Controlled Ring-Opening Polymerization of L-lactide and 1,5-Dioxepan-2-one Forming a Triblock Copolymer

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ABSTRACT: Novel elastomeric A-B-A triblock copolymers were successfully synthesized in a new two-step process: controlled ring-opening polymerization of the cyclic ether–ester 1,5-dioxepan-2-one as the amorphous middle block (B-block) followed by addition and polymerization of the two semicrystalline L-lactide blocks (A-block). A 1,1,6,6-tetra-*n*-butyl-1,6-distanna-2,5,7,10-tetraoxacyclodecane initiator system was utilized and the reaction was performed in chloroform at 60 °C. A good control of the synthesis was obtained, resulting in well defined triblock copolymers. The molecular weight and chemical composition were easily adjusted by the monomer-to-initiator ratio. The triblock copolymers formed exhibited semicrystallinity up to a content of 1,5-dioxepan-2-one as high as 89% as determined by differential scanning calorimetry. WAXS investigation of the triblock copolymers showed a crystal structure similar to that of the pure poly(L-lactide). © 2000 John Wiley & Sons, Inc. J Polym Sci A: Polym Chem 38: 1774–1784, 2000

Keywords: ring-opening polymerization; triblock copolymer; solution polymerization; thermal properties; differential scanning calorimetry

INTRODUCTION

Ring-opening polymerization of lactones and lactides has been a major research area for the production of new biodegradable materials designed for medical use. Different approaches have been evaluated in order to create materials with desired properties. Poly(lactide) is one of the most intensively studied biodegradable synthetic materials because of its beneficial mechanical properties and adjustable hydrolyzability.[1] Copolymerization of L-lactide with different types of cyclic monomers provides an important contribution to the already existing materials in that it combines the inherent properties of each homopolymer.[2] In particular, block copolymerization may offer a broader spectrum of mechanical and degradation properties in order to meet the demands of the larger number of biomedical applications. Blocks with different physical properties, for example, one soft, amorphous, and one hard, semicrystalline segment, can be utilized to modulate the basic material behavior.[3] The mechanical properties of the polymer are enhanced by a phase-separated morphology. The soft phase gives elasticity and the degradation behavior, whereas the rigid phase gives mechanical strength and also acts as a physical crosslinker. In many medical applications there is a need for degradable materials that are similar to human tissue with respect to tensile strength and elasticity.

The scientific literature reports the synthesis of block copolymers either from prepolymers[4] or by a sequential living polymerization technique.[5–7] In a previous work,[8] a synthetic route to poly(ϵ-caprolactone-*b*-1,5-dioxepan-2-one-*b*-ϵ-caprolactone) was developed. The proposed method was based on the sequential addition of monomers to a living polymerization system initiated with aluminum tri-isopropoxide, which gave a good control of the synthesis and made it possible

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to tailor the final product. However, this method was not suitable for producing triblock copolymers in which L-lactide rather than ϵ-caprolactone was one of the components. The difference in reactivities of the monomers made it impossible to first polymerize a L-lactide block and then a 1,5-dioxepan-2-one block.[9]

The aim of this study was to synthesize an triblock copolymer, poly(L-lactide-*b*-DXO-*b*-L-lactide), by controlled ring-opening polymerization in a new two-step process: polymerization of the 1,5-dioxepan-2-one (DXO) followed by the addition and polymerization of L-lactide (L-LA). Triblock copolymers were obtained using 1,1,6,6-tetra-*n*-butyl-1,6-distanna-2,5,7,10-tetraoxacyclodecane as difunctional initiator in chloroform at 60 °C. The products were characterized by ^{1}H NMR, ^{13}C NMR, SEC, differential scanning calorimetry and X-ray diffraction. The hydrolytically degradable polymer backbone makes this copolymer a potential thermoplastic elastomer.

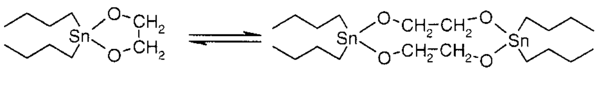
EXPERIMENTAL

Materials

Dibutyltin oxide (Aldrich, Germany) and ethylene glycol (Merck, Germany) were obtained commercially and were used as received. Toluene (Merck, Germany) was dried over Na-wire before use. Chloroform (Aldrich, Germany), stabilized with 2-metyl-2-butene, was dried by stirring over CaH_2 for at least 24 h prior to distillation in an inert atmosphere. L,L-lactide (L-LA) was obtained from Serva Feinbiochemica, Germany. Tetrahydro-4H-pyran-4-one was purchased from Maybridge Chemical, UK and used as received.

Monomers

L,L-lactide (L-LA) was purified by recrystallization in dry toluene. The monomer was dried for 20 h under reduced pressure (10^{-2} mbar) at room temperature prior to polymerization. 1,5-dioxepan-2-one (DXO) was synthesized from tetrahydro-4H-pyran-4-one through Baeyer–Villiger oxidation according to the literature.[10] The 1,5-dioxepan-2-one prepared was purified by two distillations, recrystallization from dry diethyl ether, and evaporation of residual solvent under reduced pressure. The monomer was dried over calcium hydride (CaH_2) for 24 h prior to a final distillation.



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Scheme 1. 1,1,6,6-tetra-*n*-butyl-1,6-distanna-2,5,7,10-tetraoxacyclodecane (**2**) shown as an equilibrium between the monomer (**1**) and the dimeric (**2**) complex.

Initiator

1,1,6,6-tetra-*n*-butyl-1,6-distanna-2,5,7,10-tetraoxacyclodecane (**2**) was prepared from dibutyltin oxide and ethylene glycol, as previously described in the literature.[11,12] Characterization by ^{1}H NMR and mass spectroscopy confirmed the formation of the expected structure. The initiator exists in an equilibrium between the monomeric (**1**) and the dimeric (**2**) complex according to Scheme 1.

Block Copolymerization of L-lactide and 1,5-Dioxepan-2-one

The desired amount of DXO and initiator was weighed into a silanized round-bottomed flask under a nitrogen atmosphere inside a drybox. The flask was fitted with a magnetic stirring bar and sealed with a three-way valve. Chloroform was transferred to the flask using a syringe. Polymerization was started by immersing the flask into a thermostated oil bath. The second monomer, L-lactide, was charged into a round-bottomed flask, as described above. The monomer was dissolved in chloroform and transferred with a syringe to the reaction vessel containing the initiator-polymer complex after almost complete conversion of DXO. All glassware was flame-dried prior to use. The polymer formed was isolated and purified by three consecutive precipitations in a hexane–methanol (95:5) mixture.

INSTRUMENTAL METHODS

Nuclear Magnetic Resonance

The monomer conversion was determined by ^{1}H NMR spectroscopy from the relative intensities of the resonance peaks for the monomer and the polymer protons. The molecular weight was determined from the relative intensities of the —OCH_2CH_2O— group in the copolymer backbone and the polymer peaks. The chemical structure and the monomer sequence of the block copolymers were determined with ^{13}C NMR spectroscopy. ^{1}H NMR spectra were obtained using a Bruker AC-400 Fourier-Transform Nuclear Magnetic Resonance spectrometer (FT NMR) operating at 400 MHz. A 25-mg sample was dissolved in 0.5 mL deutero-chloroform ($CDCl_3$) in a 5-mm diameter sample tube. Nondeuterated chloroform was used as an internal standard ($\delta = 7.26$ ppm). The 100.61 MHz ^{13}C NMR spectra were obtained with a 100-mg sample dissolved in 0.5 mL $CDCl_3$ using a BrukerAC-400 FT-NMR spectrometer.

Size Exclusion Chromatography

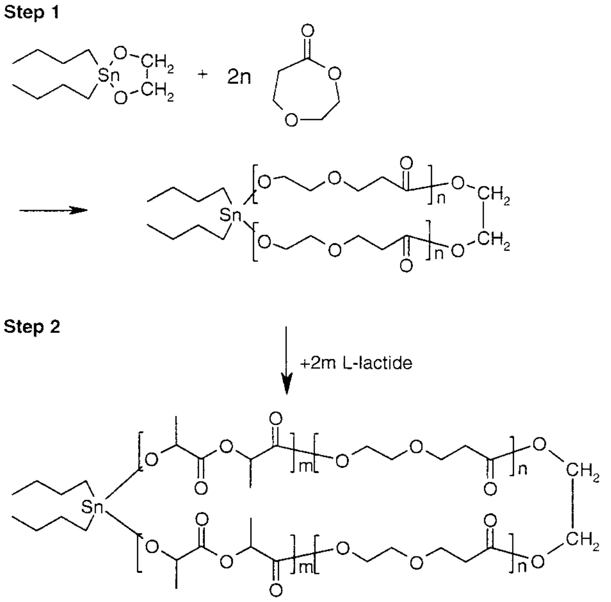
Size exclusion chromatography (SEC) was used to monitor the molecular weight change during polymerization. Polymers were analyzed with a Waters 717 plus autosampler and a Waters model 510 apparatus equipped with two PLgel 10μm mixed-B columns, 300 × 7.5 mm (Polymer Labs., UK). Spectra were recorded with an PL-ELS 1000 evaporative light scattering detector (Polymer Labs., UK) connected to an IBM-compatible PC. Millennium[32] version 3.05.01 software was used to process the data. Chloroform was used as eluent, at a flow rate of 1.0 mL/min. Narrow MWD polystyrene standards were used for calibration, range 1,700–706,000 g/mol. SEC measurements were performed on both cyclic and deactivated chains (i.e., into hexane/methanol precipitated chains). The PL-ELS 1000 detector gives the molecular weight of the polymers relative to polystyrene standards.

Differential Scanning Calorimetry

The thermal properties of the synthesized triblock copolymers were investigated by differential scanning calorimetry (DSC), using a Mettler–Toledo DSC instrument with a DSC 820 module. A scanning rate of 10 °C/min was used and the samples were heated in a nitrogen atmosphere. The second scan was used to record the heat of fusion. In evaluating the crystallinity of the triblock copolymer, it was assumed that the only contribution to the heat of fusion was from the poly(L-lactide) segments. According to earlier results obtained by DSC, poly(DXO) is totally amorphous having a T_g between -35 and -40 °C.

X-Ray Diffraction

Wide-angle X-ray diffraction analysis was performed on a Philips generator PW 1830, nickel-filtered Cu $K\alpha$-radiation ($\lambda = 1.542$ Å), with a Warhus camera.



Scheme 2. Reaction scheme for the ring-opening polymerization of poly(L-lactide-*b*-DXO-*b*-L-lactide). In the first step, the middle poly(DXO) block was polymerized through ROP initiated with tin alkoxide **1/2**. In the second step, the L-lactide was added and subsequently polymerized giving a triblock copolymer.

RESULTS AND DISCUSSION

Block Copolymerization of DXO and L-lactide

Thermoplastic elastomeric[13] poly(L-lactide-*b*-DXO-*b*-L-lactide)s of different molecular weights and compositions were successfully obtained in a two-step process according to Scheme 2. In the first step, the middle block consisting of DXO was polymerized through ROP to high monomer conversion (<99%) and in the second step the L-lactide was added and subsequently polymerized giving a triblock copolymer. The use of a cyclic difunctional initiator resulted in a triblock copolymer with hydroxyl functionalities at both chain ends after precipitation and termination, that is, cleavage of the bond between the polymer and initiator.

The major difficulty in producing triblock copolymers through ring-opening polymerization is the difference in reactivities between the different monomers. This leads to difficulties to synthesize triblock copolymers by the sequential addition of

Table I. Triblock Copolymerization of L-lactide and 1,5-Dioxepan-2-one Initiated with Tin-alkoxide 1 in Chloroform at 60 °C

Polym. No.	[M]/[I][a] L-LA/ DXO/L-LA	Reaction Time [hours] DXO/L-LA	Conversion[b] [%] DXO/L-LA	Yield[c] [%]	DXO/L-LA[d] [mol %]
1	50/200/50	8/28	>99/98,2	73,1	73/27
2	25/300/25	12/14	>99/91,4	69,0	93/7
3	50/300/50	12/28	>99/97,6	78,3	80/20
4	75/300/75	12/42	>99/99,5	76,1	75/25
5	50/400/50	16/28	>99/71,6	82,1	89/11

The initial concentration of [DXO] = 1*M;* the initial concentration of [L-LA] = 0,14–0,36*M*.

[a] Monomer-to-initiator ratio (DXO) = [DXO]/[I]; monomer-to-initiator ratio (L-LA) = [L-LA]/[I] for the different polymer blocks.

[b] Monomer conversion of the DXO and L-LA determined by ^{1}H NMR.

[c] Amount of block copolymer formed after precipitation in hexane/methanol.

[d] Molar composition of the precipitated block copolymer as determined by ^{1}H NMR.

the monomers to a living polymerization system. The macroinitiators formed must initiate polymerization of the following polymer block. Diblock copolymers may be produced but polymerization of the third block often fails. For instance, the reactivity ratios for copolymerization between L-LA and DXO were determined in an earlier work as $r_{L\text{-}LA} = 10$ and $r_{DXO} = 0.1$,[9] when stannous octoate was used as catalyst. As a result of the large difference in reactivity ratios, it was impossible to first polymerize a L-lactide block and then initiate and synthesize a 1,5-dioxepan-2-one block. This restriction led us to develop a new polymerization method based on a two-step procedure. Triblock copolymers of these two components were obtained according to Scheme 2, that is, synthesis of the DXO middle block, which acts as a very efficient macroinitiator for the polymerization of L-LA with the formation of triblock copolymers with narrow molecular weight distributions. As a result, at the end of the polymerization, the polymer chains contain only hydroxyl end groups.

The initiator **1/2** has previously been shown to polymerize the cyclic ether–ester 1,5-dioxepan-2-one (DXO) to high conversion and in good yield (>90%).[12] The experimental conditions used in the block copolymerization of DXO and L-lactide are given in Table I. All the experiments were conducted in chloroform at 60 °C with an initial concentration of DXO of 1 mol/l. The concentration of the L-lactide monomer varied, depending on the amount of monomer used. It was advantageous to perform the polymerizations at low temperature to avoid side-reactions such as inter- and intramolecular transesterification reactions. Because of the low reaction temperature, a solvent was necessary to dissolve the monomer and initiator to obtain a homogeneous polymerization mixture. As soon as full conversion was achieved, the polymerization was terminated by precipitation in a hexane/methanol mixture to minimize the amount of side reactions.

Table I shows the result of the sequential addition block copolymerization between L-LA and DXO. The molar composition of the isolated block copolyesters was examined by ^{1}H NMR. Good separation of the polymer peaks was obtained and this simplified the investigation. The amounts of poly(DXO) and poly(L-LA) were calculated by comparing the peak areas at 2.6 ppm and 5.0 ppm originating from the poly(DXO) methylene and the poly(L-LA) methine protons, respectively. The isolated copolymers contained slightly lower amount of L-lactide than expected, taking into account the conversion of the respective monomers. One event partly contributing to this observation could be the hydrolysis of the poly(L-LA) block by the methanol during the precipitation. However, the SEC analysis of the polymer before and after precipitation revealed no significant change in peak shape or position. The yield of the copolymer was lower than expected from the monomer conversion. This was due to the repeated precipitation in hexane/methanol, performed to remove residual monomer and the initiator from the copolymer.

Figure 1 shows a typical SEC trace of the poly(DXO) block and the triblock copolymer poly(L-LA-*b*-DXO-*b*-L-LA). Chloroform was used as eluent. The peak at elution time of 14.6 min corresponds to poly(DXO), and the second peak at 14.4 min corresponds to the triblock copolymer. The number-average molecular weight ($\bar{M}_n$), and

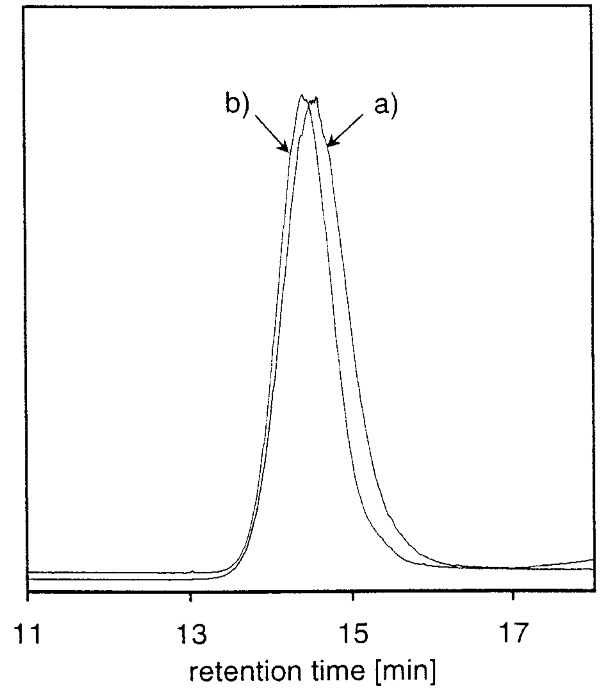


Figure 1. Typical SEC traces of (a) the poly(1,5-dioxepan-2-one) block and (b) the triblock copolymer poly(L-lactide-*b*-1,5-dioxepan-2-one-*b*-L-lactide). Chloroform was used as eluent, flow 1 mL/min.

molecular weight distribution (MWD) of the poly(L-LA-*b*-DXO-*b*-L-LA) block copolymers formed are given in Table II. It follows from the SEC analysis that the addition of the L-LA gave an increase in the molecular weight. The SEC chromatograms also showed that no homopolymers were formed. The poly(DXO) macroinitiator formed easily initiated polymerization of L-LA. The NMR analysis shows that the molecular weight of the DXO block was close to the expected from the monomer-to-initiator ratio. The molecular weight of the L-LA block was slightly lower than expected. The SEC was calibrated with polystyrene standards, and the SEC results were therefore used mainly as a quantitative tool to check the peak shape, distribution and increase in molecular weight after addition and polymerization of the L-lactide monomer.

The proposed polymerization procedure also gave a good control over the MWD. The MWD for the triblock copolymer actually decreased compared to that of the first block consisting of poly(DXO). Fractionation resulting from the repeated precipitation of the polymer formed into the hexane methanol mixture probable contributed to the lower MWD.

NMR Analysis

All block copolymers were analyzed by ^{1}H NMR spectroscopy in order to confirm the incorporation of the —OCH_2CH_2O— bridge into the polymer[12] and to determine the polymer composition. Figure 2 shows a typical ^{1}H NMR spectrum of the synthesized polymer and the peak assignments. In all cases, the ^{1}H NMR spectra revealed the existence of —OCH_2CH_2O— bridges at $\delta = 4.28$ ppm. Characteristics of the proton spectra include four triplets at 4.20, 3.73, 3.64, and 2.59 ppm originating from the methylene protons in the DXO unit. Methine protons of lactide units appear at 5.13 ppm as a quartet. A doublet from the lactide methyl protons emerges at 1.55 ppm.

The aim of the ^{13}C NMR analysis was to determine the structure of the resulting polymers. Figure 3 shows the ^{13}C NMR spectrum of poly(L-lactide-*b*-1,5-dioxepan-2-one-*b*-L-lactide). The

Table II. Molecular Weight Determination of Triblock poly(L-lactide-*b*-1,5-dioxepan-2-one-*b*-L-lactide) by ^{1}H NMR and SEC Analysis

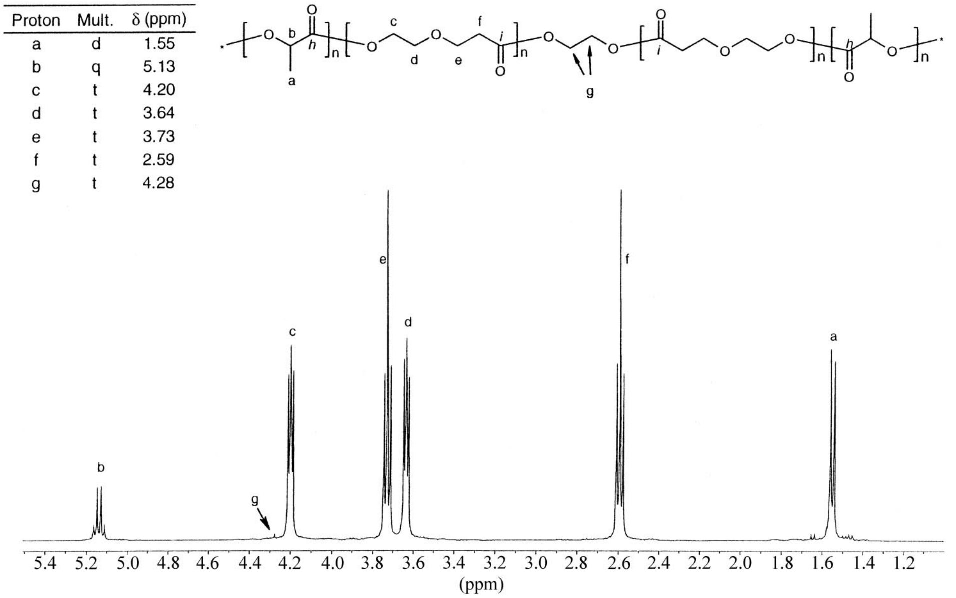
Polym. No.	$\bar{M}_n$ (DXO-block)[a]	$\bar{M}_n$ (L-LA-block)[a]	$\bar{M}_n$ (DXO-block)[b]	MWD[c]	$\bar{M}_n$ (DXO + L-LA)[b]	MWD[c]
1	23500	9800	43000	1.30	54700	1.27
2	33400	2700	58500	1.35	63100	1.29
3	33500	9800	59500	1.36	69100	1.30
4	36500	15700	61700	1.33	78600	1.26
5	42800	6100	75800	1.26	76400	1.25

Molecular weight measurements were performed on precipitated samples.

[a] Number-average molecular weight determined by ^{1}H NMR.

[b] Number-average molecular weight determined by SEC, calibration with polystyrene standards.

[c] Molecular weight distribution, determined by SEC, chloroform used as eluent.

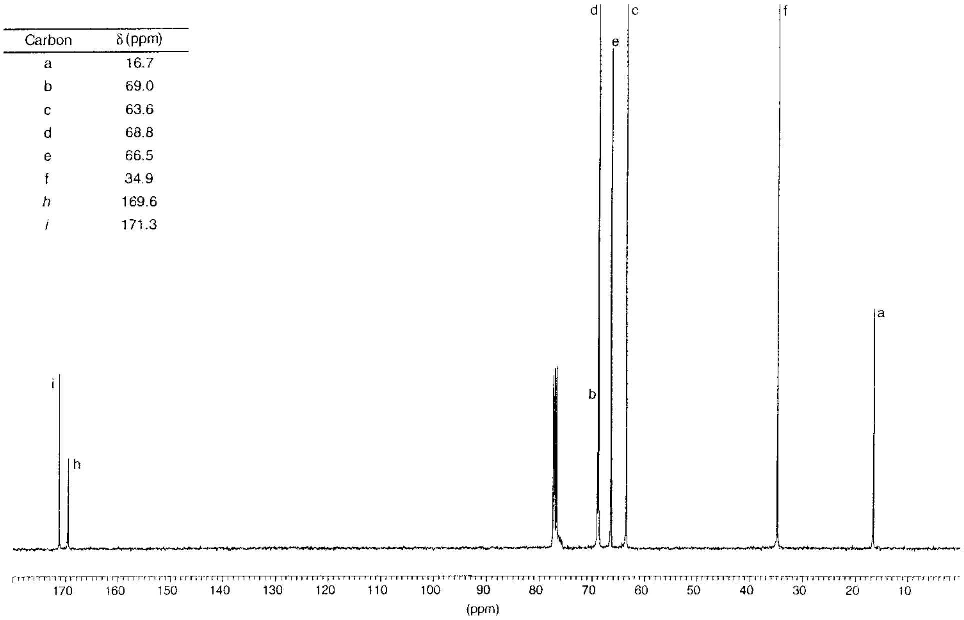


Proton	Mult.	δ (ppm)
a	d	1.55
b	q	5.13
c	t	4.20
d	t	3.64
e	t	3.73
f	t	2.59
g	t	4.28

Figure 2. 400 MHz ^{1}H NMR spectrum of the block copolyester poly(L-lactide-*b*-1,5-dioxepan-2-one-*b*-L-lactide) and the peak assignments.

spectrum shows the presence of the two carbonyl groups at 171.3, and 169.6 ppm, the four carbon atoms of the main chain of the poly(DXO) block at 68.8, 66.5, 63.6, and 34.9 ppm, and the methyl group substituent and the methine group in the main chain poly(L-LA) blocks at 16.7 and 69.0 ppm, respectively. The carbons were identified through comparison with spectra of the homopolymers of DXO,[10] L-LA,[14] and random poly(DXO-*co*-L-LA).[9]

It is well established that a number of physical properties of poly(lactide)s are associated with their stereochemical microstructure. Knowledge of the structure is therefore very important for an



Carbon	δ (ppm)
a	16.7
b	69.0
c	63.6
d	68.8
e	66.5
f	34.9
h	169.6
i	171.3

Figure 3. The 100 MHz ^{13}C NMR spectrum of L-lactide-block/1,5-dioxepan-2-one triblock copolymer in $CDCl_3$.

understanding of the macroscopic behavior. Several research groups have studied the effect of stereosequence distribution on the ^{13}C and ^{1}H NMR spectra.[15–17] Assignments have been obtained with high-resolution NMR spectroscopy. The polymerization of stereoisomers can proceed with retention or inversion of configuration during the reaction. In the case of L-lactide, it has been shown that most of the metal alkoxide initiators open the cyclic monomer through O-acyl bond cleavage with retention of the configuration. ^{13}C NMR analysis of the block copolymers supports the hypothesis that no racemization occurs. Examination of the ^{13}C NMR spectra of the triblock copolymers revealed that only isotactic poly(L-lactide) was formed.

Inter- and intramolecular transesterification reactions frequently occur in ring-opening polymerization. The tin alkoxide initiators used in ROP normally cause a higher degree of transesterification reactions than, for example, aluminum, zinc, or titanium alkoxide initiators.[18] Observations indicate that in the polymerization of L-LA initiated with tin alkoxides [15] propagation proceeds with extensive transesterification above polymerization temperatures of 100 °C. According to Kricheldorf et al.,[19] carbonyl carbons are generally the atoms that are most sensitive to sequence effects. The fine structure of the triblock copolymers was investigated from expansions around the main peaks. Figure 4 shows the carbonyl region of the ^{13}C NMR spectra, and it exhibit only two signals assigned to the DXO-DXO-DXO (DDD) and L-LA-L-LA-L-LA (LLL). This reveals that an insignificant amount of transesterification was taking place during the reaction under the mild polymerization conditions used, since transesterification reactions would give rise to copolymer signals DDL, LDL, LLD and DLD. These peaks have previously been shown to occur at 170.8, 170.7, 170.1, respectively, 169.7 ppm.[9] When the L-LA was added to the poly(DXO) macroinitiator, the polymerization took place at the tin-alkoxide end groups to give the desired A-B-A block copolymers in high yields.

All these findings may be interpreted in terms of a mechanism involving complexation of a monomer as a first step, followed by insertion through acyl-oxygen cleavage. The complex formed was negligibly active towards inter- or intramolecular transesterification reactions, resulting in a distinct triblock copolymer.

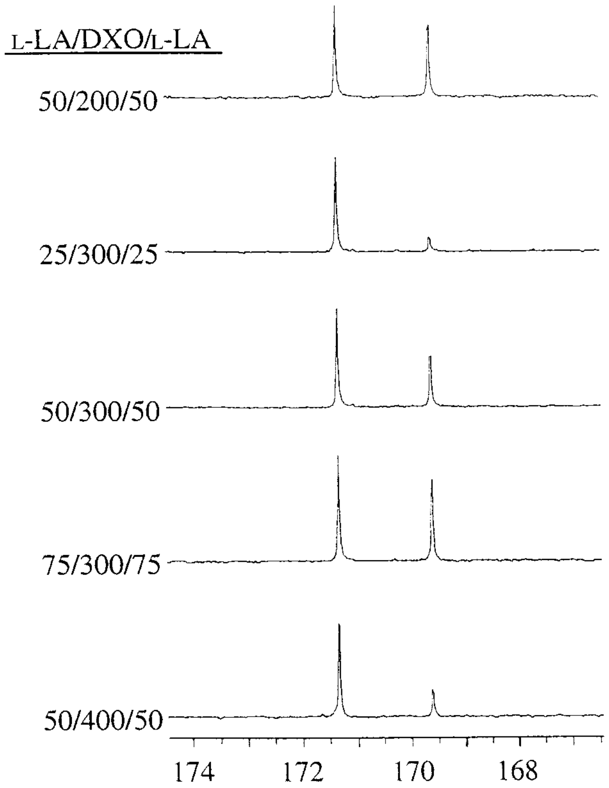


Figure 4. The 100 MHz ^{13}C NMR spectra of the carbonyl region of the L-lactide-block/1,5-dioxepan-2-one block copolymers of different compositions recorded in $CDCl_3$. Feed average block lengths (DP) are shown in the figure.

Ring-Opening Polymerization of L-lactide or 1,5-Dioxepan-2-one Initiated with 1/2 and Conducted with H_2O as Transfer Agent

Control of the ring-opening polymerization of cyclic esters, that is, a predictable molecular weight and a narrow molecular weight distribution, is important from an industrial viewpoint. It is consequently important to investigate the influence of small amounts of water on the polymerization and the prepared polymer if the material is to be produced on a large scale. Table III shows the results from the homopolymerization of L-lactide or DXO with and without the addition of water. The addition of 1 equivalent of water caused the $\bar{M}_n$ to decrease to about 10,000. The MWD was not greatly affected by deliberate contamination with water. The reaction mixture was homogeneous even at low monomer conversion and the polymerization proceeded to high monomer conversion.

As previously reported for metal alkoxide compounds, free hydroxyl compounds effectively in-

Table III. The Influence of Water on the Outcome of Polymerization

Monomer	Amount H_2O^a	Reaction Time [min]	Conversion[b] [%]	Yield [%]	$M_n{}^c$	MWD[c]
L-LA	–	1440	93,3	82,1	29400	1,12
L-LA	1 equiv.	1440	73,5	66,9	9700	1,15
DXO	–	360	90,3	79,1	29400	1,46
DXO	1 equiv.	360	91,7	49,4	10000	1,65

Polymerizations conducted in chloroform at 60 °C, initial monomer concentration = 0.5*M*.

[a] Compared to amount of Sn.

[b] Determined by ^{1}H NMR from crude reaction mixture.

[c] Number-average molecular weight determined by SEC; $CHCl_3$ was used as eluent; flowrate 1.0 mL/min.

terchange with alkoxide groups covalently bonded to the metal.[20] Thus, the free hydroxy-terminated macromolecules were exchanged for the growing alkoxide species during the polymerization process. Since the MWD was not altered, the exchange reaction between the free hydroxyl-terminated species and the alkoxide was rapid with regard to the propagation reaction. The decrease in molecular weight was a consequence of an increase in the total number of polymer chains formed when water was added. By choosing the appropriate chain-transfer agent, the polymer $\bar{M}_n$ can be altered in a preferred direction. However, it is essential to exclude water when L-LA and DXO are block copolymerized because diblock copolymers or homopolymers might be formed.

Thermal Characteristics of Poly(L-LA-*b*-DXO-*b*-L-LA)

Poly(L-LA-*b*-DXO-*b*-L-LA) triblock copolymers of different compositions and different molecular weights were analyzed by differential scanning calorimetry (DSC). After polymerization, the polymer formed was precipitated in a cold hexane–methanol mixture. Before the DSC measurements, the polymer samples were dried at room temperature under vacuum for 1 month in order to remove all remaining solvent. Figure 5 shows a typical DSC trace recorded for the poly (L-LA-*b*-DXO-*b*-L-LA) during the second scan, Table I Polym. No. 4. It was detected that the block copolymer exhibited a glass transition and a single endothermic melting peak at about 153 °C during the calorimetric scan. The thermal behavior of the other polymers was similar but the a melting peak appeared at lower temperature as the poly(L-LA) block length was reduced.

Figure 6 shows the melting temperature as a function of the amount of L-LA in the triblock copolymer. Crystallinity was observed for the triblock copolymers containing a minimum of 11 mol % L-LA, as determined by DSC. For the block copolymer with 7 mol % L-LA, the endothermic melting peak was absent and the DCS curves demonstrated only a glass transition. The peak melting temperature observed for the triblock copolymers was much lower than that of pure poly(L-LA), for which a T_m value of 169 °C was reported in the literature.[21] The difference was attributed partly to the central DXO block, which tended to limit the crystal thickness and perfection. The appearance and intensity of the endothermic peak also depended on the length of the poly(L-LA) segment, an increase in the block length resulted in a rise in the melting temperature and a higher degree of crystallinity. Low molecular weight poly(L-LA) showed a strong dependence of the melting point on the molecular weight.[22]

As is shown in Figure 7, the T_g dependence on the composition for the triblock copolymer was

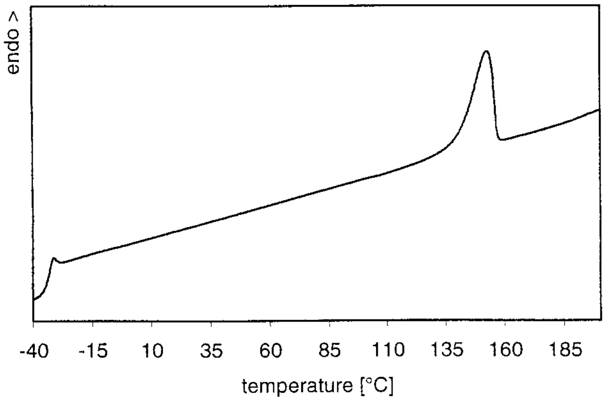


Figure 5. The DSC thermogram registered for the poly(L-LA-*b*-DXO-*b*-L-LA) during the second scan, Table IV Polym. No. 4.

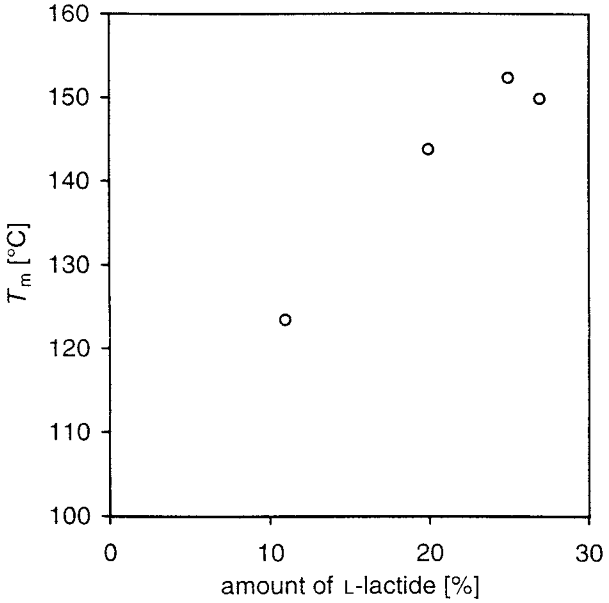


Figure 6. The melting temperature (T_m) as a function of the amount of L-lactide in the triblock copolymer. T_m was measured by DSC during the second scan.

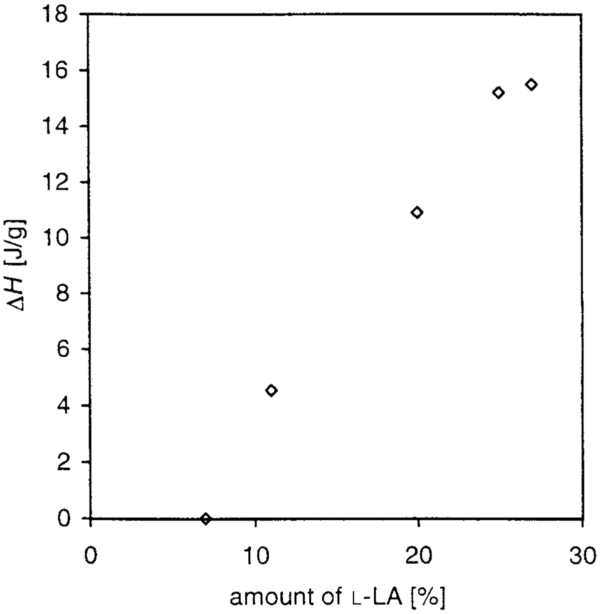


Figure 8. The heat of fusion for the L-lactide/1,5-dioxepan-2-one block copolymers as a function of the amount of L-lactide in the copolymer. The heat of fusion was measured by DSC during the second scan.

different from that of random copolymers of DXO and L-LA. As previously reported, an increase in the amount of DXO resulted in a decrease in T_g for the random copolymers. However, the T_g was not altered much by the change in the triblock copolymer composition. A variation within 2 °C was observed over the range of compositions investigated. This behavior is typical of triblock copolymers containing one A unit and two B units, one of them being able to crystallize and the other being totally amorphous.

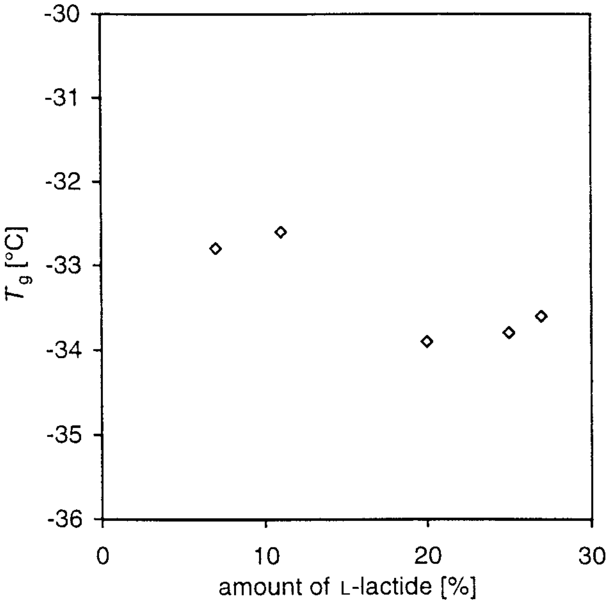


Figure 7. Glass-transition temperature of L-lactide/1,5-dioxepan-2-one block copolymers versus the amount of L-lactide in the block copolymer measured by means of differential scanning calorimetry during the second scan.

Figure 8 shows that the heat of fusion (ΔH) was linearly dependent on the amount of L-LA in the block copolymer. Table IV summarizes the thermal properties of the block copolymers. In block copolymers of DXO and L-LA of comparable poly(L-LA) block lengths (DP = 50), the melting temperature decreased as the DXO block length increased.

X-Ray Diffraction Patterns

The crystalline structure was determined by wide-angle X-ray diffraction on solvent cast films. The prepared films were dried at room temperature under vacuum in order to remove volatile residues. Several layers of films were used in order to avoid any orientation introduced by the method of preparing the polymer films.

Figure 9 shows the X-ray diffraction patterns of the block copolymers with the highest and lowest degrees of crystallinity. The crystal patterns

Table IV. Thermal Properties of Block Copolymers of L-lactide and 1,5-Dioxepan-2-one Initiated by Cyclic Tin Alkoxide in Chloroform at 60 °C

Polym. No.	$\bar{M}_n$[a]	L-lactide[b] [%]	T_g[c] [°C]	T_m[c] [°C]	ΔH[c] [J/g]
1	33300	27	−33,6	149,8	15,5
2	36100	7	−32,8	–	–
3	43300	20	−33,9	143,7	10,9
4	52200	25	−33,8	152,3	15,2
5	48900	11	−32,6	123,4	4,52

[a] Molecular weight of the triblock copolymer determined by ^{1}H NMR.
[b] Percentage L-LA in copolymer determined by ^{1}H NMR spectroscopy.
[c] Determined by differential scanning calorimetry, heating rate 10 °C/min.

were found to be similar for all the polymers prepared, with four major peaks at 2θ values of 5.44, 17.2, 19.7, and 22.8°. The X-ray pattern of the block copolymer revealed a crystal structure similar to that reported for the homopolymer made from L-lactide but additional weak, broad reflections were also observed. The diffraction peaks of the pure poly(L-LA) are reported to appear at 2θ values at about 15, 16, 18.5, and 22.5°.[23] Regardless of the structure and the molecular weights of the DXO and L-LA blocks, all the block copolymers showed the same crystalline peaks, which means that the DXO block and the L-LA block were phase-separated in the crystalline state.

From the X-ray analysis it was concluded that the block copolymers were semicrystalline at all compositions. The intensity of the crystalline scattering peaks diminished as the poly(L-LA) block length was reduced, but the 2θ values remained the same, independent of the composition. It was clear from the diffraction patterns that the polymer comprising 7 mol % L-LA (Table No. IV. Polym. No. 2 L-LA/DXO/L-LA = 25/300/25) shows some degree of crystallinity, which was not observed by DSC.

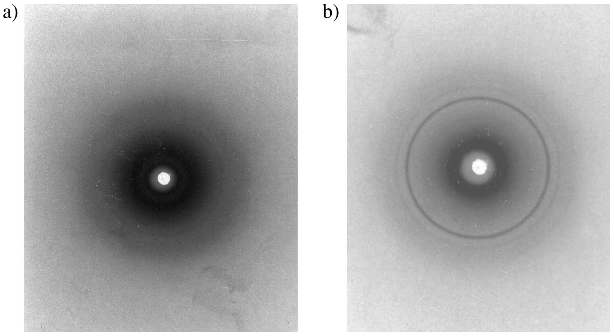


Figure 9. Wide-angle X-ray diffraction patterns of the block copolymer (a) 25/300/25, and (b) 50/200/50.

A previous study showed that random/segmented copolymers of DXO and L-LA exhibit crystallinity up to a DXO content of 50%.[9] When the amount of DXO was further increased, the polymer formed was totally amorphous. In this study, the investigated triblock copolymers had a DXO content between 73 and 93 mol %. All polymers demonstrated some degree of crystallinity, indicating that the poly(L-LA) blocks easily phase-separated and formed crystalline domains.

CONCLUSIONS

A new family of A-B-A block copolymers containing poly(1,5-dioxepan-2-one) (B) and poly(L-lactide) (A) blocks have been synthesized. The polymerization procedure was based on a two-step sequential addition of monomers to a controlled polymerization system initiated with the cyclic tin alkoxide 1,1,6,6-tetra-*n*-butyl-1,6-distanna-2,5,7,10-tetraoxacyclodecane (**1/2**). The proposed method gave a good control of the synthesis and made it possible to tailor-make the final product. The novel triblock copolymers were obtained in high yield by a controlled synthesis at moderate temperature in chloroform. No side-reactions, such as inter- or intramolecular transesterification reactions, were detected.

DSC and WAXD analyses indicated that the poly(L-LA) blocks formed crystalline domains in the solution-cast films by microphase separation. WAXD studies indicated that all the polymer compositions exhibited some degree of crystallinity. Even at the lowest L-LA content of 7%, X-ray diffraction showed the characteristic patterns of crystalline poly(L-LA). The glass-transition temperature was only slightly affected by the increase in the amount of L-LA, although, the melting temperature and the heat of fusion decreased as the L-LA block length was reduced.

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