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Microstructure analysis and thermal properties of L-lactide/ε-caprolactone copolymers obtained with magnesium octoate

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ABSTRACT

A series of copolymers with various compositions were prepared by the ring opening copolymerization of L-lactide (L-LA) and ε-caprolactone (ε-CL) using nontoxic magnesium octoate as a catalyst in bulk. The copolymerization process and the influence of transesterification on the chain microstructure were examined by ^{1}H and ^{13}C NMR. A tapered block or gradient copolymer is expected to be formed on the basis of the reactivity difference between L-LA and ε-CL. Two modes of transesterification occurred and played an important role in the redistribution of comonomer sequences but not a completely random distribution. The CLC sequence formed by the second mode of transesterification was observed at the end of reaction. The coefficient of the second mode of transesterification (T_{II}) increased as the feed mole fraction of ε-CL increased. In terms of the overall feed compositions, the L_{LL}^r values of lactidyl sequences calculated from the reactivity ratio exceeded the L_{LL}^e values determined from the product, however, the L_C^r values of caproyl sequences were identical or shorter than the L_C^e values. The thermal properties and crystallinities of the obtained copolymers were investigated by DSC and WAXD. The thermal properties and crystallinities depend on both the composition and the chain microstructure. The L-LA/ε-CL copolymer with intermediate composition exhibited some blocky character by DSC. Only single T_g was observed for each copolymer and in agreement with the calculated value from Fox equation, indicating that the amorphous region of the copolymers is miscible. The obtained copolymers can best be described as random copolymers with more or less blocky chain structure.

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1. Introduction

Over the past decade the use of aliphatic polyesters as biomaterials has increased dramatically [1,2]. Poly(ε-caprolactone) (PCL) is semi-crystalline polymer with outstanding permeability to drugs and thermal properties, however, its degradation rate is very slow. In contrast, poly(L-lactide) (PLLA) is hardly permeable to most drugs, and its half-life time is much shorter. Thus, combining PCL permeability and relatively faster biodegradation of PLLA may lead to a wide range of drug carries with adjustable properties [3,4].

Copolymerization of L-lactide (L-LA) and ε-caprolactone (ε-CL) is an effective strategy to produce materials with intermediate properties between those of the parent homopolyesters by varying its total composition and the distribution of the comonomer repeat units along the copolymer chain [5–9]. In practice, tin compounds, especially stannous octoate (Sn(Oct)$_2$), are frequently used as catalysts for copolymerization of L-LA and ε-CL [10–14]. However, the cytotoxicity and difficulty in removal of the catalysts from the obtained polymers have limited their use in many cases [15].

Therefore, many efforts have been devoted to the development of new catalysts and/or initiators that would be well tolerated by the organism [15–17]. Much less toxic is the zinc catalyst [18] used to prepare the L-LA and ε-CL copolymers. Kricheldorf [19] conducted the copolymerization of L-LA with ε-CL and glycolide in the presence of zinc lactate. Kowalski [20] also introduced the commercially available zinc octanoate for the synthesis of PLLA and PCL with high molecular weight.

Nevertheless, it is essential to search for initiators containing metals which are not harmful for the human organism, especially those taking part in metabolic processes, such as Ca, Fe, and Mg. Hence, a great lot of papers were published on the polymerization of lactide in the presence of calcium, ferric, and magnesium compounds as catalysts [21–32]. Organic amino calcium compounds [21], calcium acetylacetonate [22], calcium complex

[23] were also used for lactide polymerization. The useness of iron (III) acetylacetonate, iron (II) lactate and ferric alkoxides catalysts enabled to obtain copolymers with yields up to 100% and possessing good mechanical properties [24,25].

In the latest studies, the results of the lactide polymerization in the presence of well-defined magnesium β-diiminate complexes [26], magnesium alcoholates [27], magnesium aryloxides [28], magnesium benzyl alkoxides [29] were presented as well as dibutylmagnesium and Grignard compounds as catalysts [30–33]. The polymerization proceeds in the solution very fast; however, there are no reports on application of the described methods for obtaining biodegradable random copolymers.

The aim of this paper was to present a new catalyst for L-LA/ε-CL copolymer synthesis with nontoxic magnesium octoate (Mg(Oct)$_2$). We firstly traced the copolymerization process and analyzed the corresponding microstructure by ^{1}H and ^{13}C NMR. Then, we synthesized a series of copolymers with various compositions and investigated their microstructure and thermal properties by ^{13}C NMR, DSC, and WAXD. Since physical properties of copolyesters are strongly connected with their chain microstructure, special attention has been paid to the influence of the polymerization time and copolymer composition on the chain microstructure of the obtained copolymers.

2. Experimental

2.1. Materials

L-lactide (L-LA, Purac) was recrystallized twice from dried ethyl acetate and then dried in a vacuum oven at room temperature. ε-Caprolactone (ε-CL, Acros Organics) was dried over calcium hydride and distilled under reduced pressure and then stored over molecular sieves under a nitrogen atmosphere. Magnesium octoate (Mg(Oct)$_2$, 2.3 wt% Mg in toluene, Strem Chemical.) and other reagents were used as received without further purification.

2.2. Copolymerization procedure

Copolymerizations were carried out in a previously flamed and nitrogen purged glass ampoules. Designed amounts of L-LA and ε-CL were weighted into the ampoules purged with dry nitrogen. Mg(Oct)$_2$ diluted in toluene was added as a catalyst by a syringe. The ampoules were heated under reduced pressure to remove the toluene and purged with dry nitrogen three times. Then the ampoules were immersed into a thermo stated oil bath at 130 °C for 48 h. The products were isolated by dissolving in chloroform and precipitating in hydrochloric acidic mixture of hexane and diethyl ether and dried in vacuum at 50 °C for 24 h. To trace the L-LA/ε-CL copolymerization process, samples for ^{1}H and ^{13}C NMR were withdrawn from the reaction mixture at various intervals.

2.3. Measurements

The conversion of comonomers, copolymer compositions and monomer sequences were determined by ^{1}H and ^{13}C NMR spectroscopy. Spectra were recorded on a Bruker Avance II 400M NMR spectrometer (Bruker, Switzerland) using CDCl$_3$ as solvent and TMS as internal reference at 25 °C, and sample concentrations of ca. 10% (w/w). ^{1}H NMR spectra were recorded at a 400 MHz resonance frequency with 32 scans, a 4.0 s acquisition time and a 6.5 μs pulse width. ^{13}C NMR spectra were recorded at a resonance frequency of 100 MHz with 17,000 scans, a 1.4 s acquisition time and a 6.5 μs pulse width.

The molecular weight and polydispersity were measured by GPC-220 (Polymer Lab, UK) equipped with Ultrastyragel® columns

and differential refractometer. Tetrahydrofuran (THF) was used as the eluent at a flow rate of 1.0 ml/min at 40 °C. The molecular weight calibration curve of polymers was obtained with narrow molecular weight distribution polystyrene standards.

Differential scanning calorimetry (DSC) was carried out on a Mettler Toledo DSC 822^e (Mettler Toledo, Switzerland) instrument in nitrogen atmosphere. The samples were heated for the first run from −60 to 200 °C at 10 °C/min, then cooled to −60 °C, and heated again for the second run from −60 to 200 °C at 10 °C/min. Before and after cooling, the temperature was kept constant for 5 min. The melting temperature (T_m) and entropy of fusion (ΔH_m) were measured on the first heating, and glass transition temperature (T_g) on the second one.

Wide-angle X-ray diffraction (WAXD) was performed on a Dmax-Ultima+ X-ray diffractometer (Rigaku, Japan) with Ni-filtered Cu/K-α radiation (= 0.15418 nm). The operating target voltage was 40 kV and the tube current was 100 mA. The scanning rate was 0.02°θ/s from 5.0° to 50.0°.

3. Results and discussion

3.1. Trace the L-LA/ε-CL copolymerization process

To obtain deeper insight into the process of the formation of the final microstructure of the obtained copolymers, we used ^{1}H and ^{13}C NMR techniques to trace the reaction progress of the copolymerization of L-LA and ε-CL catalyzed with Mg(Oct)$_2$ in bulk at 130 °C, as shown in Figs. 1 and 2. The dependence of the conversion of particular comonomers on the total conversion showed that the process of copolymerization had a much higher reactivity of L-LA in comparison with ε-CL (Fig. 3). L-LA polymerized preferentially at the initial stage of the reaction and ε-CL incorporated chain later, i.e., a copolymer containing mainly lactidyl units was formed at the initial stage. The copolymerization of L-LA and ε-CL catalyzed with Mg(Oct)$_2$ occurred at a fairly high reaction rate, however, it was considerably slower than that catalyzed by Sn(Oct)$_2$ [5]. The conversion of L-LA was almost quantitative by 8 h, whereas the conversion of ε-CL was only 30% at 8 h and nearly complete after 48 h. With reaction progress, the mole fraction of lactidyl units in copolymers decreased and that of caproyl increased with increasing of the total conversion of comonomers.
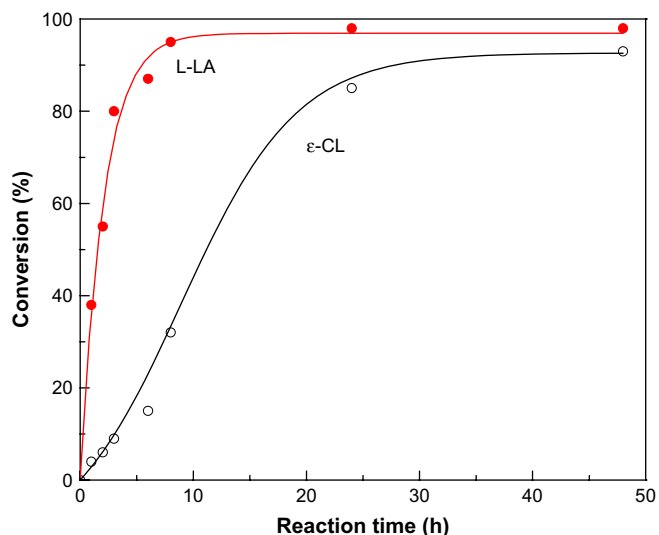

Fig. 1. Time-conversion curves of Mg(Oct)$_2$-catalyzed copolymerization of L-LA and ε-CL (mole ratio = 38:62) in bulk at 130 °C.
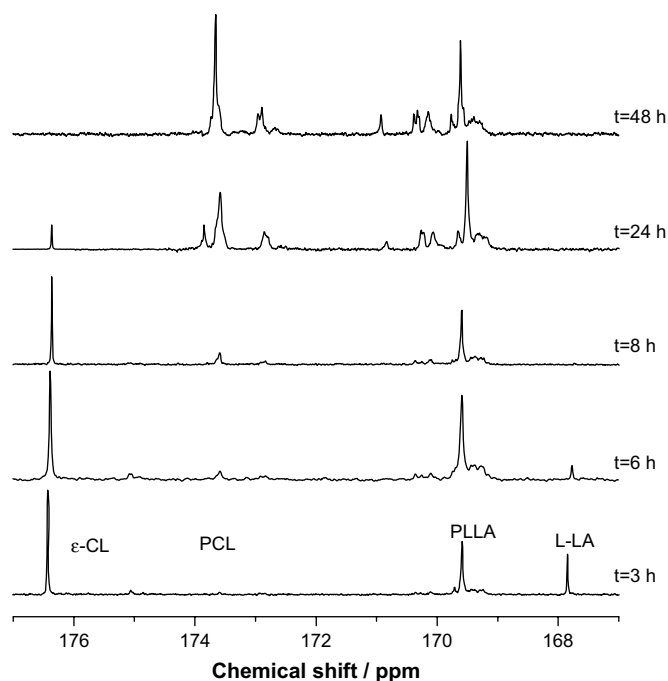
Fig. 2. CO signals in ^{13}C NMR spectra for the reaction progress of the copolymerization of L-LA and ε-CL (mole ratio = 38:62) in bulk at 130 °C.

When the structure of the copolyesters was estimated by ^{13}C NMR at progressing conversion, a sudden decrease in the average length of lactidyl blocks (L_{LL}^e), accompanied by a rapid growth in the average length of caproyl blocks (L_C^e), was observed at the initial stage (Fig. 4, the detailed calculation method shown in the following section). Thereafter, both L_C^e and L_{LL}^e decreased slightly at later. These effects were reflected by changes in signal intensities of the appropriate sequences in ^{13}C NMR spectra with reaction time (Fig. 2). The decrease in lactidyl average block length was still observed even when unreacted lactide molecules were absent in the reaction mixture. It indicated that transesterification occurred during copolymerization even after lactide molecules have been consumed. It is necessary to assume that in the first stage of
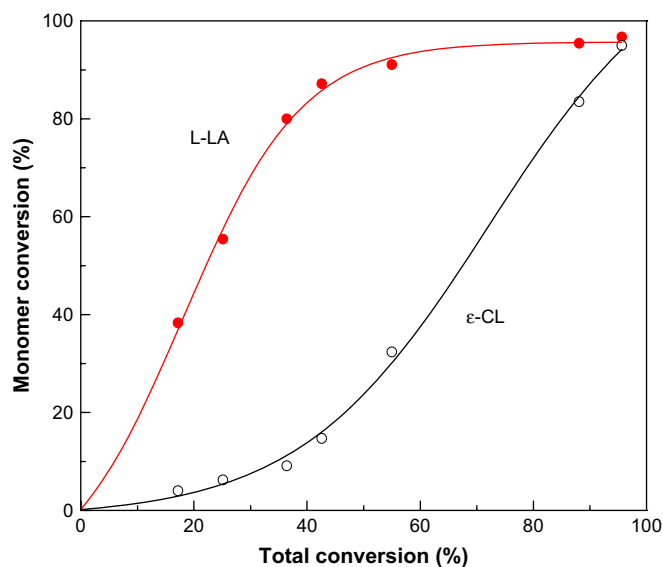

Fig. 3. Dependence of conversion of L-LA and ε-CL on total conversion. (Mole ratio L-LA to ε-CL = 38:62) in bulk at 130 °C.
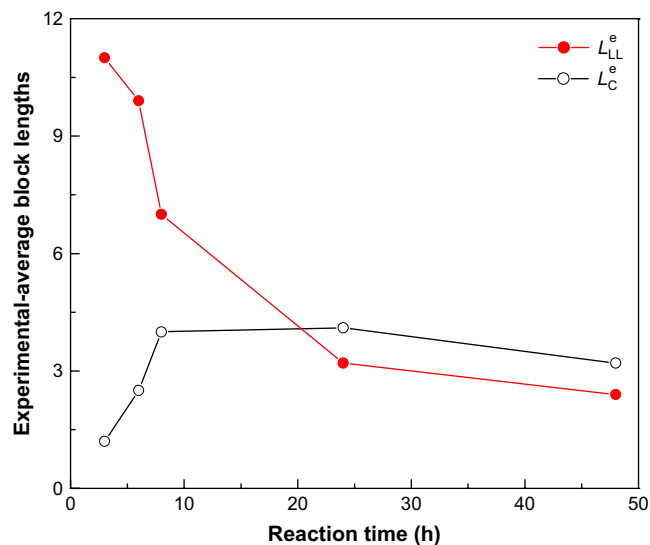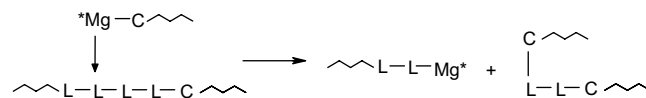

Fig. 4. Experimental number-average block length as a function of reaction time. (Mole ratio L-LA to ε-CL = 38:62) in bulk at 130 °C.

reaction mainly the first mode of transesterification runs, since typical "anormal" sequences, such as CLC, as a result of the second mode of transesterification were insignificant until the end of the reaction (Scheme 1) [34–36].
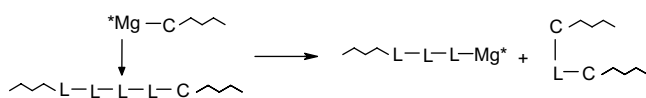
The average length of caproyl blocks (L_C^e) increased sharply at first and then decreased gradually, as a result of the competition between propagation reaction and transesterification in the polymerization of ε-CL. In the later of the reaction, a significant peak corresponding to the CLC sequences was observed in the ^{13}C NMR spectra (Fig. 2), which testified the attack of active caproyl ends on forming lactyl sequences (the second mode of transesterification, Scheme 1). The more ε-CL molecules incorporated into the copolymer chains, the higher probability of occurrence of the transesterification between lactidyl units and caproyl units.

According to the reactivity ratios previously published data [5,6] and the above results, a tapered block or gradient copolymer is expected to be formed. It undoubtedly belonged to the "separate" type of copolymerization reaction, which prefers formation of long lactidyl blocks at the beginning of the reaction and formation of long caproyl blocks at the end of reaction. However, the transesterification reaction rearranges the comonomer sequences and leads to randomization, but this effect is not complete. A more

Scheme 1. Two modes of transesterification reactions.

detailed analysis of the obtained copolymers is further presented in the following section.

3.2. Microstructure analysis of the L-LA/ε-CL copolymers

As previously discussed, transesterification plays an important role in the redistribution of monomer sequences, thereby influencing the microstructure [37,38]. To investigate the effect of transesterification on the redistribution of monomer sequences in the copolymerization and the effect of chain microstructure on copolymer properties, a series of copolymers with various compositions was prepared via the copolymerization of L-LA and ε-CL catalyzed by Mg(Oct)$_2$ in bulk at 130 °C. The results in Table 1 showed that all the copolymers had moderate molecular weights and their yields exceeded 93%. It indicated that Mg(Oct)$_2$ is an efficient catalyst with moderate activity for the copolymerization of L-LA and ε-CL. Due to the difference in the hydrodynamic volumes of the aliphatic polyesters and PS macromolecules with identical molar masses, the M_n values determined with a refractive-index (RI) detector and polystyrene (PS) standards show typical deviation from the actual values [39–42]. Although a ratio of the actual molecular weight to the determined value between 0.45 and 0.56 has been proposed by several research groups [39–42], the actual molecular weight of the obtained could be used as most drug carriers, which high molecular weight is always unnecessary and even undesirable [31,43].

Chain microstructure and the randomizing effects of transesterification reactions were studied by means of ^{13}C NMR, since this technique is very sensitive to monomer sequencing and is therefore a powerful tool for determining the average sequence length for each type of comonomer unit [6,11,12,34,35,44–48]. In particular, the carbonyl carbon signals (between 175 and 165 ppm) are the most sensitive to the sequence distribution of the lactidyl (LL) and caproyl (C) units. The average lengths of the LL and C sequences were determined on the basis of the attribution of the peaks in the ^{13}C NMR spectrum, as previously described by Kricheldorf and Kreiser [44] and Kasperczyk and Bero [35].

As shown in Scheme 1, two types of transesterification reactions were recognized, referred to as the first and second modes [35], in which a LL unit undergoes bond cleavage leading to the formation of anomalous sequences of CLC and CLLLC, both with an odd number of lactyl (L) units. These odd-number L sequences cannot be formed by the opening of LA rings alone during the growth reaction of the copolymer chains. The coefficient of the second mode of transesterification reaction (T_{II}) is defined as [35]:

$$T_{II} = CLC/CLC_R \quad (1)$$

Where CLC is the experimentally determined concentration of

the CLC sequences from the ^{13}C NMR spectrum and CLC$_R$ is the theoretical concentration for completely random chains as calculated via Bernoullian statistics:

$$CLC_R = k^2/(k+1)^3 \quad (2)$$

Where $k = C/L$.

Fig. 5 showed the assignment of peaks in ^{13}C NMR spectra of the obtained copolymers, as reported by Kasperczyk and Bero [45]. Since the spectra of the L-LA/CL copolymers in this work showed not only peaks due to the LLL (Fig. 5a) and CCC (Fig. 5 g) sequences but also intermediate peaks due to CCL, LCL, CLL and CLC sequences, it confirmed that copolymerization has indeed occurred. Although some pentads can be detected on the spectra, triad determination is accurate enough for the sequential analysis of the L-LA/CL copolymers to be reliable [6]. The experimental number-average lengths of the lactidyl (L_{LL}^e) and caproyl (L_C^e) sequences were calculated from the following equations [6,44]:

$$L_{LL}^e = \frac{1}{2}\left[\frac{I_{LLL} + (I_{CLL} + I_{LLC})/2}{(I_{CLL} + I_{LLC})/2 + I_{CLC}} + 1\right] \quad (3)$$

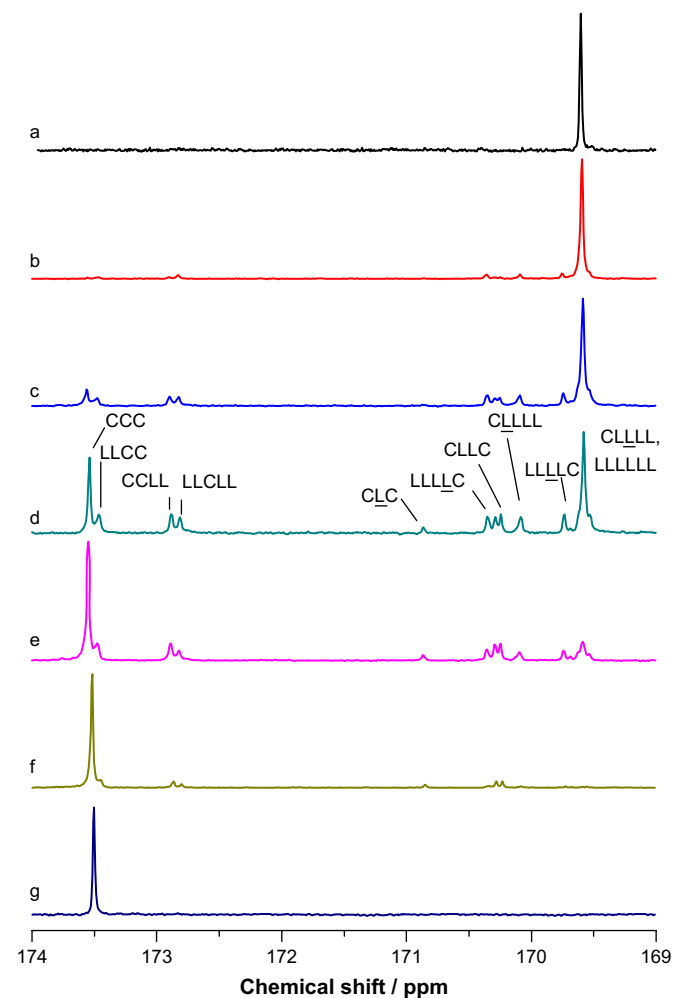$$L_C^e = \frac{I_{CCC} + I_{LCC}}{I_{CCL} + I_{LCL}} + 1 \quad (4)$$

Table 1
Copolymerizations of L-LA and ε-CL at various feed monomer ratios catalyzed by Mg(Oct)$_2$ at 130 °C for 48 h.[a]

No.	Sample	f_{CL}	F_{CL}	Yield	M_n	M_w/M_n	L_C^e	L_{LL}^e	T_{II}
a	PLLA	0	0	0.98	20100(11300)	1.81	0	∞	0
b	P(LLA-co-CL)1	0.10	0.083	0.93	19200(10800)	1.72	1.5	10.2	0
c	P(LLA-co-CL)2	0.35	0.359	0.94	17300(9700)	1.88	2.4	4.6	0.03
d	P(LLA-co-CL)3	0.55	0.545	0.97	18500(10400)	1.98	3.1	3.1	0.13
e	P(LLA-co-CL)4	0.75	0.768	0.95	20800(11600)	1.86	5.2	1.8	0.15
f	P(LLA-co-CL)5	0.95	0.946	0.98	21500(12000)	1.75	12.4	1.2	0.24
g	PCL	1	1	0.96	19400(10900)	1.85	∞	0	0

[a] Other reaction conditions: in bulk, Mg(Oct)$_2$: 1 mol%; f_{CL}: feed mole fraction of ε-CL; F_{CL}: mole fraction of caproyl units in copolymers; L_C^e: average length of caproyl blocks; L_{LL}^e: average length of lactidyl blocks; T_{II}: yield of the second mode of transesterification. M_n obtained from GPC analysis, values in parentheses are multiplied by a factor of 0.56 [40].

Fig. 5. CO signals in ^{13}C NMR spectra of PLLA, PCL and L-LA/CL copolymers: (a) PLLA; (b) P(LLA-co-CL)1; (c) P(LLA-co-CL)2; (d) P(LLA-co-CL)3; (e) P(LLA-co-CL)4; (f) P(LLA-co-CL)5; (g) PCL.

The values of L_{LL}^e and L_C^e were summarized in Table 1. Both L_{LL}^e and L_C^e increased as the relative proportions of their respective monomers increased. Obviously, the copolymer composition has a profound influence on the values of L_{LL}^e and L_C^e.

In comparison, the average lengths of the LL and C sequences for chains with a random distribution of units, as would be obtained by complete transesterification via the first and second modes, may also be calculated from the following equations [35]:

$$L_{LL}^R = (k+1)/2k \tag{5}$$

$$L_C^R = k+1 \tag{6}$$

Comparisons between the experimental and calculated average sequence lengths based on Bernoullian statistics and assuming a completely random distribution showed significant differences (Fig. 6). The experimental L_{LL}^e and L_C^e values were significantly higher than the calculated L_{LL}^R and L_C^R values for every copolymer composition studied, again possibly due to the higher reactivity of L-LA compared with ε-CL, not equal to one, as previously described [49]. Consequently, transesterification reaction did not lead it to reach a completely random distribution.

We can also calculate the average sequence lengths of the lactidyl (L_{LL}^r) and caproyl (L_C^r) units from reactivity ratios of $r_{LA} = 23$ and $r_{CL} = 0.22$ reported in our previous paper [49] as the following equations [50,51]:

$$L_{LL}^r = r_{LA}\frac{f_{LA}}{f_{CL}} + 1 \tag{7}$$

$$L_C^r = r_{CL}\frac{f_{CL}}{f_{LA}} + 1 \tag{8}$$

These calculated sequence lengths are proportional not only with the monomer feed ratio but also with the reactivity ratios. Thus, the L_{LL}^r and L_C^r values describe the behavior of the lactidyl and caproyl chain lengths in the initial stage of copolymerization. In terms of the overall feed compositions, the L_{LL}^r values calculated from the reactivity ratio exceeded the L_{LL}^e values determined from the polymeric product, as shown in Fig. 6. However, the L_C^r values were identical or shorter than the L_C^e values.

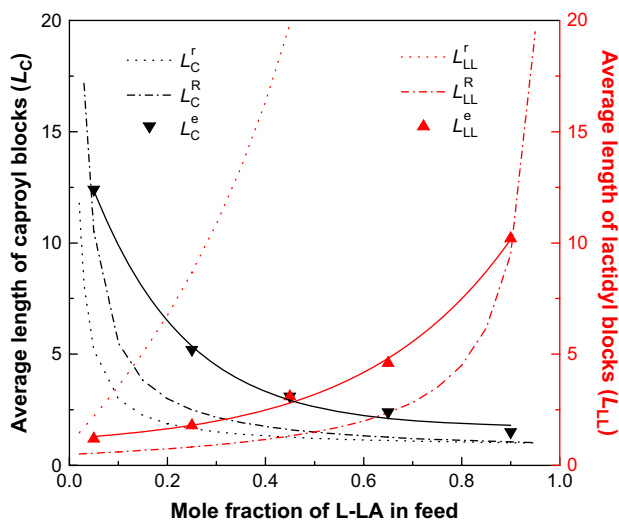Brief summary, it is relevant to note that the synthesized copolymers here are more random, as evidenced by their ^{13}C NMR spectra (Fig. 5) and interpreted by Kaspercyzk and Bero [45], but with some blocky character as reflected by comparisons of their three kinds of microblock lengths (Fig. 6).

3.3. Thermal properties and crystallinities of the obtained copolymers

The thermal properties of the obtained copolymers were investigated by DSC, the second heating scan was obtained after quench cooling of the sample following the first heating scan. The melting temperature (T_m), heat of melting (ΔH_m) and glass transition temperature (T_g) are marked in the corresponding DSC curves in Figs. 7 and 8. PLLA and PCL are both intrinsically semi-crystalline polymers. A broad melting peak at 171 °C was observed with PLLA (Fig. 7a), while PCL showed a sharp and strong melting peak at 61 °C (Fig. 7 g).

The copolymer composition and chain microstructure have a profound influence on the thermal properties and crystallinities of the obtained copolymers. When PLLA component was dominant, the samples PCLA1 and PCLA2 with L-LA/ε-CL 0.90/0.10 and 0.65/0.35 showed a T_m peak at 157 °C and 126 °C from PLLA, but no T_m peak from PCL (Fig. 7b and c). This is probably because the ε-CL unit sequences were not long enough and/or required longer relaxation times to crystallize following melt-quenching. While at the higher ε-CL content, Samples PCLA4 and PCLA5 with ratios of L-LA/ε-CL 0.25/0.75 and 0.05/0.95 showed single melting peaks in the range of $T_m = 45$–60 °C (Fig. 7e and f). This, in turn, implies that the lactidyl sequences were not long enough to form PLLA crystalline microdomain. In contrast, PCLA3 containing a comparative composition showed two distinct melting endotherms, indicating the existence of both PLLA and PCL crystalline microdomains.
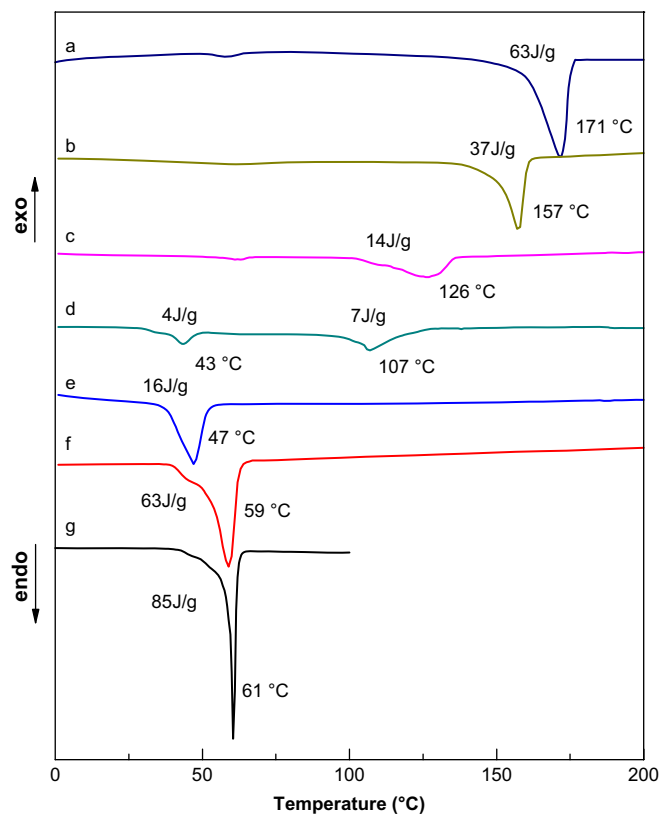

Fig. 6. Average block length as a function of L-LA in feed with theoretical (dashed curves) and experimental (dots) values.

Fig. 7. First heating of DSC curves for PLLA, PCL and L-LA/CL copolymers: (a) PLLA; (b) P(LLA-co-CL)1; (c) P(LLA-co-CL)2; (d) P(LLA-co-CL)3; (e) P(LLA-co-CL)4; (f) P(LLA-co-CL)5; (g) PCL.

Fig. 8. Second heating of DSC curves for PLLA, PCL and L-LA/CL copolymers: (a) PLLA; (b) P(LLA-co-CL)1; (c) P(LLA-co-CL)2; (d) P(LLA-co-CL)3; (e) P(LLA-co-CL)4; (f) P(LLA-co-CL)5; (g) PCL.
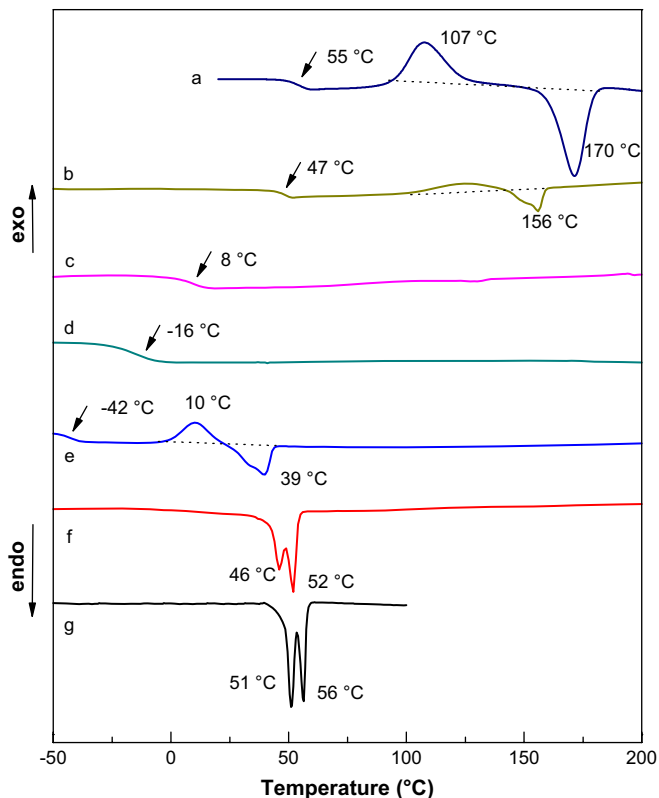

Fig. 10. WAXD patterns of PLLA, PCL and L-LA/CL copolymers: (a) PLLA; (b) P(LLA-co-CL)1; (c) P(LLA-co-CL)2; (d) P(LLA-co-CL)3; (e) P(LLA-co-CL)4; (f) P(LLA-co-CL)5; (g) PCL.

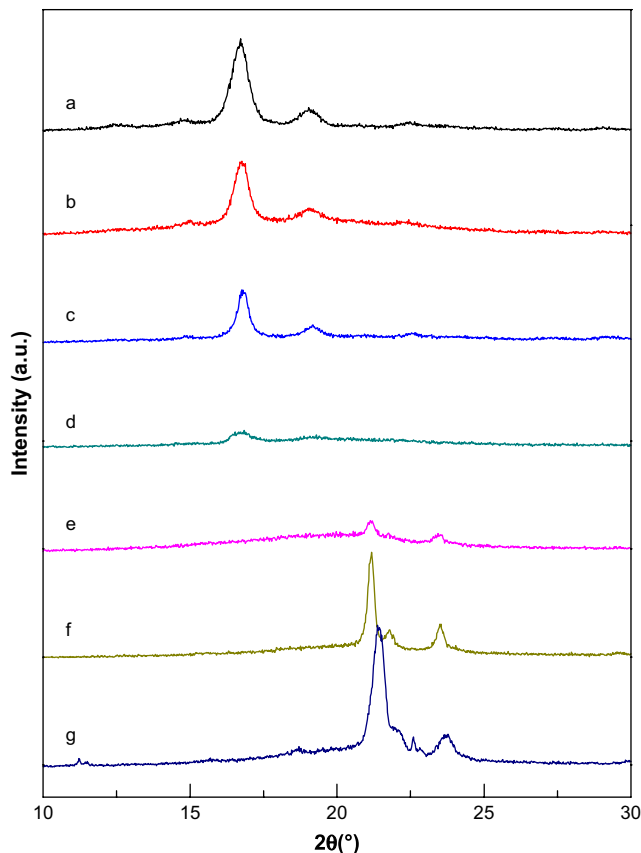However, this two weak melting endotherms observed on the first heating scan (Fig. 7d) disappeared on the second heating scan after cooling (Fig. 8d). Combining with the above analysis results of chain microstructure in Table 1, it illuminated that ca. three repeating units of lactidyl and caproyl in PCLA3 is long enough to allow their crystallization to occur, but their crystallizability is quite weak in rapid cooling process.

It can be found from Figs. 7 and 8 that the increasing presence of one type of block decreases the crystallize ability and ΔH_m value of the other type, as would be expected on thermodynamic grounds. Both T_m and ΔH_m values increased with the L-LA/ε-CL ratio, while the width of the melting range decreased as the L-LA-rich crystalline domains became more uniform and less disordered. Fig. 9 showed the composition dependence of the T_m of the copolyesters measured by DSC during the first heating scan. A linear relationship between the T_m of the PLLA or PCL blocks and the concentration of L-LA or ε-CL, respectively, was observed. These results are consistent with the higher L_{LL}^e and L_C^e values and lower transesterification coefficient of the copolymer from ^{13}C NMR. Hence, the values of ΔH_m and T_m are significantly affected not only by the copolymer composition but also by L_{LL}^e and L_C^e values.

It is well known that a block copolymer usually exhibits two T_gs, in contrast to a random one, the unique T_g of which is predicted by the Fox equation.

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \tag{9}$$

Where T_g is the glass transition of the copolymer, w_i and T_{gi} are the weight content for compound i and T_g for the parent homopolymer, respectively.
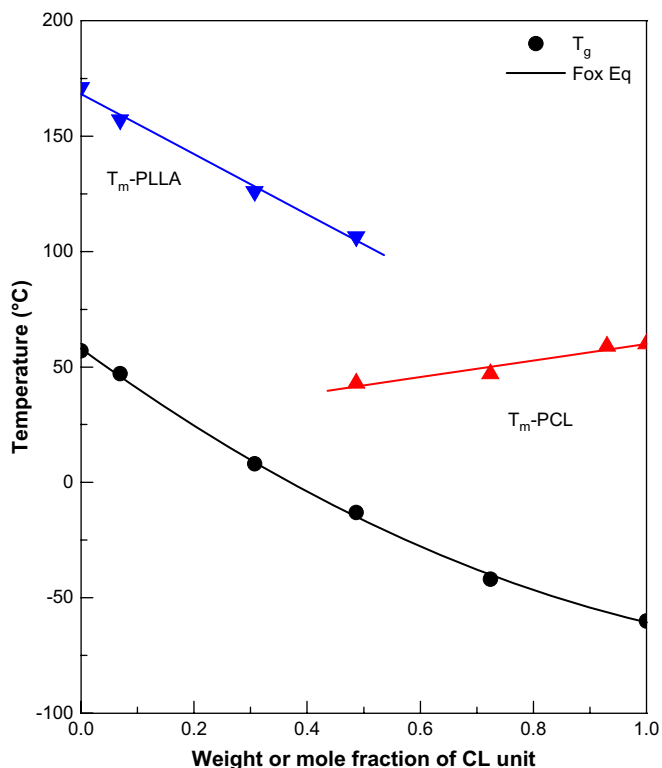

Fig. 9. Phase diagram of L-LA/CL copolymers with experimental values of T_g and T_m.

Only a T_g for each copolymer was observed during the second heating curves (Fig. 8). The single T_g values are significant in that they are an indication that the amorphous domains of the copolymers are miscible and there is no phase separation between PCL and PLLA crystalline domains. Fig. 9 showed that experimental T_g changes with the PCL percent of the copolymer and fitted the Fox equation within the limits of experimental errors, which is in favor of a random structure. It may also be possible that the copolymers are random, or comprise a mixture of compatible block copolymers.

The WAXD patterns of copolymers at various comonomer compositions and their PLLA and PCL homopolymers were depicted in Fig. 10. With pure PLLA, as shown in Fig. 10a, the peaks at $2\theta = 16.8$ and $18.8°$ are characteristic of crystalline PLLA. Due to the interference from the PCL unit, the relative intensity of these two peaks decreases with increasing ε-CL unit fraction in the copolymers, vice versa. The observation of characteristic peaks of crystalline PCL at $2\theta = 21.6$ and $23.8°$ (Fig. 10e and f) in PCLA4 and PCLA5 indicated that the formation of a PCL crystalline phase as in pure crystalline PCL (Fig. 10g). The WAXD patterns of the copolymers were consistent with the thermal properties by DSC measurement, but little difference existed between WAXD and DSC results for PCLA3. A small and broad peak of PLLA was observed, which indicated that the sample has lower crystallinity than others with longer PLLA block lengths. However, no obvious characteristic reflection peaks for crystalline PCL appeared, which indicated that PCL crystalline was undetectable by WAXD (Fig. 10d). This contradiction may be due to the difference in the sensitivity of both methods. In DSC, the change of heat flow is measured, whereas X-ray diffraction occurs when the periodic structure exists [52].

4. Conclusions

The L-LA/ε-CL copolymers with various compositions were prepared by the copolymerization of L-lactide and ε-caprolactone using nontoxic magnesium octoate as a catalyst. As for as their pharmaceutical application is concerned, the obtained polymers without containing any toxic heavy metal ions are reasonably desirable and high molecular weight is always unnecessary and even undesirable. The obtained copolymers with moderate molecular weight, although not yet satisfactory, could be as alternative for the ones by tin catalyst, especially used as drug carriers. In addition, we believed that the L-LA/ε-CL copolymers with much higher molecular weight could be obtained by using high vacuum technique instead of nitrogen-filled atmosphere. Thus, the above results showed that magnesium octoate is an efficient catalyst with moderate activity for the copolymerization of L-LA and ε-CL. A tapered block or gradient copolymer is expected to be formed due to the differences in the reactivity of comonomers. Transesterification reaction played an important role in the redistribution of monomer sequences to more random, but this randomizing effect did not lead to a complete random chain. The obtained copolymers can best be described as random copolymers with some compatible blocky character. The thermal properties and crystallization depend on both the composition and the chain microstructure.

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