Melt Block Copolymerization of ε-Caprolactone and L-Lactide

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SYNOPSIS

AB block copolymers of ε-caprolactone and (L)-lactide could be prepared by ring-opening polymerization in the melt at 110°C using stannous octoate as a catalyst and ethanol as an initiator provided ε-caprolactone was polymerized first. Ethanol initiated the polymerization of ε-caprolactone producing a polymer with ε-caprolactone derived hydroxyl end groups which after addition of L-lactide in the second step of the polymerization initiated the ring-opening copolymerization of L-lactide. The number-average molecular weights of the poly(ε-caprolactone) blocks varied from 1.5 to 5.2 × 10^3, while those of the poly(L-lactide) blocks ranged from 17.4 to 49.7 × 10^3. The polydispersities of the block copolymers varied from 1.16 to 1.27. The number-average molecular weights of the polymers were controlled by the monomer/hydroxyl group ratio, and were independent on the monomer/stannous octoate ratio within the range of experimental conditions studied. When L-lactide was polymerized first, followed by copolymerization of ε-caprolactone, random copolymers were obtained. The formation of random copolymers was attributed to the occurrence of transesterification reactions. These side reactions were caused by the ε-caprolactone derived hydroxyl end groups generated during the copolymerization of ε-caprolactone with prepolymers of L-lactide. The polymerization proceeds through an ester alcoholysis reaction mechanism, in which the stannous octoate activated ester groups of the monomers react with hydroxyl groups.

Keywords: block copolymers • ring-opening polymerization • ε-caprolactone • L-lactide • stannous octoate

INTRODUCTION

It is known that in the stannous octoate initiated ring-opening polymerization of lactones, hydroxyl compounds act as initiators.[1-4] This provides the possibility to synthesize linear AB and ABA block copolymers using mono- and difunctional alcohols, respectively. The synthesis of ABA triblock copolymers from poly(ethylene glycol) and D, L- or L-lactide using stannous octoate as a catalyst has been reported.[5,6] In this case the hydroxyl end groups of poly(ethylene glycol) initiate the ring-opening polymerization of lactide, resulting in a growing polymer chain of lactide units at both sides of the poly(ethylene glycol) macroinitiator. Alternatively, a lactone may be polymerized using stannous octoate and an alcohol as a catalyst and an initiator, respectively, to give a prepolymer with a hydroxyl end group. After completion of the first polymerization step an amount of a second lactone can be added, whereupon the hydroxyl end group of the prepolymer initiates the copolymerization of the second lactone and an AB block copolymer may be obtained. Using this technique star-shaped block copolymers of D,L-lactide and various other lactones have been synthesized by sequential melt ring-opening polymerization of the corresponding monomers using stannous octoate as a catalyst and pentaerythritol as an initiator.[7]

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Linear AB and ABA block copolyesters have been synthesized by sequential ring-opening polymerization of lactones in solution, using various anionic catalysts under anhydrous reaction conditions.[8-14] In principle, the block copolymerization of lactones using stannous octoate and a hydroxyl compound as a catalyst/initiator does not require strictly anhydrous reaction conditions and can be performed in the melt. Therefore sequential copolymerization of lactones with stannous octoate/hydroxyl compounds as an initiating system is an attractive alternative to prepare block copolymers in a more convenient way. In this study the possibility of synthesizing linear AB block copolymers of ε-caprolactone and L-lactide via sequential ring-opening polymerization in the melt of the corresponding monomers using stannous octoate as a catalyst and ethanol as an initiator was investigated.

EXPERIMENTAL

Materials

ε-Caprolactone (Merck, Darmstadt, Germany) was distilled under reduced pressure ($P = 5 \times 10^{-2}$ mBar) and subsequently stored in a dry argon atmosphere. L-Lactide was purchased from Purac Biochem BV, Gorinchem, The Netherlands, and was dried over P_4O_{10} *in vacuo*. Stannous octoate (Sigma Chem. Corp., St. Louis, MO) was used as received, and stored in a dry argon atmosphere. Ethanol (analytical grade, Merck, Darmstadt, Germany) was dried over molecular sieves (3 Å).

Methods

All analyses were performed with samples of the crude polymerization products.

^{1}H-NMR spectroscopy was carried out with a Bruker AC 250 spectrometer. ^{13}C-NMR spectroscopic measurements were performed with a Varian Unity 400 WB apparatus. $CDCl_3$ was used as a solvent for the NMR measurements. The GPC measurements were carried out with $CHCl_3$ as the eluent (1.5 mL/min) using a Waters 510 pump, a HP 1050 autosampler, four Waters μStyragel columns (10^5, 10^4, 10^3, and 5×10^2 Å) in series, a Waters 410 differential refractometer, and a Viscotek Viscometer Detector H502. Calibration was effected with polystyrene standards with a narrow molecular weight distribution. Molecular weights were determined according to the universal calibration principle.

The DSC measurements were performed with a Perkin-Elmer DSC-7 apparatus calibrated with indium and gallium. Samples of the copolymers (10 mg) were quenched to −90°C and kept at this temperature for 10 min. Subsequently the samples were heated to 220°C at a rate of 20°C/min.

Preparations

Synthesis of Prepolymers

L-Lactide or ε-caprolactone (100 mmol), stannous octoate [0.1 mmol, monomer/catalyst ratio (M/C) = 1000], and ethanol [10, 5, or 2.5 mmol, to give a monomer/initiator (M/I) ratio of 10, 20, or 40, respectively] were weighed into a round-bottomed flask equipped with a magnetic stirring bar. The flask was purged with dry argon, closed with a glass stopper and a clamp, and immersed in an oil bath at 110°C for 24 h.

Copolymerizations

An amount of prepolymer [poly(ε-caprolactone) or poly(L-lactide)] equivalent to 10 mmol of the corresponding monomer units and 90 mmol of either L-lactide or ε-caprolactone were weighed into a round-bottomed flask equipped with a magnetic stirring bar. When a M/C of 1000 was used in the copolymerization reaction (see Table I) an additional amount of 0.09 mmol stannous octoate was also weighed into the flask. The flask was purged with dry argon, closed with a glass stopper and a clamp, and immersed in oil bath at 110°C for 24 or 504 h (see Table I).

RESULTS AND DISCUSSION

For the synthesis of block copolyesters it is required that transesterification reactions do not occur during the polymerization. Recently Kricheldorf et al.[15] reported that in the stannous octoate catalyzed ring-opening polymerization of D,L-lactide, no transesterification reactions occurred at reaction temperatures below 120°C. Therefore it was decided to perform all polymerizations at 110°C.

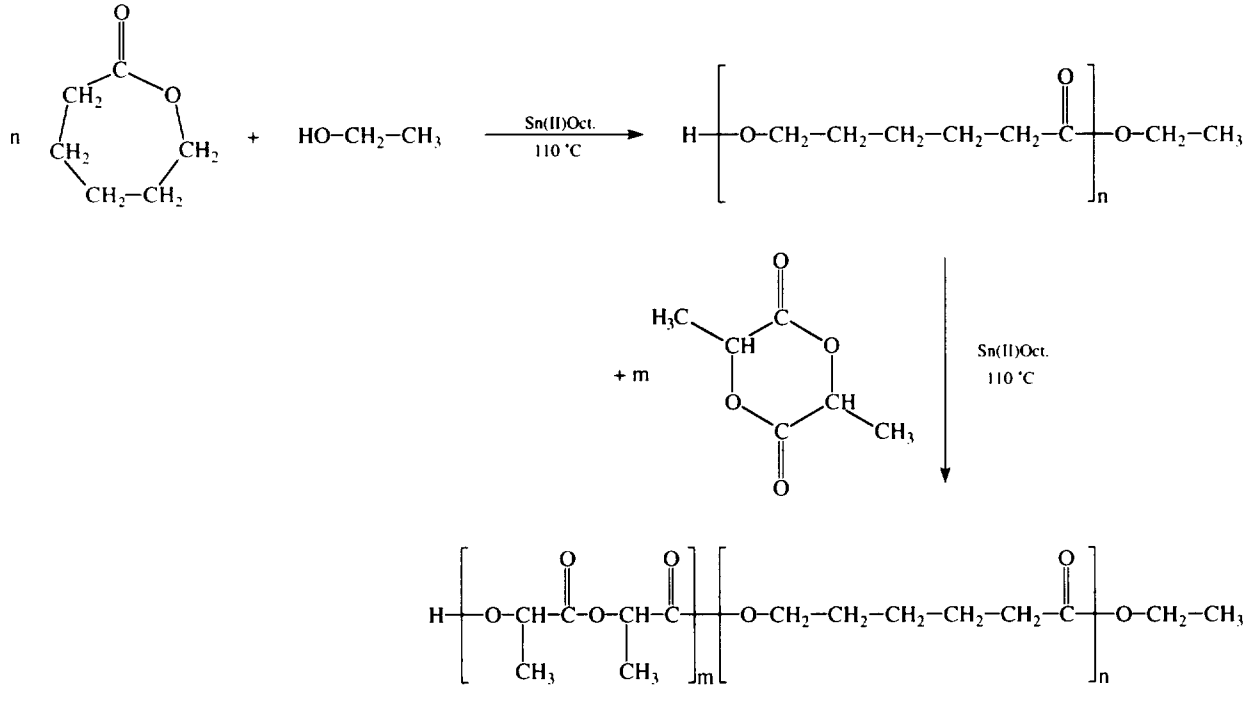
Initially the preparation of block copolymers of ε-caprolactone and L-lactide was investigated by synthesizing poly(ε-caprolactone) as the first block, and subsequently copolymerizing this prepolymer with L-lactide (Scheme 1). ε-Caprolactone was reacted with stannous octoate (monomer/catalyst molar ratio M/C = 1000) and ethanol in the melt at 110°C for 24 h. To obtain ε-caprolactone prepolymers with different molecular weights the molar ratio of ε-caprolactone and ethanol (M/I) was varied

Table I. Block Copolymerization of ε-Caprolactone (Cap) and L-Lactide (Lac) in the Melt (T = 110°C) using Stannous Octoate (C) as a Catalyst and Ethanol (I) as an Initiator: First Block ε-Caprolactone, Second Block L-Lactide

Code	M/I (mol/mol)	Lac/Cap (mol/mol)	M/C (mol/mol)	Reaction Time (h)	Monomer Conversion (%)	$M_{n,calc}$[a] ×10^{-3}	$M_{n,NMR}$[b] ×10^{-3}	$M_{n,GPC}$[c] ×10^{-3}	M_w/M_n	$T_{m,LAC}$[d] (°C)	ΔH_{Lac}[d] (J/g)
C-1	10	0	1000	24	100	1.1	1.5	nd[e]	nd	—	—
CL-1.1	—	9	9000	504	99	13.9	19.5	20.9	1.21	192	99
CL-1.2	—	9	1000	24	99	14.0	17.4	16.6	1.23	174	58
C-2	20	0	1000	24	100	2.3	2.8	nd	nd	—	—
CL-2.1	—	9	9000	504	99	28.0	27.8	25.9	1.16	198	103
CL-2.2	—	9	1000	24	99	28.1	31.2	26.4	1.27	181	60
C-3	40	0	1000	24	100	4.6	5.2	nd	nd	—	—
CL-3.1	—	9	9000	504	99	53.0	40.6	28.8	1.25	186	78
CL-3.2	—	9	1000	24	98	54.1	49.7	39.0	1.21	180	61

[a] Expected number-average molecular weight calculated from conversion and monomer/hydroxyl group ratio.
[b] Number-average molecular weight determined by ^{1}H NMR end group analysis.
[c] Number-average molecular weight determined by GPC measurements using the universal calibration technique.
[d] Peak melting temperatures ($T_{m,Lac}$) and heats of fusion (ΔH_{Lac}) of the poly[(L)-lactide] part of the block copolymers measured by DSC at a heating rate of 20°C/min.
[e] nd = Not determined.

(M/I = 10, 20, and 40). Independent from the M/I ratio the conversion of ε-caprolactone was always 100% after 24 h reaction time as indicated by ^{1}H-NMR analysis of the crude polymerization products. The number-average molecular weights ($M_{n,NMR}$, Table I) were calculated from the intensity ratios of the OCH_2 methylene proton signals (δ = 4.05) and the $HOCH_2$ methylene proton signals (δ = 3.65) in the ^{1}H-NMR spectra of the crude ε-caprolactone prepolymers [Fig. 1(a)]. The $M_{n,NMR}$ values were somewhat higher compared to the expected number-average molecular weights ($M_{n,calc}$). ^{1}H-NMR anal-



Scheme 1. Sequential block copolymerization of ε-caprolactone and L-lactide with stannous octoate and ethanol as a catalyst and initiator, respectively.

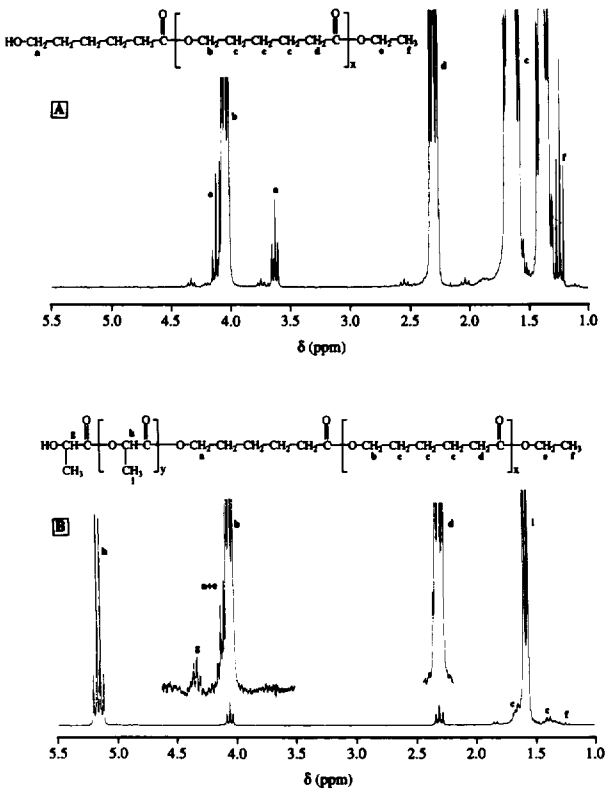


Figure 1. Expanded ^{1}H-NMR spectra ($CDCl_3$) of: (A) prepolymer of ε-caprolactone (M/I = 20, C-2), and (B) corresponding block copolymer of ε-caprolactone and L-lactide (CL-2.2).

ysis demonstrated that the ratio of the signals of the terminal $HOCH_2$ methylene protons and the methyl protons of the ethyl ester end group (δ = 1.25) was equal to 2 : 3. Also the methyl and methylene proton signals of ethanol at δ = 1.20 and δ = 3.60, respectively, were completely absent. This demonstrates that the ethanol present in the reaction mixture had completely reacted with ε-caprolactone. The differences between the $M_{n,calc}$ and the $M_{n,NMR}$ values are explained by partial evaporation of the ethanol during the experimental procedure and/or polymerization.

Next the ε-caprolactone prepolymers were copolymerized with L-lactide (Lac) in the melt at 110°C. To accomplish complete dissolution of the poly(ε-caprolactone) in the L-lactide melt a Lac/Cap ratio of 9 (mol/mol) was used. One series of copolymerizations was conducted without an additional amount of stannous octoate (M/C = 9000, CL-1.1, CL-2.1, and CL-3.1 in Table I). A second series of copolymerizations was performed with the addition of extra stannous octoate to give a M/C of 1000 (CL-1.2, CL-2.2, and CL-3.2). The crude polymerization products were characterized by ^{1}H-NMR, ^{13}C-NMR, GPC, and DSC.

For all copolymerizations the conversion of L-lactide, as determined by ^{1}H-NMR spectroscopy, was higher than 98%. When a M/C of 9000 was employed 98% conversion was reached after 504 h reaction time. In contrast to this the reaction was already completed after 24 h when a M/C of 1000 was used.

In the ^{1}H-NMR spectra of the copolymerization products [Fig. 1(b)] the $HOCH_2$ methylene proton signals belonging to the ε-caprolactone prepolymers (δ = 3.65) could not be detected. Furthermore, the presence of a new proton signal at δ = 4.10 of the terminal OCH_2 methylene group of an ε-caprolactone polymer chain bound to a L-lactide moiety clearly demonstrated that the terminal ε-hydroxyl caproyl groups had initiated the ring-opening polymerization of L-lactide. The copolymer chains were terminated by a L-lactide derived hydroxyl group, as demonstrated by the HOCH methine proton signals at δ = 4.35. The intensity ratios of these terminal methine proton signals and the methyl proton triplet of the ethyl ester end-groups of poly(ε-caprolactone) at δ = 1.25 were always equal to 1 : 3. Consequently each polymer chain has a hydroxyl lactyl end-group on one end and an ethyl ester end group on the other chain end as end groups.

The $M_{n,NMR}$ values of the copolymers (Table I) were calculated from the sum of the $M_{n,NMR}$ values of the ε-caprolactone prepolymers and the number-average molecular weight of the corresponding poly(L-lactide) part of the copolymers determined from the intensity ratios of the OCH methine proton signals (δ = 5.15) and the HOCH terminal methine proton signals (δ = 4.35). The $M_{n,NMR}$ values and the number-average molecular weights measured by GPC ($M_{n,GPC}$) were in good accordance for the copolymers with lower molecular weights (CL-1.1, CL-1.2, CL-2.1, and CL-2.2). For the copolymers with the highest molecular weights (CL-3.1 and CL-3.2) the $M_{n,GPC}$ values were considerably lower compared to the $M_{n,NMR}$ values. For the copolymers with the highest molecular weights the $M_{n,NMR}$ and $M_{n,GPC}$ values were lower compared to the $M_{n,calc}$ values. On the other hand the copolymers with the lowest molecular weights (CL-1.1 and CL-1.2) the $M_{n,NMR}$ and $M_{n,GPC}$ values were somewhat higher compared to the expected number-average molecular weights. Only for the copolymers with intermediate molecular weights (CL-2.1 and CL-2.2) were the expected and determined number-average molecular weights in good agreement. In conclusion, the differences between the calculated and the determined molecular

weights were the largest for the copolymerizations carried out with a M/C of 9000.

The copolymers had rather narrow molecular weight distributions with M_w/M_n ratios varying from 1.16 to 1.25 (Table I). This indicates that no transesterification and/or backbiting reactions occurred during the copolymerizations. These results also suggest that the initiation rate is at least comparable to the propagation rate. Comparison of the GPC profiles of the copolymers with the profiles of 9 : 1 (mol/mol) mixtures of the same copolymers and the corresponding ε-caprolactone prepolymers (Fig. 2) evidently proved the absence of prepolymer in the copolymers, and corroborated the results of the ^{1}H NMR analysis.

Although both ^{1}H-NMR and GPC measurements indicated the formation of block copolymers in the copolymerization of caprolactone prepolymers and L-lactide this was not considered as undoubted evidence. Recently Bero et al.[13,16,17] reported that ^{13}C-NMR analysis of copolymers of ε-caprolactone and L-lactide gave distinct information on the sequence distribution of ε-oxycaproyl and lactyl units. Especially the carbonyl carbon signals were most sensitive to sequence effects. If an AB block copolymer is formed during the copolymerization of a hydroxyl-terminated prepolymer of ε-caprolactone and L-lactide, only ε-oxycaproyl-lactyl sequences arising from the reaction of the ε-hydroxyl caproyl end-group with L-lactide must be present, whereas ε-oxycaproyl-lactyl sequences due to transesterification reactions must be absent. This implies that in the ^{13}C-NMR spectra of the copolymers the carbonyl carbon signals belonging to Lac–Cap–Cap (LCC) and LLC sequences (see Fig. 3) must be present, and the signals originating from CCL, LCL, CLC, and CLL sequences must be absent. The ^{13}C-NMR spectra of the copolymers [Fig. 3(a)] undoubtedly confirmed the formation of block copolymers, because the carbonyl carbon signals of the LCC and LLC sequences were present and the signals indicating the occurrence of transesterification reactions were completely absent. In addition the carbonyl carbon signals belonging to the hydroxyl lactyl end-group sequence (H–LLL) could be distinguished.

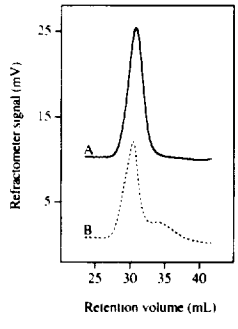


Figure 2. GPC curves of: (A) block copolymer of ε-caprolactone and L-lactide (CL-2.2), and (B) a 9 : 1 mixture of the same block copolymer and the corresponding ε-caprolactone prepolymer.

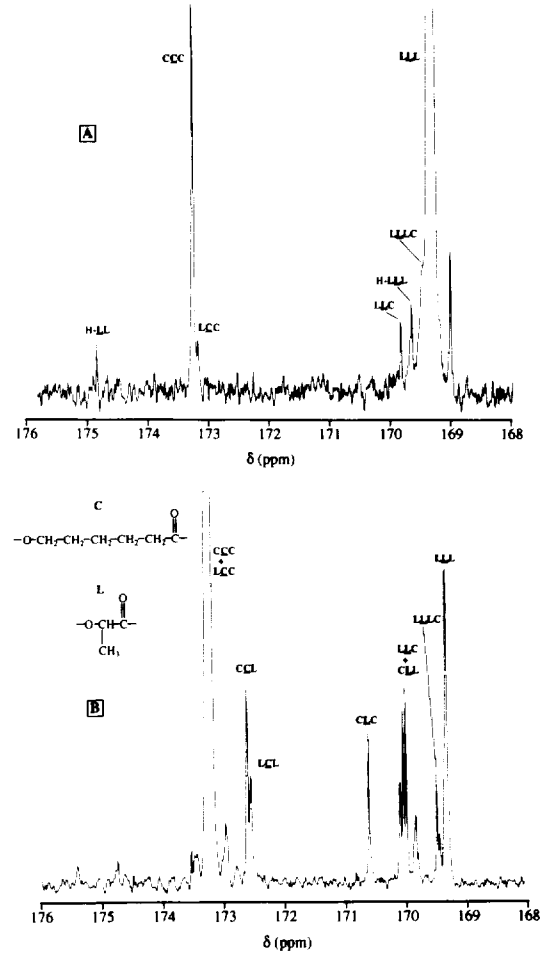


Figure 3. Expanded ^{13}C-NMR spectra ($CDCl_3$) of: (A) block copolymer prepared by copolymerization of a ε-caprolactone prepolymer with L-lactide (CL-1.2), and (B) random copolymer obtained after copolymerization of a prepolymer of L-lactide (M/I = 10) with ε-caprolactone (Lac/Cap = 1 : 9).

In the synthesis of the block copolymers not only the ε-hydroxyl caproyl groups may initiate the ring-opening polymerization of L-lactide. The total hydroxyl content in the polymerization reaction increases both upon addition of L-lactide, and an additional amount of stannous octoate to give a M/C of 1000 in the second step. The L-lactide has a hydroxyl content of about 0.1 mequiv/mol due to the presence of impurities like lactyl lactate. The stan-

nous octoate contains about 2 wt % water. It is calculated that at a M/I ratio of 10 and a M/C ratio of 1000 in the second step of the block copolymerization, 6 mol % poly(L-lactide) homopolymer can be formed when these introduced hydroxyl containing compounds co-initiate the ring-opening polymerization of L-lactide. Using a M/I ratio of 40 and a M/C ratio of 1000, the formation of poly(L-lactide) may become 22 mol % of the total polymerization mixture.

However, the intensity ratio in the ^{1}H-NMR spectra between the terminal methine proton signal of the lactide derived hydroxyl end-group and the ethyl ester end group of the poly (e-caprolactone) block (1 : 3) will decrease when poly (L-lactide) homopolymer is formed. Such a decrease in intensity ratio has not been observed. Furthermore, in the ^{13}C-NMR spectra of the block copolymers no signals at δ 174.3 belonging to poly (L-lactide) carboxylic acid end groups have been observed. The spectroscopic analysis is not regarded absolute evidence for the absence of poly (L-lactide) in the polymer mixture. Extensive fractionation experiments in different solvents are necessary to determine the absence or presence of small amounts of the poly (L-lactide).

As an alternative to synthesize block copolymers of ε-caprolactone and L-lactide the polymerization sequence of the monomers was inverted. Thus, L-lactide was polymerized first using stannous octoate as a catalyst (M/C = 1000) and ethanol (M/I = 10) as an initiator at 110°C for 24 h with 100% conversion. Subsequently the hydroxyl-terminated L-lactide prepolymer ($M_{n,\mathrm{NMR}}$ = 1700) was reacted at 110°C with ε-caprolactone using a Lac/Cap molar ratio of 1 : 9 and stannous octoate with a M/C of 1000. In the ^{13}C-NMR spectrum of the resulting copolymer [Fig. 3(b)] carbonyl carbon signals belonging to ε-oxycaproyl-lactyl sequences LCL, CLC, and LLC emerging from transesterification reactions were present, clearly proving that a random copolymer had been formed. In the ^{1}H-NMR spectrum of the copolymer methine proton signals of the hydroxyl lactyl end groups still were present after copolymerization with ε-caprolactone. The $HOCH_2$ methylene proton signals of the ε-caprolactone derived end groups were also present, though hardly detectable. Apparently the ε-hydroxyl caproyl end groups generated during the copolymerization of ε-caprolactone with prepolymers of L-lactide are reactive towards the ester groups in the polymer chains.

Obviously, when conducting a ring-opening polymerization in the melt using stannous octoate/alcohol as an initiating system, block copolymers of ε-caprolactone and L-lactide can only be prepared when ε-caprolactone is polymerized first. This conclusion has some resemblance with the results reported on the block copolymerization of ε-caprolactone and L-lactide in solution using aluminum tris(isopropoxide) as an initiator.[8,11] With this anionic initiator, block copolymers could only be prepared if ε-caprolactone was polymerized first. Actually ε-caprolactone did not polymerize at all when added to the living poly (L-lactide) chains. This was attributed to a much lower reactivity of the L-lactide derived end groups compared to the end groups derived from ε-caprolactone.

In Figure 4 a DSC heating curve typical for the copolymerization products of the prepolymer of ε-caprolactone with L-lactide is presented. For the poly (ε-caprolactone) block a small melting endotherm was found at ca. 60°C. The melting temperature of the poly (L-lactide) part of the block copolymers ($T_{m,\mathrm{Lac}}$) varied between 174 and 198°C (Table I). The $T_{m,\mathrm{Lac}}$ values and the heats of fusion of the block copolymers synthesized with a M/C of 9000 were higher compared to the $T_{m,\mathrm{Lac}}$ values of the copolymers prepared with a M/C of 1000. These differences can be explained by the much longer reaction times required to accomplish complete conversion of L-lactide for the copolymerizations carried out with a M/C of 9000 compared to the reactions performed with a M/C of 1000 (504 and 24 h, respectively). This means that the poly (L-lactide) crystallites of the block copolymers prepared with the lowest catalyst concentration are growing slower and are annealed over a much longer period at 110°C resulting in polymers with higher melting points and crystallinities.

Several experimental observations gave rise to consider the reaction mechanism of the stannous octoate/alcohol initiated ring-opening polymerization of ε-caprolactone and L-lactide: (1) the formation of monomer derived hydroxyl end groups and alcohol derived ester end groups, (2) the dependence

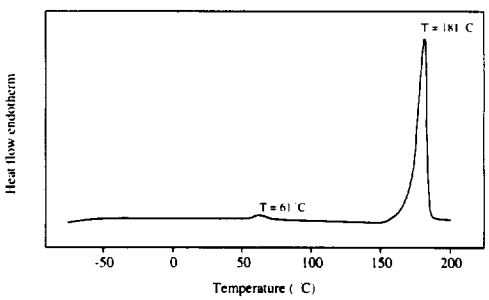


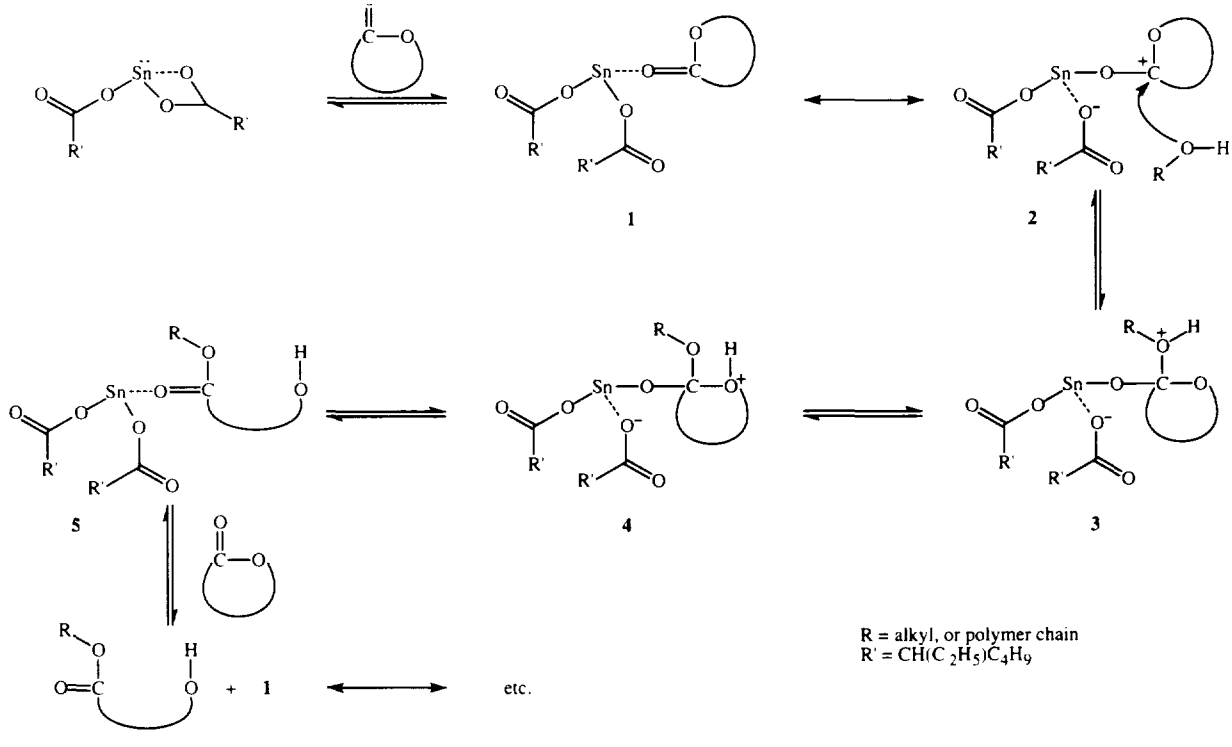
Figure 4. Typical DSC heating curve of a block copolymer of ε-caprolactone and L-lactide) (CL-2.2).

of the occurrence of transesterification reactions on the sequence of polymerization of ε-caprolactone and L-lactide, (3) the independence of the molecular weights of the polymers on the stannous octoate concentration. Recently Nijenhuis et al.[4] reported that hydroxyl containing impurities in the catalyst and monomer were the true initiators in the ring-opening polymerization of L-lactide with stannous octoate. They proposed a Lewis acid catalyzed transesterification reaction mechanism for the stannous octoate/hydroxyl compound initiated polymerization. Most of the experimental observations mentioned above can be explained by the reported reaction mechanism.

The reaction mechanism outlined in Scheme 2, describing an ester alcoholysis mechanism, may account for the occurrence of transesterification reactions in the copolymerization of the hydroxyl-terminated prepolymer of L-lactide with ε-caprolactone. According to the literature[18,19] for tin(II) carboxylates, the most likely environment for the tin atom in these compounds would be pyramidal structures with a three-coordination of the tin atom and a non-bonding electron pair. Most likely the tin atom of stannous octoate coordinates through either a *p*-orbital or a *d*-orbital with the carbonyl oxygen atom of the lactone (**1**). Due to the coordination with tin the carbonyl carbon atom becomes more positive (**2**), resulting in an increased susceptibility to nucleophilic attack by a hydroxyl group (**3**). In the initiation reaction, the hydroxyl group containing compound is the added alcohol or a prepolymer with a hydroxyl end group, whereas in the propagation reaction the hydroxyl group is the end-group of a growing polymer chain.

After proton transfer (**4**) and the actual ring-opening of the monomer by acyl-oxygen cleavage (**5**), a linear molecule with an alcohol-derived ester end-group and a lactone-derived hydroxyl end group is formed. The ester of the ring-opened monomer still coordinated to the tin atom exchanges with a second monomer molecule, whereafter the process starts again at **1**. Consequently a stannous octoate molecule is not bound to one particular polymer chain, but constantly changes from one to another growing polymer chain. Therefore the molecular weight of the polymer will not be determined by the stannous octoate concentration, but by the hydroxyl group concentration only.

The higher reactivity of the ε-caprolactone derived hydroxyl end groups compared to the (L)-lactide-derived hydroxyl end-groups can be explained



Scheme 2. Proposed reaction mechanism for the ring-opening polymerization of ε-caprolactone and L-lactide using stannous octoate as a catalyst and a hydroxyl compound as an initiator.

by electronic and steric aspects. For ε-hydroxyl caproyl end groups the electron density at the oxygen atom of the hydroxyl group is higher compared to the hydroxyl lactyl end groups. The electron density of the oxygen atom of the ε-hydroxyl caproyl end groups is increased by the electron donating C_5H_{10} alkyl group, making the attacking hydroxyl group more nucleophilic. On the other hand the carbonyl group in α-position to the hydroxyl lactyl group withdraws electrons, resulting in a less nucleophilic hydroxyl group. An electron-withdrawing R-group will also have a destabilizing effect on derivative **3.** In addition, the α-methyl group of the lactyl end group may sterically hinder the nucleophilic attack of the hydroxyl lactyl end-group.

The tin atom of stannous octoate will not only be able to coordinate with the ester group of the monomer,but also will form a coordination complex with ester functions somewhere in the polymer chains. Moreover, as the reaction proceeds and more of the lactone is converted to polymer, stannous octoate will increasingly coordinate with ester groups of the polymer chains. As a result these ester groups will also be more susceptible to nucleophilic attack by hydroxyl groups and transesterification reactions may occur. The occurrence of transesterification reactions will to a large extent depend on the reactivity of the hydroxyl end groups present in the reaction mixture.

CONCLUSIONS

This study demonstrates that block copolymers of ε-caprolactone and L-lactide can be prepared by ring-opening polymerization in the melt using stannous octoate/ethanol as an initiating system, provided ε-caprolactone is polymerized first. When the sequence of polymerization is reversed, random copolymers of L-lactide and ε-caprolactone are obtained. The formation of random copolymers is due to transesterification reactions which were caused by the ε-caprolactone-derived hydroxyl end groups generated during the copolymerization of ε-caprolactone with prepolymers of L-lactide. The L-lactide-derived hydroxyl end-groups are less reactive compared to the ε-caprolactone-derived hydroxyl end groups. Consequently, in the copolymerizations of L-lactide with prepolymers of ε-caprolactone with only hydroxyl lactyl end-groups present, transesterification reactions do not occur. Initiation and polymerization proceed by an ester alcoholysis reaction mechanism, in which the stannous octoate activated ester groups of the monomers react with hydroxyl groups.

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