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Copolymers of *rac*-Lactide and ϵ -Caprolactone: Conventional Copolymerization vs. Macroinitiator Copolymerization

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Copolymers of *rac*-lactide (*rac*-LA) and ϵ -caprolactone (CL) were synthesized with tin(II) 2-ethylhexanoate and 1,4-butanediol at 130°C using two methods of copolymerization: conventional copolymerization and sequential polymerization using poly(CL) as a macroinitiator for *rac*-LA. Conventional copolymerizations showed a retarded rate of CL conversion until *rac*-LA reached high conversion. The macroinitiator method led to reduced overall reaction time to reach high conversion of both monomers. At a low CL comonomer ratio, the copolymers synthesized by the two different methods were very similar but, as the comonomer ratio was increased, differences in monomer sequencing (e.g. random vs. blocky) as determined by ¹³C-NMR and glass transition were observed. Additionally, macroinitiator synthesis carried out at 150°C in an effort to promote transesterification did not show any significant differences from the copolymer synthesized at 130°C.

Keywords: Biodegradable polymer, polylactide, poly(ϵ -caprolactone), poly(lactide-co- ϵ -caprolactone), macroinitiator

1 Introduction

Biodegradable polymers such as polylactide (PLA), polyglycolide (PGA), and poly(ϵ -caprolactone) (PCL) are of great interest because of their biomedical and general consumer thermoplastic applications. Copolymers derived from combinations of lactide, glycolide, and ϵ -caprolactone are likewise of interest since copolymerization is an effective and inexpensive way to customize such properties as glass transition, extent of crystallinity, and biodegradation rate. For copolymerizations that tend toward random incorporation of the two comonomers, the physical and thermal properties of the resultant copolymer will generally be intermediate between those of either homopolymer (1). However, variations in the degree of randomness of the copolymer can arise, largely dependent upon the copolymerization behavior of the comonomer pair. These effects are often magnified for high conversion copolymerizations due to comonomer drift as a result of early incorporation of the monomer that is more reactive in copolymerization. Ring opening copolymerizations are additionally complicated

by the significance of various equilibria among monomer, cyclic oligomer, and polymer (propagation-depropagation equilibrium).

The copolymerization of *rac*-lactide (*rac*-LA) and ϵ -caprolactone (CL), catalyzed by tin(II) 2-ethylhexanoate, is the primary focus of this investigation. It is known that CL homopolymerizes at a faster rate than does *rac*-LA, (2, 3) but in copolymerization *rac*-LA polymerizes to nearly $[rac-LA]_{eq}$ before significant conversion of CL is observed (2, 4–6). This behavior indicates that the growing chain end, whether it is lactoyl- or caproyl-based, is more reactive toward *rac*-LA than CL. In a practical sense, this creates the possibility for compositional drift, and it causes the copolymerization rate to be lower than either homopolymerization rate; thus, inconveniently long reaction times are often necessary to achieve full conversion of the CL monomer. A significant practical advantage of the copolymerization is that the equilibrium concentration of *rac*-LA is much lower than in the homopolymerization of *rac*-LA under similar conditions.

As would be expected, the polymerization catalyst can affect the behavior of the copolymerization, affecting both the rate of the reaction and the sequence distribution of the comonomers. There have been a number of investigations into various catalysts to improve the randomness of poly(*rac*-LA-co-CL). Some examples include rare earth-chloride-propylene oxide, (7) bismuth(III) *n*-hexanoate, (8)

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as well as Al and Zn-based catalysts (6, 9). Randomization is achieved in part due to transesterification. Two types of transesterification can occur: the first mode of transesterification is that which does not produce a CLC or CLLC sequence (C = caproyl, L = lactoyl) and the second mode of transesterification is that which does produce a CLC or CLLC sequence, requiring the division of one lactide unit to produce an odd number of L units between C units (9). Although these systems did improve the randomness of the copolymer, in most cases long reaction times were required. Tin(II) 2-ethylhexanoate is perhaps the most widely used catalyst (or co-initiator) for lactone polymerizations. Kricheldorf et al. have observed that at low reaction temperatures ($\leq 120^\circ\text{C}$) no transesterification is observed, which would lead to blocky copolymer, but at higher temperatures randomization does occur (10).

Conventional copolymerizations are performed by initiation of a comonomer charge containing the full compliment of both monomers and allowing the copolymerization to proceed to some overall conversion. In a previous paper, we reported a method whereby a macroinitiator formed from one monomer can be used to initiate the polymerization of a second monomer (11). For the case of initiation of *rac*-LA by a poly(ϵ -caprolactone) macroinitiator, we have recently observed that the total polymerization time to create the macroinitiator (ϵ -caprolactone polymerization plus subsequent *rac*-LA polymerization) was less than that required to create a copolymer with the same molecular weight and comonomer composition by the conventional method. The goal of this work is to address the following proposition: if Sn(Oct)₂-catalyzed polymerization of *rac*-LA is initiated by a pre-formed poly(ϵ -caprolactone) macroinitiator, is transesterification sufficient to yield a copolymer that is essentially the same as that obtained using a conventional copolymerization? To this end, the rate of *rac*-LA and CL conversions in conventional copolymerizations was compared to the rate of *rac*-LA polymerizations using a poly(ϵ -caprolactone) macroinitiator to initiate the *rac*-LA. The sequence distributions of the resulting copolymers were investigated using ¹³C carbon nuclear magnetic resonance (¹³C-NMR). Additionally, differential scanning calorimetry was used to observe glass transition behavior of the different copolymers.

2 Experimental

2.1 Materials

1,4-Butanediol (BD) and tin(II) 2-ethylhexanoate (SnOct, Aldrich) were used as received. *rac*-Lactide was generously donated by Ortec, Inc. in Easley, SC and was used as received. ϵ -Caprolactone (TONE, Dow) was vacuum distilled from calcium hydride (Aldrich) and stored under nitrogen prior to use.

2.2 Procedures

2.2.1. Calibration of Refractive Index (RI) response to *rac*-lactide and ϵ -caprolactone

The response of the SEC refractive index (RI) detector toward both *rac*-LA and CL was determined by measuring RI peak height produced by monomer solutions in THF of known concentration. This will be described in detail for ϵ -caprolactone (the procedure was similar for *rac*-lactide): Five solutions of CL in THF were prepared at the following concentrations: 1.0, 1.8, 3.4, 4.9, and 6.2 mg/mL. A 100 μL injection of each solution was introduced into the SEC mobile phase, and the height (in arbitrary units) of the peak eluting at 19.3 mL was recorded. The five data points were then plotted as RI peak height vs. injected mass (g), resulting in a straight line defined by the following equation: RI Peak Height = $-0.01421 + 721.32 \times \text{Injected Mass CL}$ ($R^2 = 0.9997$). The corresponding equation for *rac*-lactide was RI Peak Height = $0.00433 + 493.11 \times \text{Injected Mass } rac\text{-LA}$ ($R^2 = 0.9997$).

The method for calculating monomer conversion of a polymerization aliquot will now be described for the 50/50 mol% conventional copolymerization, which is representative: An aliquot from the bulk copolymerization was removed from the reactor after 6 min of reaction time using a pipette and rapidly cooled to quench further reaction. A solution of the aliquot was prepared in THF with a concentration, c , of 26.5 mg/mL, and 100 μL of that solution was injected into the SEC mobile phase. The resulting chromatogram is shown in Figure 1. From the observed peak height at 19.3 mL, the mass of CL in the aliquot, m_{CL} , was calculated to be 1.0×10^{-3} g; likewise, from the observed peak height at 18.2 mL, the mass of *rac*-LA in the aliquot, m_{LA} , was calculated to be 9.8×10^{-5} g. For a 100 μL injection, the total mass of the aliquot, m_{Tot} , was 2.65×10^{-3} g. The original mass fraction of CL in the reaction, f_{CL} , was 0.442 for a 50/50 mol% copolymer feed. Thus, the conversion of CL in the aliquot, p_{CL} , was calculated as 0.145 using the following equation:

$$p_{\text{CL}} = \frac{f_{\text{CL}}m_{\text{Tot}} - m_{\text{CL}}}{f_{\text{CL}}m_{\text{Tot}}}$$

In an analogous manner, the conversion of *rac*-LA, p_{LA} , was calculated to be 0.934.

2.2.2. Conventional copolymerization of *rac*-lactide and ϵ -caprolactone

Reactions were formulated within a Vacuum Atmospheres Company Dri-Lab glove box under an inert N₂ atmosphere. A representative procedure for a 90/10 (mol/mol) *rac*-lactide/ ϵ -caprolactone copolymer was as follows: 66.847 g (0.464 mol) of *rac*-lactide and 5.882 g (0.0516 mol) of ϵ -caprolactone were added to a 100 mL, 2-neck round bottom flask. The flask was then equipped with an overhead stirrer, and immersed into a 130°C thermostated oil bath, contained within a dry N₂ glove box, for ~20 min to fully

melt the monomers. Then, 1.335 g (0.0148 mol) of BD was injected and the mixture was stirred briefly. SnOct, 0.025, (0.062 mmol, 100 ppm Sn) was then injected into the flask and the polymerization was carried out for 24 h. Aliquots of the reactor contents were collected at the following time intervals: 30 s, 2, 4, 6, 8, 10, 15, 20, and 40 min, 1, 1.5, and 2 h, and then hourly up to at least 8 h and lastly sometime between 22–24 h. Aliquots were collected in scintillation vials and cooled to room temperature in the antechamber of the glove box.

2.2.3. Macroinitiator copolymerization of rac-lactide and ϵ -caprolactone

Reactions were formulated within a Vacuum Atmospheres Company Dri-Lab glove box under an inert N₂ atmosphere. A representative procedure for a 90/10 (mol/mol) rac-lactide/ ϵ -caprolactone copolymer was as follows: 23.530 g (0.206 mol) of ϵ -caprolactone and 5.341 g (0.0593 mol) BD were added to a 100 mL, 2-neck round bottom flask. Then, 66.868 g (0.464 mol) of rac-lactide was added to a second 100 mL, 2-neck round bottom flask. The first flask, containing the ϵ -caprolactone, was then equipped with an overhead stirrer, and immersed into a 130°C thermostated oil bath, contained within a dry N₂ glove box, for ~5 min to heat the monomer. Then, 0.102 g (0.20 mmol, 100 ppm Sn in final polymer) of SnOct was injected into the flask and the polymerization was carried out for 1 h. Aliquots were collected at 1, 5, 10, 20, 30, 45, and 60 min. Aliquots were collected in scintillation vials and cooled to room temperature in the antechamber of the glove box. At an elapsed time of 40 min, the second flask containing rac-lactide, was immersed into a 130°C thermostated oil bath, contained within a dry N₂ glove box, to melt the lactide monomer. After the 60 min aliquot had been collected from the first flask, 7.246 g of the reaction mixture was added to the second flask. During the reaction in the second flask, aliquots were collected at the following time intervals: 30 sec, 2, 4, 6, 8, 10, 15, 20, and 40 min, 1, 1.5, and 2 h, then hourly up to at least 8 h, and lastly sometime between 22–24 h. Aliquots were collected in scintillation vials and cooled to room temperature in the antechamber.

2.3 Instrumentation

2.3.1. Size exclusion chromatography

Monomer conversions were determined using a SEC system consisting of a Waters Alliance 2695 Separations Module, an on-line multi-angle laser light scattering (MALLS) detector (MiniDAWNTMTREOS, Wyatt Technology Inc.), an interferometric refractometer (RI detector, Optilab DSPTM, Wyatt Technology Inc.) and two mixed E (pore size range 50–103 Å, 3 μ m beads) PLgelTM (Polymer Laboratories Inc.) SEC columns connected in series. Freshly distilled THF served as the mobile phase and was delivered at a flow rate of 1.0 mL/min. Sample concentrations were

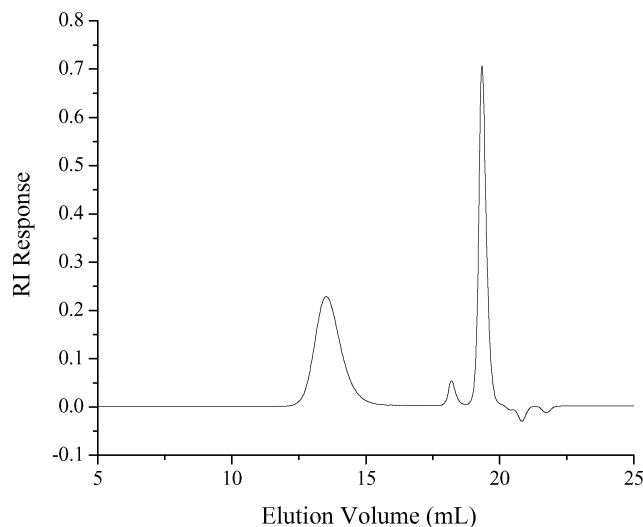


Fig. 1. SEC chromatogram of 50/50 mol% rac-LA/CL conventional copolymerization at 6 min.

ca. 7–40 mg of polymer/mL of THF, and the injection volume was 100 μ L. The detector signals were simultaneously recorded using ASTRATM 5.3 software (Wyatt Technology Inc.).

2.3.2. Nuclear magnetic resonance spectroscopy

¹³C-NMR spectra were obtained using a 300 MHz Varian Mercury plus spectrometer operating at 75.5 MHz for carbon. The samples were prepared in 5-mm (o.d.) glass tubes and the concentration was approximately 10–25% (w/w) in *d*-chloroform. Carbon signals were reported against the published solvent lock resonance of 77.16 ppm.

3 Results and Discussion

The macroinitiator and conventional copolymerization methods were compared with regard to rate of polymerization and monomer sequence distribution at a reaction temperature of 130°C. Two compositions of copolymer were studied: 90/10 and 50/50 mol% rac-LA/CL. The macroinitiator method was carried out by first polymerizing the ϵ -caprolactone, utilizing the full complement of initiator and SnOct for 1 h. The resulting oligo(ϵ -caprolactone) was then added to the appropriate amount of molten rac-LA to continue the polymerization. The conventional method was carried out by fully melting and mixing the monomers with the initiator prior to starting the polymerization by the addition of catalyst.

SEC was utilized to analyze reaction aliquots, such that the conversions of rac-LA and CL could be monitored independently of each other. The conversions calculated from the aliquots are plotted vs. time for each of the four copolymerizations in Figures 2–5. The plot in Figure 2, for the conventional copolymerization with initial comonomer

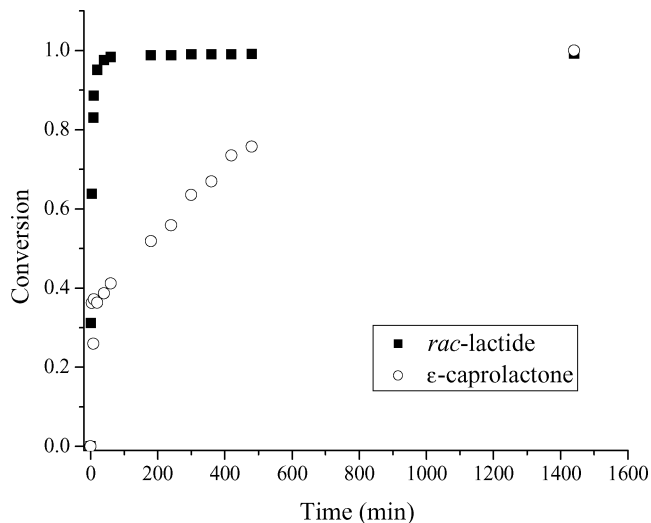


Fig. 2. Conversion vs. time of conventional copolymerization of 90/10 mol% *rac*-LA/CL. $T = 130^{\circ}\text{C}$; $[\text{SnOct}] = 0.837 \text{ mol/kg}$.

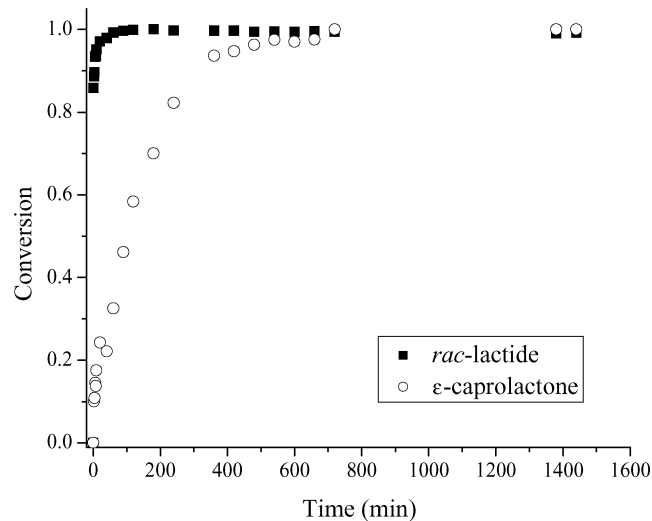


Fig. 4. Conversion vs. time of conventional copolymerization of 50/50 mol% *rac*-LA/CL. $T = 130^{\circ}\text{C}$; $[\text{SnOct}] = 0.837 \text{ mol/kg}$.

feed of 90/10 mol% *rac*-LA/CL, indicates that the *rac*-LA conversion reached equilibrium in about 120 min, while the CL conversion was only about 75% at 480 min. We estimate that the CL reached maximum conversion in approximately 1,200 min. Using the macroinitiator method as displayed in Figure 3, the CL was completely converted in 60 min and then added to the *rac*-LA. The *rac*-LA then reached maximum conversion in an additional 90 min for a total reaction time to reach maximum conversion of both monomers of 150 min.

The same trends were observed for the 50/50 mol% *rac*-LA/CL copolymerizations in Figures 4 and 5. The *rac*-LA reached maximum conversion in 120 min, while the CL took 720 min in a conventional copolymerization. The

macroinitiator method achieved full conversion of CL in 60 min. The macroinitiator was then added to *rac*-LA, which reached maximum conversion in an additional 120 min, for a total reaction time of 180 min to fully convert both monomers as opposed to 720 min for the conventional copolymerization.

The kinetic comparisons clearly showed that the macroinitiator method offers a significant advantage in terms of time of reaction. The next issue to address was whether the copolymers produced via the macroinitiator method were sufficiently randomized by transesterification to be essentially the same as those produced by the conventional copolymerization. To this end, differential scanning calorimetry (DSC) was used to compare each pair

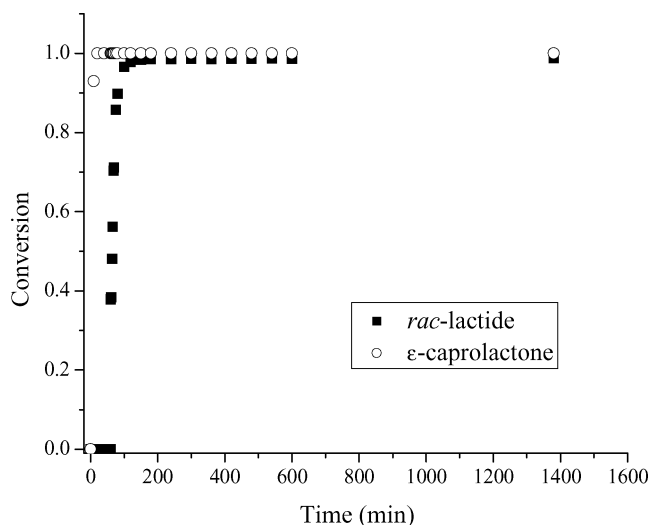


Fig. 3. Conversion vs. time of macroinitiator copolymerization of 90/10 mol% *rac*-LA/CL. $T = 130^{\circ}\text{C}$; $[\text{SnOct}] = 0.837 \text{ mol/kg}$.

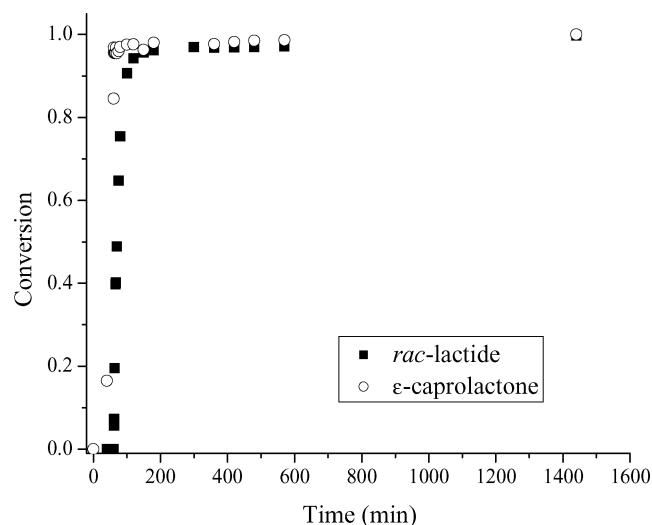


Fig. 5. Conversion vs. time of macroinitiator copolymerization of 50/50 mol% *rac*-LA/CL. $T = 130^{\circ}\text{C}$; $[\text{SnOct}] = 0.837 \text{ mol/kg}$.

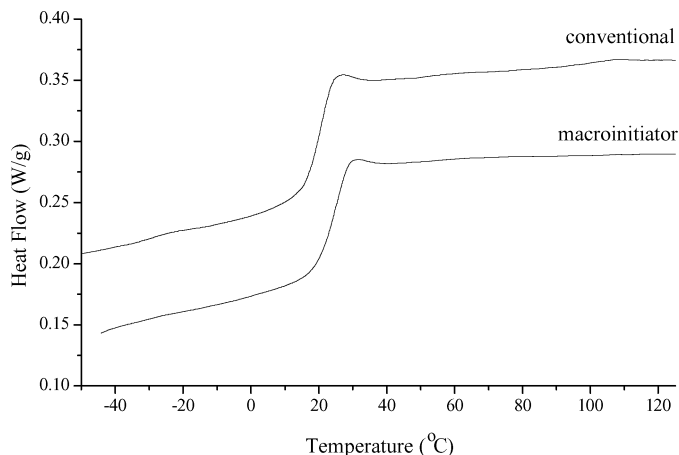


Fig. 6. DSC of 90/10 mol% *rac*-LA/CL copolymers.

of copolymers in terms of the position and breadth of the glass transition. Completely random copolymers are predicted to display one glass transition temperature (T_g) somewhere between that of the two respective homopolymers as defined by the Fox equation. In contrast, a well phase-separated block copolymer should exhibit two individual T_g s. The 90/10 mol% *rac*-LA/CL copolymers both showed one T_g at 21 and 25°C for the conventional and macroinitiator methods, respectively (Figure 6). The minor difference in T_g s does suggest that there are differences in the randomness of the copolymers, but neither were blocky enough to exhibit two distinct T_g s. The 50/50 mol% *rac*-LA/CL copolymers also showed one T_g (Figure 7); however, the T_g of the macroinitiator copolymer was a very broad transition compared to that of the conventional copolymer. The T_g of the conventional copolymer was -20°C and the T_g of the macroinitiator copolymer was -28°C . The lower T_g s as compared to the 90/10 system are characteristic of the higher content of CL. Not surprisingly, there was a larger difference in T_g between the two meth-

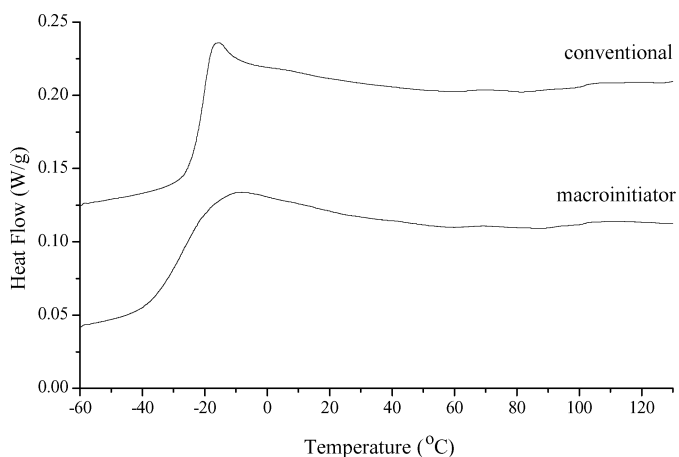


Fig. 7. DSC of 50/50 mol% *rac*-LA/CL copolymers.

ods of copolymerization than what was observed in the 90/10 system; although, in contrast to the 90/10 system, in the 50/50 system, the macroinitiator copolymer displayed the lower T_g . The temperature difference and the shape of the transition both indicate that there are significant differences in the backbone sequencing between the two 50/50 copolymers.

^{13}C -NMR was used to analyze the differences in comonomer sequencing between the copolymers from the macroinitiator method versus the conventional copolymerization. One might expect a blocky nature in either case since most of the CL is incorporated toward the end of the conventional copolymerizations, and by definition, all of the CL is incorporated at the beginning of the macroinitiator method. Figures 8 and 9 show the carbonyl region of the ^{13}C -NMR spectra of the 90/10 and 50/50 mol% *rac*-LA/CL copolymers, respectively. Since the goal of the macroinitiator copolymerization method was to produce a polymer similar to that of a conventional copolymerization in a shorter time, the NMR spectra displayed are those of each polymer when both monomers reached maximum conversion. Evidence of transesterification was observed in all of the copolymers indicated by a monomer sequence with one or three lactoyl units (L, one lactic acid moiety) between two caproyl units (C). Interestingly, only the 50/50 conventional copolymer showed the CLC sequence, which would result from backbone cleavage at the first or last

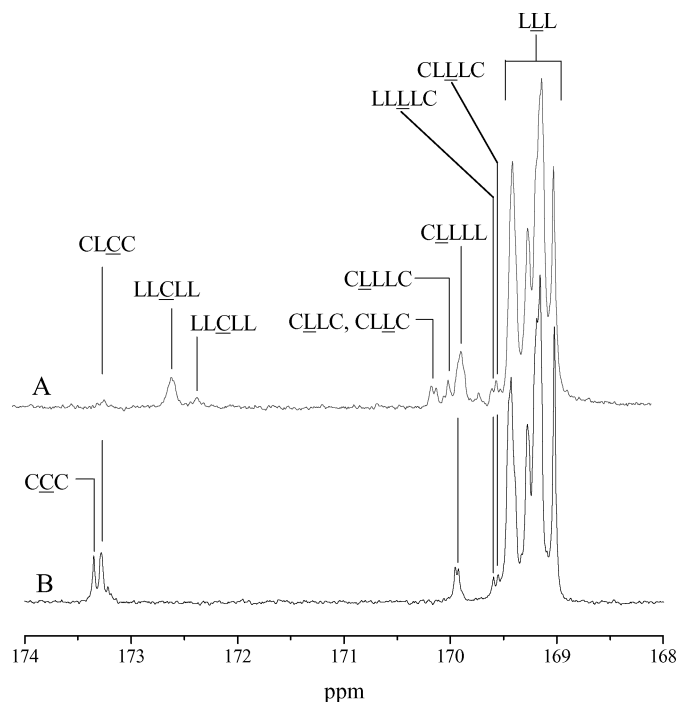


Fig. 8. Carbonyl region of the ^{13}C NMR spectra of 90/10 mol% *rac*-LA/CL copolymers produced by conventional copolymerization (A) and macroinitiator method (B).

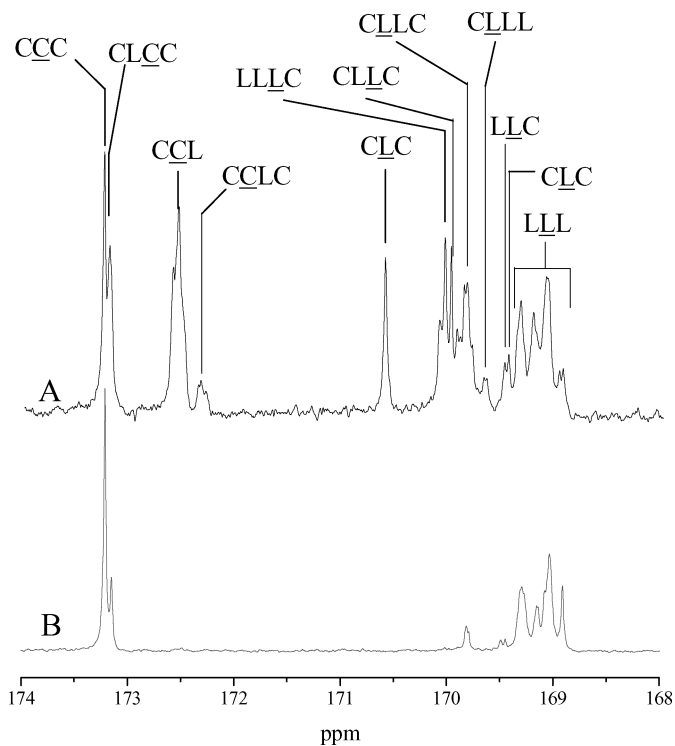


Fig. 9. Carbonyl region of the ^{13}C NMR spectra of 50/50 mol% *rac*-LA/CL copolymers produced by conventional copolymerization (A) and macroinitiator method (B).

ester linkage within any continuous sequence of two or more lactoyl units (6, 8).

Based on the sequencing of caproyl units in Figure 8, it was evident that the macroinitiator copolymer was incompletely randomized since it still retained CCC sequences, which are statistically unlikely at this composition and are in fact absent in the conventional copolymer. Also, there was no LCL sequences in the macroinitiator copolymer where one C was between two lactidyl groups. Neither 90/10 copolymer exhibited much observable transesterification (as indicated by CLC or CLLC sequences) due to the low CL content.

The 50/50 copolymers displayed in Figure 9 showed more pronounced differences. Most obvious was the very blocky nature of the macroinitiator copolymer with the vast majority of the sequences being CCC or LLL. Conversely, the 50/50 conventional copolymer showed a wide array of sequences including a number of sequences only obtainable by transesterification. The wide distribution of monomer sequencing indicated a very random copolymer.

Since the 50/50 mol% *rac*-LA/CL macroinitiator polymerization yielded a very blocky copolymer at 130°C, the procedure was repeated at a reaction temperature of 150°C and for longer times to promote transesterification reactions. The conversion vs. time plot in Figure 10 showed that maximum *rac*-LA conversion was reached at a total reaction time of 120 min, which was faster than the reaction

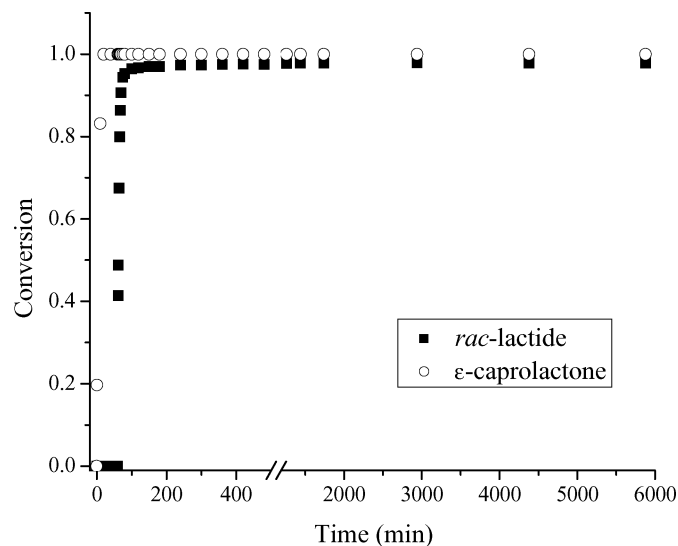


Fig. 10. Conversion vs. time of macroinitiator copolymerization of 50/50 mol% *rac*-LA/CL. $T = 150^\circ\text{C}$; $[\text{SnOct}] = 0.837 \text{ mol/kg}$

at 130°C, as expected. The DSC thermogram in Figure 11 indicated a very broad T_g centered at -28.9°C , very similar to the 130°C reaction. The ^{13}C -NMR spectrum in Figure 12 was also very similar to that for the 130°C reaction, indicating a very blocky copolymer. At 24 h of reaction time, there was no distinct difference between the spectra of the 130 and 150°C products. In an attempt to further promote transesterification, the 150°C polymerization was carried out to very long reaction times. However, essentially no differences were observed in the product after 72 and even 97 h, compared to 24 h, and particularly, no evidence of second mode transesterification was observed in terms of a CLC sequence at 170.5 ppm.

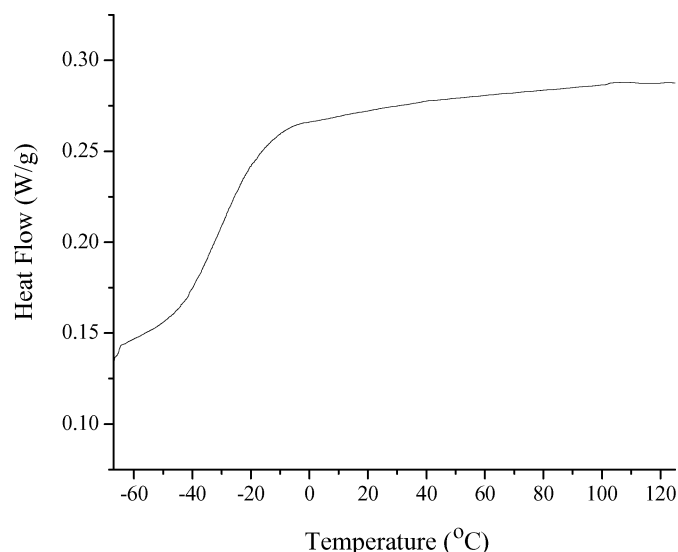


Fig. 11. DSC of 50/50 mol% *rac*-LA/CL macroinitiator copolymer synthesized at 150°C, 24 h reaction time.

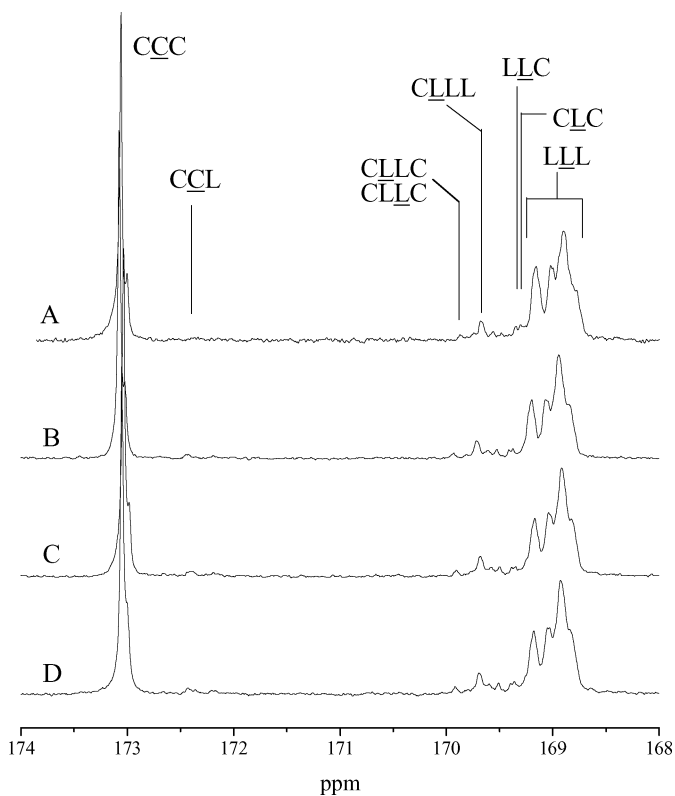


Fig. 12. Carbonyl region of the ^{13}C -NMR spectrum of macroinitiator 50/50 mol% *rac*-LA/CL synthesized at 150°C ; reaction time: (A) 24 h, (B) 48 h, (C) 72 h, and (D) 97 h.

4 Conclusions

For *rac*-lactide/ ϵ -caprolactone copolymers with low CL comonomer compositions, such as 90/10 mol% *rac*-LA/CL, it is possible to obtain copolymers by the macroinitiator method that have very similar properties to corresponding copolymers synthesized by the conventional method, and the macroinitiator method significantly reduces the overall reaction time needed to reach maximum conversion of both monomers. However, there are detectable differences in the comonomer sequencing as observed using ^{13}C -NMR, and slight differences in the observed T_g by DSC. In contrast, a copolymer produced from an equimolar *rac*-LA/CL comonomer feed varies greatly depending on which method of synthesis is used. The macroinitiator method polymer had a very broad T_g region in the DSC thermogram unlike the conven-

tional copolymer that had a very distinct, sharp transition. Also, ^{13}C -NMR analysis indicated that the macroinitiator copolymer had a very blocky nature; while the conventional copolymer had a wide array of monomer sequences indicative of a random copolymer. Additionally, increasing the polymerization temperature for the 50/50 *rac*-LA/CL macroinitiator synthesis to 150°C and extending the polymerization time to as long as 97 h resulted in essentially the same copolymer structure as that obtained at 130°C at 24 h, with no evidence of increased transesterification. In summary, the copolymers synthesized by the macroinitiator method were different than the copolymers synthesized by the conventional method; however, as would be expected, the difference diminished as the CL composition decreased.

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References

1. Odian, G. *Principles of Polymerization*, Wiley-Interscience: New York, 1991.
2. Duda, A., Libiszowski, J., Mosnacek, J. and Penczek, S. (2005) *Macromol. Symp.*, 226, 109–119.
3. Kowalski, A., Duda, A. and Penczek, S. (1998) *Macromolecules* 31, 2114.
4. Vanhoorne, P., Dubois, P., Jerome, R. and Teyssie, P. (1992) *Macromolecules*, 25, 37.
5. Chamberlin, B.M., Jazdzewski, B.A., Pink, M., Hillmyer, M.A. and Tolman, W.B. (2000) *Macromolecules*, 33, 3970–3977.
6. Bero, M. and Kasperczyk, J. (1996) *Macromol. Chem. Phys.*, 197, 3251–3258.
7. Shen, Y., Zhu, K.J., Shen, Z. and Yao, K.-M. (1996) *J. Polym. Sci. Part A: Polym. Chem.*, 34, 1799–1805.
8. Kricheldorf, H. R., Bornhorst, K. and Hachmann-Thiessen, H. (2005) *Macromolecules*, 38, 5017–5024.
9. Kasperczyk, J. and Bero, M. (1993) *Makromol. Chem.*, 194, 913–925.
10. Kricheldorf, H.R., Boettcher, C. and Tonnes, K.-U. (1992) *Polymer*, 33, 2817–2824.
11. Storey, R.F., Mullen, B.D., Desai, G., Sherman, J.W. and Tang, C.N. (2002) *J. Polym. Sci. Part A: Polym. Chem.*, 40, 3434.