermoscientific Co.) using the attenuated reflectance (ATR) technique using a ZnSe crystal. Spectra were recorded at room temperature between 4,000 and 650 cm^{-1}, with a 4 cm^{-1} resolution and 100 scans.

The melting point (T_m) and enthalpy of fusion (ΔH_f) of polymers and copolymers were determined by differential scanning calorimetry by means of a PerkinElmer DSC-7 (PerkinElmer Inc.). Experiments were conducted under nitrogen atmosphere (20 mL/min flow rate), performing a first heating from 0°C to 110°C at a heating rate of 10°C/min. Then, the sample was cooled to 0°C at a cooling rate of 10°C/min. Later, a second heating run was performed under the same conditions of the first one. Crystallinity percentage for PCL and PDL was calculated by taking the ratio of fusion enthalpy (ΔH_f) of the sample to the fusion enthalpy of 100% crystalline polymer (ΔH_f°) as given in following equation:

$$\text{Crystallinity (\%)} = \frac{\Delta H_f}{\Delta H_f^\circ} \tag{1}$$

where ΔH_f° for PCL = 139.3 J/g and ΔH_f° for PDL = 233 J/g (11).

The thermal stability of polymers and copolymers was evaluated through the thermogravimetric analysis (TGA) using a TGA 8000 PerkinElmer equipment (PerkinElmer Inc.). The samples were heated from 50°C to 650°C at a heating rate of 10°C/min under nitrogen atmosphere (20 mL/min flow rate).

3 Results and discussion

3.1 Conversion

Table 2 presents the monomer(s) conversion values of the polyesters and copolyesters synthesized by microwave-assisted lipase-catalyzed ring-opening polymerization of ε-caprolactone (ε-CL) and/or (ω-PDL). As can be seen, conversion was found in the range of 91–95%, which is higher than values reported by Kerep and Ritter. (19) and by Mahapatro and Matos (20) for PCL and PPDL, respectively, during MW-assisted enzymatic ring-opening polymerization. In this regard, Kerep and Ritter (19) reported conversion values of 60–61% after 60 min using diethyl ether as a solvent. In contrast, they found that this parameter reached only 31% conversion when toluene was employed as the solvent. Similarly, Mahapatro and Matos (20) reported yields of 41% and 61% after 60 and 120 min, respectively, in the ROP of PDL catalyzed by Novozyme-435 under MW conditions.

Table 2: Conversion and thermal properties of polyesters and copolyesters synthesized by microwave-assisted lipase-catalyzed ring-opening polymerization

Sample CL-co-PDL	Conversion (%)	T_g (°C)	T_m (°C)	ΔH_f (J/g)	Crystallinity (%)	T_d (°C)
100/0*	94	−60**	52	74.4	53.4	395
100/0	95	−60**	57	77.6	55.7	408
75/25	93	−35	68	114.8	n.d.	416
50/50	92	−30	78	135.0	n.d.	421
25/75	91	−28	87	136.4	n.d.	423
0/100	94	−23	95	145.3	62.4	424
0/100*	96	−23	93	143.3	61.5	401

*Homopolymers obtained at 85°C for 24 h using Novozyme-435, without MW irradiation.
**From ref. (11).
n.d. = not determined.

The difference between conversion values obtained in this study (92–96%) and those reported by other authors (19,20) (31–61%) is attributed to differences in the synthesis conditions in this case the solvent (toluene) and the presence of molecular sieve. Kerep and Ritter reported that reactivity of MW-assisted ring-opening polymerization of ε-CL is influenced by the type of solvent, thus affecting the monomer conversion. Temperature and irradiation power can also affect the reaction yielding (19). An additional parameter that could have affected the conversion is the presence of molecular sieve in the reaction medium since it is well known that humidity has influence in the esterification reactions (3).

It is also important to note that the conversion values (91–95%) obtained after 60 min in the MW-assisted polymerization can be reached only after at least 24 h in the conventional enzyme-catalyzed polymerizations (10,11,25–27) (see values obtained for homopolymers synthesized at 85°C for 24 h using Novozyme-435, without MW irradiation in Table 2). Therefore, it is clear that under the proper conditions a synergistic effect between MW technology and enzyme catalysis helps reduce the reaction times compared with conventional ROP with a reasonable monomer conversion, and it is also suitable for the copolymerization reaction.

Monomer reactivity ratios are important parameters used in copolymerization kinetics to predict the polymerization rate and copolymer composition, among other parameters of the final product. Kumar et al. (21) studied the copolymerization of PDL and CL by means of the Novozyme-435/toluene traditional approach under thermal conditions for long time and found that reactivity ratios for PDL polymerization ($r_1 = 1.742$) was 13 times faster than CL polymerization ($r_2 = 0.135$). Despite the large difference in the reactivity of these monomers, random copolymers were formed.

It has been also reported that microwave-assisted polymerization process affects the reactivity ratios of the monomers (28,29). For instance, Oberti et al. (28) pointed out that the monomer reactivity ratios r_1 and r_2 are twofold higher under microwave conditions than those obtained under thermal conditions. Interestingly, this behavior was observed in both monomers, suggesting that a similar microstructure could be obtained in these copolymers.

3.2 Fourier transform infrared spectroscopy

FTIR spectra of PCL, PPDL, and their copolymers, synthesized by microwave-assisted lipase-catalyzed ring-opening polymerization, are shown in Figure 3. As observed, IR spectra were similar among them, and they exhibited the typical bands of the polyesters. Thus, spectra displayed a very intense band in the carbonyl region (1,700–1,750 cm^{-1}), related to ester stretching vibration, as well as peaks in the 1,200–1,000 cm^{-1} region, corresponding to C–O and C–O–C asymmetric and symmetric stretching vibrations of the ester moiety. Spectra also showed absorption bands in the wavenumber range of 2,990–2,810 cm^{-1}, which are related to C–H asymmetric and symmetric stretching vibration of methylene groups. As expected, peaks owing to methylene groups were more intense for PPDL than those observed for PCL due to the aliphatic chain length. In copolymers, these peaks become more intense as the concentration of PDL increases because the methylene groups are present in greater number than other groups in the copolymer structure. The presence of methylene groups was confirmed by the appearance of bands in the 1,480–1,380 cm^{-1} range, attributed to C–H bending vibration.

A close inspection of spectra showed that both C–H stretching vibrations and C=O stretching vibration were
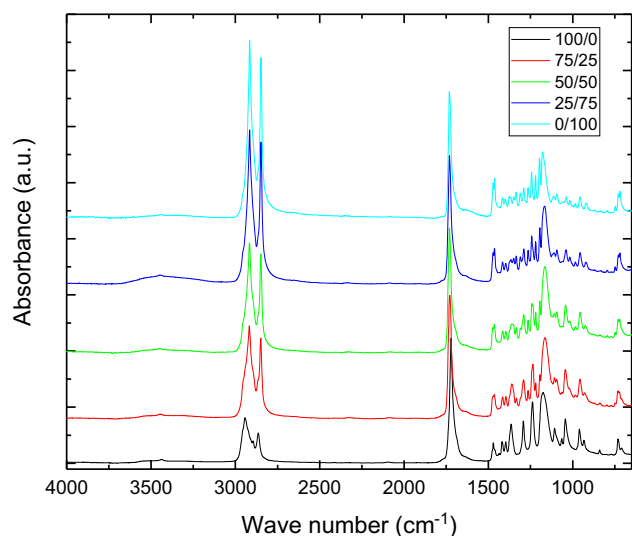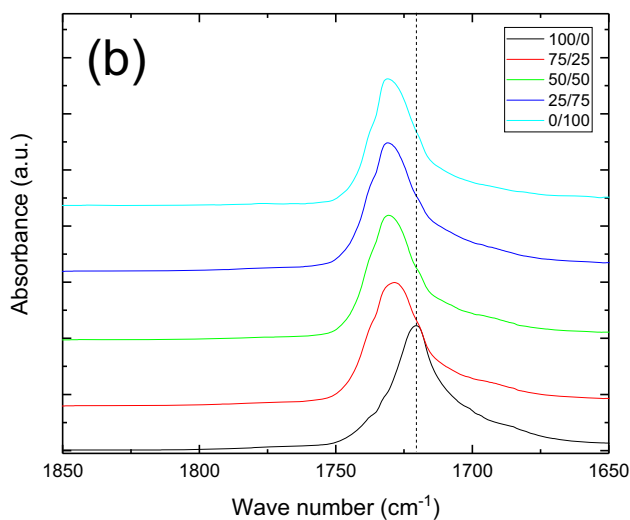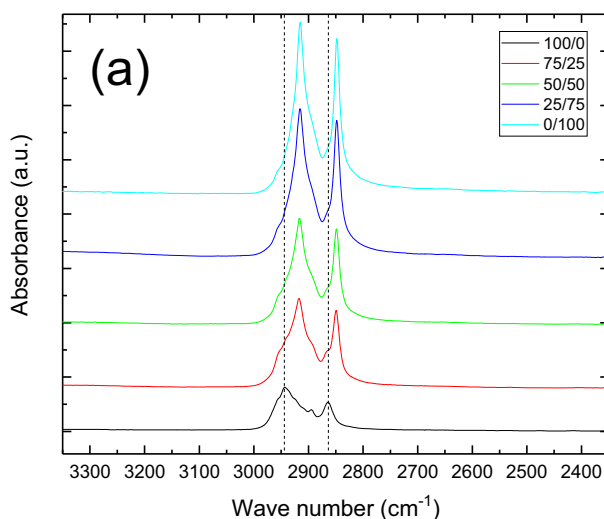
Figure 3: FTIR spectra of polyesters and copolyesters form CL–PDL synthesized by MW-assisted ROP catalyzed by N435.

shifted when PDL incorporates in increasing quantities into the copolymer structure (see Figure 4). Thus, bands at 2,945 and 2,865 cm^{-1} of the PCL homopolymer shifted to 2,915 and 2,849 cm^{-1} for PPDL homopolymer; the carbonyl band displayed a similar behavior (a shifting from 1,730 to 1,720 cm^{-1}). This phenomenon suggests that both aliphatic polyesters interact between them.

3.3 Differential scanning calorimetry (DSC)

The DSC thermograms of CL–PDL polyesters and copolyesters synthesized by MW-assisted lipase-catalyzed (ROP) are shown in Figure 5. Results revealed that all polyester samples were semi-crystalline displaying one endothermic peak, which is associated with a melting process in the polymers. PCL and PPDL exhibited T_m values at 57°C and 95°C, respectively, which are very similar to those reported by other authors for these homopolymers (3,11,5). Copolymers also exhibited only one melting peak, and their T_m values linearly increased from 57°C to 95°C as PDL concentration in the copolymer increased (see Figure 6). This fact discards that the copolymers obtained from ε-CL and ω-PDL are block copolymers and validates the formation of random copolymers. This behavior has been also reported previously for these copolymers (10,22). The melting peak was not the only parameter that increased as the PDL content in copolymers increased; heat of fusion (ΔH_f) also shows an increase from 77.6 J/g for PCL to 145.3 J/g for PPDL (see Table 2). The values for the copolymer fall in between these two limiting values


Figure 4: FTIR spectra of MW-assisted ROP copolyesters CL–PDL: (a) in the 3,300–2,400 cm^{-1} range and (b) in the 1,850–1,650 cm^{-1} region.
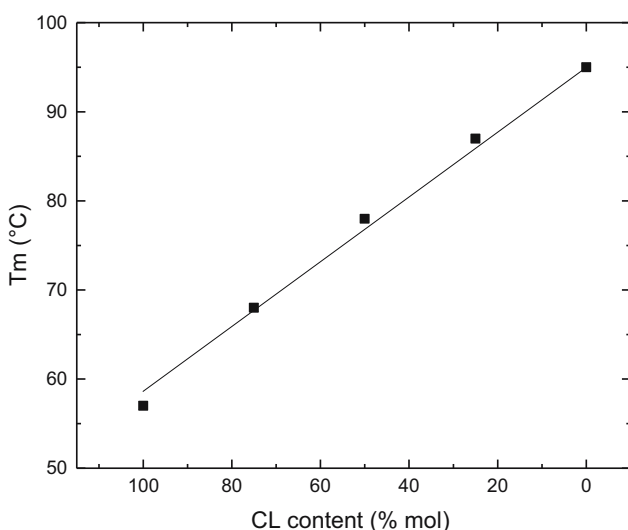
present an indication that the similarity in structure can cogenerate crystalline structures in these copolyesteres. Crystallinity percentages for PCL and PDL were similar to those reported by Ulker and Guvenilir (11).

These results are very interesting as it is well known that one way to disrupt crystallization is using co-monomers during the synthesis, as long as the co-monomer does not co-crystallize (30). A typical example comes from the copolymerization of glycolide and lactide monomers that when either monomer is present over 70 mol%, a crystalline polymer is obtained. Otherwise, amorphous copolymers will be obtained (31–33).

The fact that the copolymers exhibit only one T_m, as well as the shifting of the carbonyl band from 1,720 to 1,730 cm^{-1} observed in the FTIR spectra, validates the hypothesis of the miscibility of CL and PDL polymeric
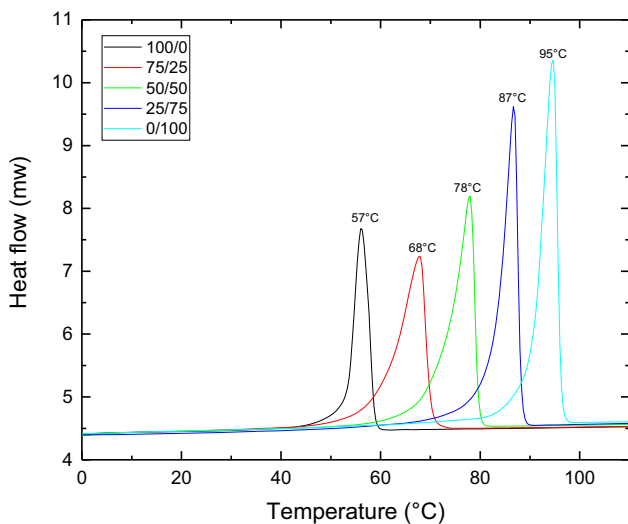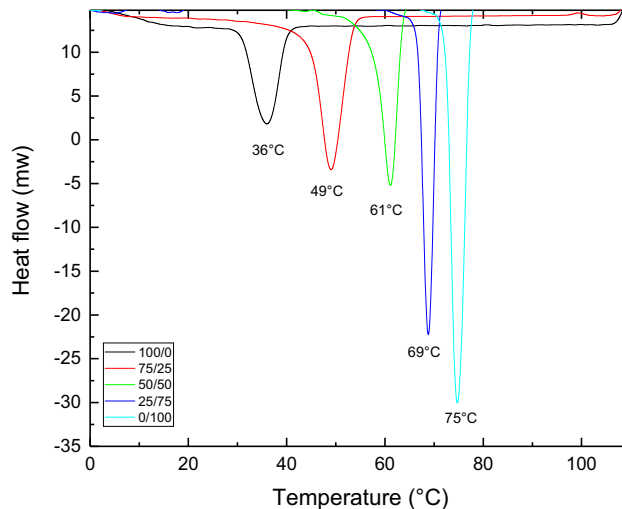
Figure 5: DSC heating curves of MW-synthesized copolyesters CL–PDL.

Figure 7: DSC cooling curves of MW-synthesized copolyesters CL–PDL.

and copolymers is a function of composition, which varies from 36°C for PCL to 75°C for PDL with the copolymers falling in between these values.

Table 2 also presents the glass transition temperature (T_g) values obtained for the polymers PCL and PDL, and the random copolymers synthesized in this work by MW. The T_g values of copolymers fall between homopolymers T_g's: −60°C reported for PCL (11) and −23°C calculated in this work for PDL. It is worth mention that the T_g value reported for PDL by other authors shows variations. Focarete et al. (2), Ulker and Guvenilir (11), Bouyahyi et al. (22), and Fernández et al. (34) reported −27°C, −29°C, −30°C, and −36°C, respectively. This discrepancy could be attributed to the molecular weight of PDL obtained.

Figure 6: Relationship between T_m and ε-caprolactone (ε-CL) content in CL–PDL copolymers.

structures when they are copolymerized. In fact, Ceccorulli and Scandola (10) reported the co-crystallization of these random copolymers; however, they did not postulate the reason for the observed results. A plausible explanation is that the aliphatic hydrocarbon chains belonging to these polyesters (PCL and PPDL) are responsible for the formation of the observed crystalline structure.

DSC cooling curves for the obtained polyesters and copolyesters were also obtained, and the results are presented in Figure 7. As observed in this figure, the thermograms exhibit an exothermic peak, which is related to the crystallization phenomenon. Remarkably, it was noticed that the crystallization temperature of homopolymers

3.4 Thermogravimetric analysis

Figure 8 shows the TGA and DTGA curves for polymers synthesized by the MW-assisted lipase-catalyzed ROP. As observed, all thermograms show a single well-defined mass loss and the degradation temperatures (T_d) increased as the concentration of PDL in CL–PDL copolymer increases. This indicates that pentadecanolactone structure improve the thermal resistance of polymer due, probably, to the longer hydrocarbon aliphatic chain. Thus, T_d increases from 408°C for PCL to 424°C for PPDL as observed in the inset of Figure 8b. This behavior was also reported by Ulker and Guvenilir (11) in samples of P (CL-co-PDL) synthesized by ring-opening polymerization using Novozyme 435 as a catalyst applying conventional heating.
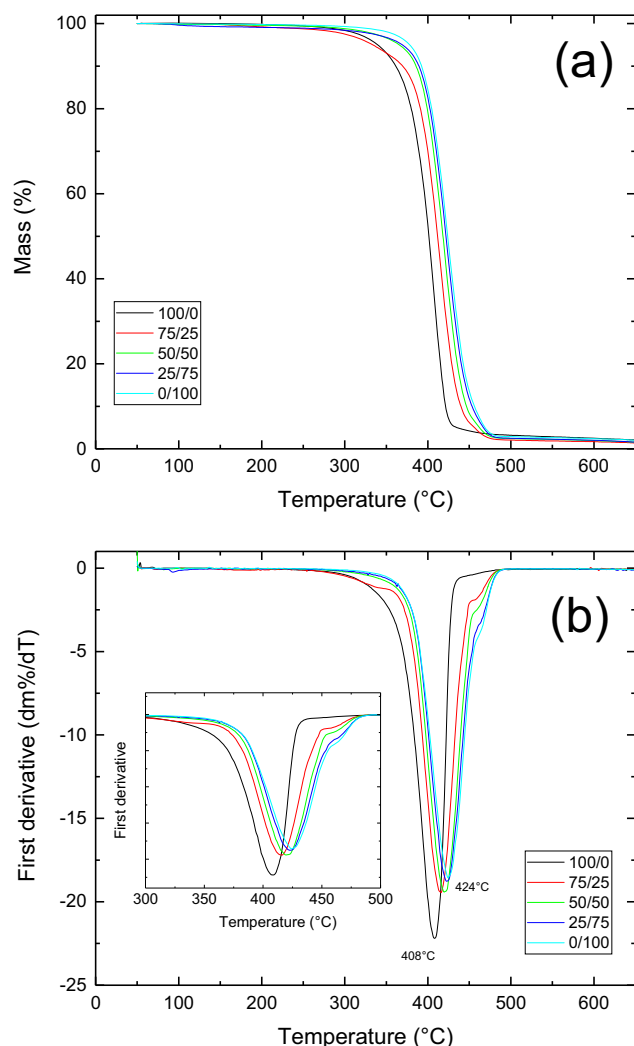
Figure 8: (a) TGA and (b) DTGA curves of MW-assisted ROP-synthesized copolyesters CL–PDL.

4 Conclusions

A series of poly(caprolactone-co-pentadecanolactone) with different molar feed ratios were synthesized by MW-assisted lipase-catalyzed ROP. Polymerizations reached high conversions (91–95%) within 60 min. FTIR spectra showed that both carbonyl band and peaks owing to methylene groups were shifted to lower wave number as PDL content increased in the copolymers CL–PDL. DSC results revealed that all polyester samples (homopolymers and copolymers) were semi-crystalline. The fact that the copolymers synthesized from ε-CL and ω-PDL exhibited only one melting peak suggests that the polymers are within a miscibility range. Thermal stability of polyesters also depended on the PDL content. An increase in PDL concentration increases the T_d of polymers.

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