Polymerization temperature effects on the properties of L-lactide and ε-caprolactone copolymers

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Summary

The large difference in reactivity of L-lactide and ε-caprolactone in ring opening polymerization with stannous octoate, leads to the formation of copolymers with blocky structures. By varying the polymerization temperature, copolymers with different average sequence lengths and molecular weights can be synthesized. It is shown that the average monomer sequence length has a large effect on the thermal and mechanical properties of these copolymers.

Introduction

Because of their use in biomedical applications (1,2,3), the preparation of copolymers and blends of L-lactide and ε-caprolactone has received much attention recently. A main application for these thermoplastic elastomers seems to be the degradable sustained drug release systems (1,4). However other applications such as meniscus prostheses, nerve guides, and burn wound coverings are also feasible (5). Throw-away objects, which degrade in the environment may also be manufactured from these polymers (6,7). In this paper the effect of the polymerization temperature on synthesis and properties of these copolymers will be discussed.

Experimental

Polymerizations

50/50 copolymers of L-lactide and ε-caprolactone were prepared by ring opening polymerization in bulk with stannous octoate as a catalyst. L-lactide (CCA, The Netherlands) was recrystallized from sodium dried toluene. ε-Caprolactone (Janssen Chimica, Belgium) was purified by drying over CaH_2 and distilling under reduced nitrogen atmosphere. To the freshly purified monomers, an amount of 1.10^{-5} mole catalyst per mole monomer was added.
Copolymerizations were conducted in evacuated silanized glass ampoules at different temperatures.

Compression Moulding

Sheets (3x10x0.1 cm) were obtained by compression moulding the bulk polymerized copolymer samples at 200 °C followed by slow cooling and annealing for 8 hours at 100 °C.

Copolymer Characterization

The intrinsic viscosities of the synthesized copolymers were measured in chloroform at 25 °C with an Ubbelohde viscosimeter.

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Monomer conversion and copolymer composition were determined by 300 MHz ^{1}H NMR of solutions in deuterated chloroform. Average sequence lengths were determined by 75 MHz ^{13}C NMR, but it was observed that 300 MHz ^{1}H NMR also showed neighbour effects of ε–caprolactone at δ=2.4 and 4.1 ppm, allowing the calculation of ε–caprolactone sequence lengths in good accordance to the ^{13}C determinations.

Thermal properties were measured on a Perkin-Elmer DSC-7, the 5-10 mg samples were heated at a rate of 20 °C per minute.

Stress-strain behaviour was examined with an Instron 4301 tensile tester. Compression moulded samples (4x50x1 mm) were tested at room temperature at a crosshead speed of 10 mm/min.

Dynamic mechanical analysis was performed on a Rheometrics RSA-II DMTA. In tension mode at a constant loading of 50 g, the compression moulded samples (4x50x1 mm) were subjected to an oscillating strain of maximum amplitude of 0.5% at a frequency of 1 Hz. The heating rate was 5 °C/min.

Results and Discussion

Copolymerizations of L–lactide and ε–caprolactone with co–ordination insertion catalysts are characterized by a larger reactivity of L–lactide (1,8,9). The relatively high value of L–lactide polymerization enthalpy can be attributed to the high ring strain in the skew boat conformation of the molecule (10).

This difference in reactivity is clearly illustrated in Figure 1. The conversion of 50/50 mixtures of both monomers at 110 °C is monitored as a function of time. It can be seen that L–lactide is preferentially polymerized, conversion being essentially complete after 48 hours. The ε–caprolactone conversion rate is much lower, and ε–caprolactone will be copolymerized after most L–lactide has been depleted. This difference in reactivity will lead to copolymers with blocky structures.
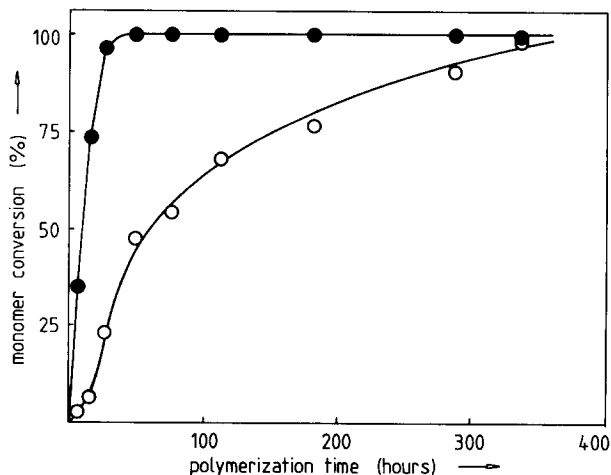
Figure 1:
L–lactide (●) and ε–caprolactone (o) conversion during copolymerization at 110 °C in the presence of stannous octoate
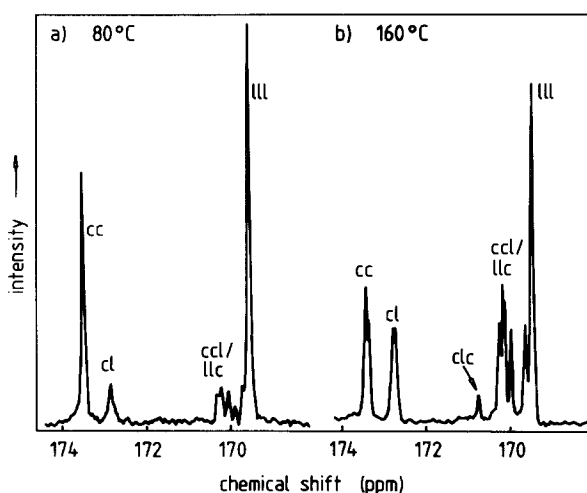
These blocky structures however, may be randomized by transesterification reactions (11). The terminal hydroxyl group of a growing polymer chain may attack an ester bond in a chain instead of adding a subsequent monomer by ring opening a lactone ester bond, especially as (reactive) monomers are depleted. It has been shown, that increasing the reaction time and temperature results in an increased extent of transesterification (12,13).

The influence of the polymerization temperature on the properties of the synthesized copolymers is given in Table 1. The time needed to achieve almost complete conversion is longer at lower polymerization temperatures. Copolymers with the highest molecular weights are obtained at the lowest polymerization temperature. This phenomenon was also observed for L-lactide homo polymers (14,15), and may be related to the temperature dependance of a keto-enol tautomerism of lactones (16).

Table 1

Influence of the polymerization temperature on 50/50 L-lactide and ε-caprolactone copolymers

pol.temp. (°C)	pol.time (days)	$[\eta]$ (dl/g)	$\overline{L}c$	$\overline{L}L$	CLC triad intensity (% of L-lac triads)
80	60	11.5	5.5	11.0	0
110	10	9.9	3.7	8.5	0.6
120	5	7.8	2.5	5.5	2.3
160	2	3.4	2.1	3.9	4.4

Figure 2:
Carbonyl region of the ^{13}C NMR spectrum of 50/50 P(LLA-ε-CL) copolymers displaying sequence effects. a) pol.temp.=80 °C, b) pol.temp.=160 °C

The average monomer sequence lengths $\bar{L}c$ and $\bar{L}L$ determined by ^{13}C NMR are greatly influenced by the polymerization conditions. The carbonyl region of the ^{13}C spectrum, Figure 2, is sensitive to sequence effects, and allows the calculation of average monomer sequence lengths (13). The average ε-caprolactone sequence length decreases with higher polymerization temperatures, indicating the formation of a more random copolymer. The presence of a CLC L-lactyl triad at higher temperatures shows that transesterification plays a larger role at higher polymerization temperatures. The extent of transesterification, given as the fraction of CLC triads, is also given in Table 1.

By placing a sample synthesized at 110 °C at a temperature of 160 °C for two days, it was shown that transesterification occurs predominantly during polymerization. The initial CLC triad fraction had not increased under these conditions.

Apart from increased transesterification reactions at higher temperatures, the blockiness of the copolymers may also decrease due to a smaller difference in reactivity of L-lactide and ε-caprolactone at higher temperatures.

Reactivity ratios were calculated assuming terminal control of lactone addition. Monomer and copolymer composition at low conversions were determined by ^1H NMR, the data was evaluated by the method derived by Kelen and Tüdõs (17). Our values determined at 80 °C and 110 °C together with data from the literature are given in Table 2.

Although at all temperatures L-lactide is more readily polymerized than ε-caprolactone, an increase in temperature leads to a decrease in the value of the product of the reactivity ratios. This implies the formation of a more random copolymer.

Table 2

Reactivity ratios of L-lactide and ε-caprolactone copolymerized with stannous octoate at different temperatures

| pol.temp. (°C)	r_{l-lac}	$r_{ε-cl}$	$r_{l-lac} * r_{ε-cl}$
80	57.1	0.39	22.3
110	42.0	0.36	15.1
130 [a]	34.7	0.24	8.3

a) data from ref. 1

As may be expected, copolymers varying in average monomer sequence length show quite distinct thermal and mechanical behaviour. The properties of copolymers synthesized at 110 °C, Copol-110, and synthesized at 80 °C, Copol-80, will be discussed.

Thermal analysis of copolymers differing in blockiness is given in Figure 3. The DSC scans were taken after compression moulding and annealing at 100 °C. The 50/50 copolymer synthesized at 110 °C with $\bar{L}c=3.7$ (A) shows a glass transition temperature at Tg=-15 °C and one at 55 °C, corresponding to two amorphous phases. The second one being rich in L-lactide, shows an enthalpy recovery peak (18,19). The melting endotherm Tm=102 °C, ΔH=4.0 J/g corresponds to fusion of small and imperfect L-lactide crystallites. The as-polymerized material was completely amorphous and displayed crystallinity only after weeks of annealing at room temperature.

Copol-80, (B), shows a single Tg at -39 °C, corresponding to an ε-caprolactone rich phase. Two melting endotherms; one at 44.3 °C, ΔH=5.8 J/g, and the other at 149 °C, ΔH=14.8 J/g can be observed. In this case ε-caprolactone sequences as well as L-lactide sequences are able to crystallize. An amorphous L-lactide phase cannot be detected.
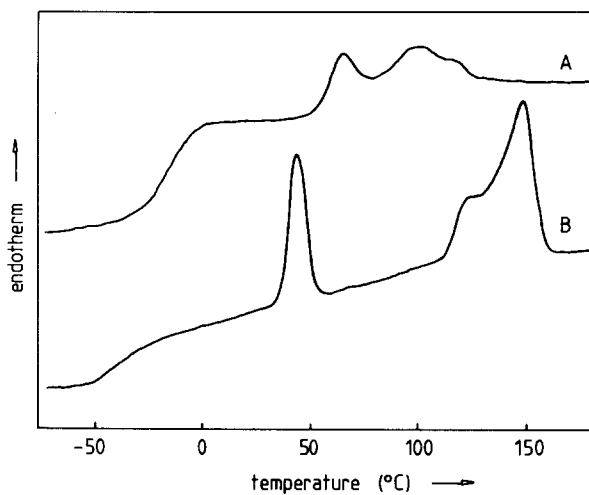
Figure 3:
DSC thermograms of 50/50 L-lactide and ε-caprolactone copolymers
A: synthesized at 110 °C, B: synthesized at 80 °C
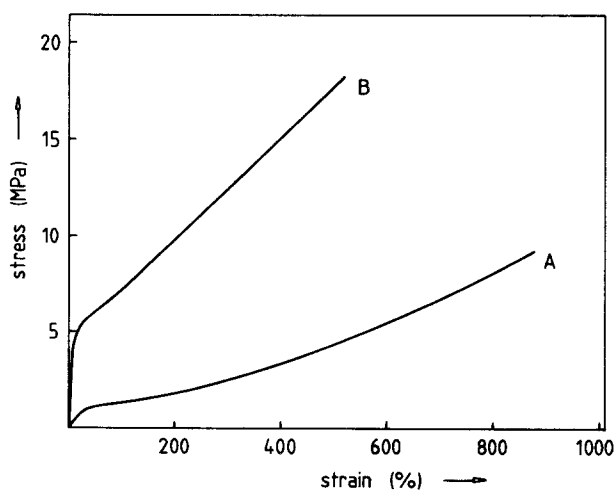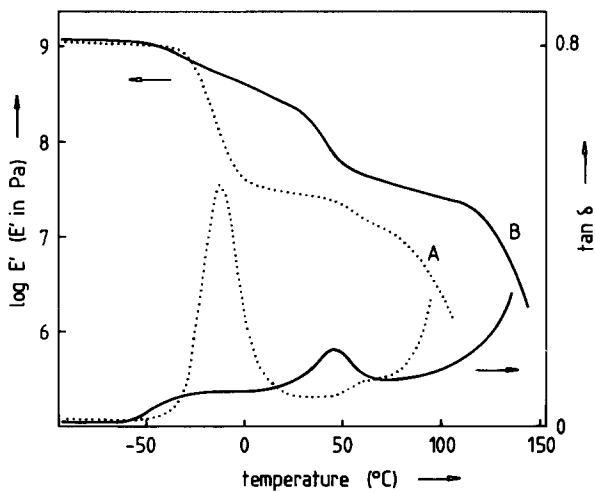

Figure 4:
Stress-strain diagrams of 50/50 L-lactide and ε-caprolactone copolymers
A: synthesized at 110 °C, B: synthesized at 80 °C

Figure 4 shows the stress–strain behaviour at room temperature of these copolymers after compression moulding and annealing. The higher average monomer sequence lengths and therefore higher crystallinity result in: higher initial modulus (84 vs. 5.2 MPa), lower strain at break (480 vs. 880 %), higher yield stress (5.0 vs. 1.0 MPa) and higher tensile strength at break (18.2 vs. 9.0 MPa) values for Copol–80 (B) in comparison to Copol–110 (A). Compression moulded specimens annealed at room temperature for several weeks displayed tensile properties comparable to those of samples annealed at 110 °C.

The dynamic mechanical behaviour of both materials is shown in Figure 5. The measured storage modulus E' and damping tan δ are given as a function of temperature.

Figure 5:
DMTA curves of 50/50 L–lactide and ε–caprolactone copolymers
A (····): synthesized at 110 °C, B (——): synthesized at 80 °C

For both copolymers the storage modulus at very low temperatures is comparable. Copol–110 (A) shows a first transition at –15 °C corresponding to the glass transition temperature of an amorphous phase consisting of L–lactide and ε–caprolactone sequences. A second transition at 50 °C due to an amorphous L–lactide rich phase can also be discerned. A rapid decrease in modulus at 100 °C can be attributed to the melting of L–lactide units, indicating a phase separated system consisting of a rubber phase and a smaller glassy phase, plus one built up of crystallites of L–lactide sequences.

Copol–80 (B) with longer average sequences, $\overline{L}c=5.5$, displays different DMTA behaviour. A low temperature glass transition at –50 °C can be observed at the inflection point of the E' curve. The corresponding tan δ peak beginning at –60 °C is very broad, indicating a rubbery phase of broad composition. Furthermore the melting of ε–caprolactone sequences at 48 °C and the melting of L–lactide units at 150 °C can be discerned.

It can be seen that at room temperature the loss modulus is a factor 10 higher than E' of copolymer A, which is in agreement with the stress–strain values. The thermal characteristics also agree very well with the DSC data.

Conclusions

The polymerization temperature has a large effect on molecular weight and average monomer sequence lengths in L-lactide and ε-caprolactone copolymers. Less blocky copolymers are formed at higher temperatures due to transesterification reactions and a less pronounced difference in reactivity of the monomers. The thermal and mechanical properties of the copolymers are hereby greatly affected.

Acknowledgements

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