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Copolymerization of 2,2-Dimethyltrimethylene Carbonate and L,L-Lactide

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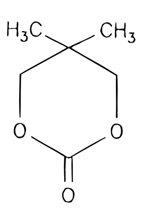
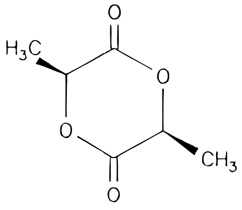
ABSTRACT: The ring-opening polymerization of mixtures of 2,2-dimethyltrimethylene carbonate (DTC) and L,L-lactide (LLA) in the melt, with diethyl zinc or dibutyltin dimethoxide as initiator, results in the formation of random copolymers. LLA polymerizes first in a fast reaction, followed by a slow polymerization of DTC. Investigations of the polymerization mechanism reveal that DTC is randomly inserted into LLA-LLA diads. The microstructure of the copolymers was determined by triad analysis of the ^{13}C NMR spectra. The thermal behavior of the copolymers, especially the dependence of the glass transition temperature on the copolymer composition, was studied, and a deviation from the behavior predicted by the Fox equation was observed.

Introduction

High molecular weight copolymers of 2,2-dimethyltrimethylene carbonate (DTC) and L,L-lactide (LLA) are expected to have a wide range of interesting mechanical and biological properties as a function of their composition and microstructure. While block copolymers are often multiphase materials that provide for additivity of the phase properties, random copolymers are known to provide new materials with new properties. Applications of these in the biomedical field as biocompatible and biodegradable materials are expected.



DTC



LLA

In order to finely adjust the properties of a copolymer, the relation between reaction conditions (especially initiator, temperature, and solvent) and microstructure are to be established. The present work aims at the mechanism of the copolymerization of DTC and LLA in the presence of aluminum-, zinc-, and tin-based catalysts. The microstructure of the copolymers was determined by means of ^{13}C NMR spectroscopy and is characterized by the distribution of triads.

Experimental Part

Materials. L,L-Lactide (LLA) and D,L-lactide (DLLA) from Boehringer GmbH, Ingelheim, and 2,2-dimethyltrimethylene carbonate (DTC) from Bayer AG were dried in vacuo before use. Dibutyltin dimethoxide [$Bu_2Sn(OMe)_2$] from Merck, diethyl zinc (1.1 M solution in toluene) from Aldrich, tri-*sec*-butoxyaluminum from Merck, and diethylaluminum ethoxide and aluminum acetylacetonate from Aldrich were used as initiators without further purification. (Usually a stock solution of the corresponding initiator in toluene was used to initiate polymerization). Toluene was freshly distilled in vacuo from a solution of *sec*-butyllithium before use as a solvent for polymerizations. Nitrogen from Linde was passed over 4 Å molecular sieves, finely distributed potassium on aluminum oxide, and BTS catalyst (from BASF) for purification.

Measurements. ^{1}H NMR and ^{13}C NMR were recorded with a Varian VXR 300 FT-NMR spectrometer at 300 and 75.4 MHz, respectively. $CDCl_3$ was used as solvent and TMS as internal standard. 507-PP Wilmad sample tubes were used, diameter 5 mm, length 175 mm.

Gel permeation chromatography (GPC) was carried out using two systems: (i) A Waters apparatus with a combined ultraviolet detector and a refractive index detector. A combination of four columns was applied with PL-gel from Polymer Laboratories; length of each column, 300 mm; diameter, 7.0 mm; diameter of the gel particles, 5 μm; pore widths, 100, 500, 10^3, and 10^4 Å. Tetrahydrofuran was the eluting solvent, with a flow rate of 0.5 mL/min. (ii) An ERC HPLC pump 64 with an ERMA 7515A refractive index detector and two columns with Jordi Gel; length of each column, 500 mm; diameter, 8.0 mm; diameter of the gel particles, 5 μm; pore widths, 100 and 10^3Å. Chloroform was the eluting solvent, with a flow rate of 1.0 mL/min. Calibration in both cases was achieved with polystyrene standards of narrow molecular weight distribution ($M_w/M_n = 1.03-1.06$) from polymer Standard Service in Mainz, Germany. The calibration curve was achieved by a semilogarithmic plot of the peak molar mass (M_p) versus elution volume (V_e).

Differential scanning calorimetry was performed with a Perkin Elmer DSC 7 apparatus, heating rate 20 K/min. The first and second heating runs showed no essential differences.

Optical rotatory data were obtained using a Perkin Elmer 141 polarimeter at 589 nm with chloroform as the solvent at room temperature ($c = 0.01$ g/mL).

General Procedure for the Polymerization in Solution. To a solution of the monomer in toluene was added at 90 °C a solution of the initiator in toluene. After a selected reaction time, the reaction mixture was cooled to room temperature and neutralized with a solution of 5 wt % phosphoric acid in methanol. Initial conditions and results are summarized in Tables 1 and 2.

Preparation of Poly(DTC)-*b*-poly(LLA). To a solution of 2.6 g (0.02 mol) of DTC in 26 mL of toluene was added at room temperature 0.24 mL of a 1.1 M solution of Et_2Zn in toluene (or 0.52 mL of a 0.5 M solution of Al(O-*sec*-Bu)$_3$ in toluene). After 10 h, the reaction mixture was heated to 90 °C, and 2.88 g (0.02 mol) of LLA was added. After another 8 h at 90 °C, the polymerization was stopped, and the polymer was isolated as described before. Yield: 84% (for Al(O-*sec*-Bu)$_3$ as initiator), 72% (for Et_2Zn as initiator).

^{13}C NMR data (cf. Figure 2a): $\delta = 169.58$ (C_a), 155.26 (C_d), 72.43 (C_e), 69.03 (C_b), 35.15 (C_f), 21.38 (C_g), 16.65 (C_c) ppm.

Preparation of Poly(DTC-*stat*-LLA). General Procedure for the Polymerization in the Melt. To a mixture of 2.6 g (0.02 mol) of DTC and 2.88 g (0.02 mol) of LLA heated to

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Table 1. Homopolymerization of DTC and LLA in Toluene[a] at 90 °C with Different Initiators: Initial Conditions, Polymer Yield, Molecular Weight, and Optical Rotation of the Polymer

monomer	initiator	[M]/[I], mol/mol	time, h:min	yield, wt %	M_{obs}[b]	$[\alpha]^{20}_{D}$[c]
DTC	Al(O-*sec*-Bu)$_3$	154	36:00	89	20 000	
DTC	Zn(Et)$_2$	154	20:00	88	35 000	
DTC	Bu$_2$Sn(OMe)$_2$	154	0:45	45	21 200	
LLA	Al(O-*sec*-Bu)$_3$	139	36:00	85	22 000	−155.6
LLA	Zn(Et)$_2$	139	0:20	95	28 000	−155.1
LLA	Bu$_2$Sn(OMe)$_2$	139	0:20	94	22 000	−155.4

[a] Initial monomer concentration 15 wt %: $[DTC]_0 = 1.15$ mol/L, $[LLA]_0 = 1.04$ mol/L. [b] From GPC, based on polystyrene standards. [c] Measured in $CHCl_3$ ($c = 0.01$ g/mL).

Table 2. Copolymerization of Equimolar Amounts of DTC and LLA in Toluene[a] at 90 °C with Different Initiators: Initial Conditions, Yield, Copolymer Composition, and Molecular Weight

initiator[b]	time, h	yield, wt %	[LLA]/[DTC][c]	M_{obs}[d]
Al(O-*sec*-Bu)$_3$	36	53	88/12	11 000
Et$_2$Al(OEt)	36	56	77/23	26 000
ZnEt$_2$	20	76	66/34	31 000
Bu$_2$Sn(OMe)$_2$	20	39	82/18	13 000

[a] Initial monomer concentration, $[DTC]_0 = [LLA]_0 = 1.04$ mol/L; $[DTC]_0 = 13.5$ wt %; $[LLA]_0 = 15$ wt %. [b] The ratio $([DTC]_0 + [LLA]_0)/[I] = 146$. [c]Molar ratio of the monomers incorporated in the polymer (as obtained from ^1H NMR). [d]From GPC, based on polystyrene standards.

Table 3. Copolymerization of Equimolar Amounts of DTC and LLA in the Melt with Different Initiators:[a] Initial Conditions, Yield, Copolymer Composition, and Molecular Weight

initiator	temp, °C	yield, wt %	[LLA]/[DTC][b]	M$_{obs}$[c]	M_w/M_n
Al(O-*sec*-Bu)$_3$	100	5	51/49	8 500	1.7
Al(acac)$_3$	130	55	100/00	50 100	
Et$_2$Al(OEt)	100	49	74/26	36 500	1.6
ZnEt$_2$	80	57	90/10	20 000	1.4
	100	78	52/48	24 000	1.6
	125	76	55/45	35 600	1.9
	130	75	57/43	32 300	1.9
Bu$_2$Sn(OMe)$_2$	80	57	80/20	20 000	1.4
	100	61	67/33	21 000	1.4
	130	78	53/47	14 000	1.7

[a] Molar ratio $([DTC]_0 + [LLA]_0)/[I] = 146$; polymerization time, 20 h. [b] Molar ratio of the monomers incorporated in the polymer (as obtained from ^1H NMR analysis). [c] From GPC, based on polystyrene standards.

temperatures between 80 and 130 °C was added 0.273 mmol of the respective initiator. After 20 h, the reaction mixture was cooled to room temperature and dissolved in 20 mL of CH_2Cl_2, which contained 0.5 mL of 5 wt % phosphoric acid in methanol. The polymer was precipitated in methanol. The results are summarized in Table 3.

^{13}C NMR data (cf. Figure 2b and Chart 1): $\delta = 169.59$ (C_1, C_3), 169.83 (C_2, C_4, C_7), 169.46 (C_5), 170.0 (C_6), 170.12 (C_8), 155.28 (C_9, C_{10}), 154.55 (C_{11}, C_{12}), 72.43 (C_{13}, C_{14}, C_{18}), 72.94 (C_{15}, C_{16}), 69.83 (C_{17}, C_{19}), 69.03 (C_{20}, C_{22}, C_{24}), 69.25 (C_{21}, C_{23}), 71.40 (C_{25}, C_{26}), 71.69 (C_{27}) ppm. Signals not assigned: $\delta = 35.15$ (C_{quat}, DTC), 21.38 (CH_3, DTC), 16.67, 16.88 (CH_3, LLA), 17.00 (CH_3, LA) ppm.

For copolymers with various [LLA]/[DTC] ratios, cf. Table 4.

Results and Discussion

The polymerization of DTC with tri-*sec*-butoxyaluminum [Al(O-*sec*-Bu)$_3$], diethylzinc (ZnEt$_2$), and dibutyldimethoxytin [Bu$_2$Sn(OMe)$_2$] in toluene as a solvent[1] reveals a clear distinction between the aluminum- and zinc-based initiators on the one hand and the tin-based initiator on the other. For tin in the active site, the rates of back-biting reactions (intramolecular transesterification) and intermolecular transesterification reactions are as high as the rate of the propagation reaction, while for the aluminum- and zinc-based initiators, the rate of the propagation reaction is much higher than that of transesterification.

Table 4. Copolymerization of LLA and DTC in the Melt at 105 °C with Et$_2$Zn as Initiator[a] ($t = 20$ h): Dependence of the Yield and Composition of Copolymers on the Composition of the Monomer Feed

no.	$[LLA]_0$, mol %	$[DTC]_0$, mol %	yield, wt %	[LLA]/[DTC][b]	M_{obs}[c]
1	89	11	76	89/11	75 000
2	78	22	77	81/19	73 000
3	68	32	77	70/30	72 000
4	58	42	78	64/36	74 000
5	47	53	78	50/50	73 000
6	38	62	78	42/58	74 000
7	28	72	77	28/72	73 000
8	18	82	78	19/81	73 000
9	11	89	79	12/88	74 000

[a] Molar ratio $([DTC]_0 + [LLA]_0)/[I] = 182$. [b] Molar ratio of the monomers incorporated in the polymer (as obtained from ^1H NMR analysis). [c] $1.5 < M_w/M_n < 1.8$ (from GPC, based on polystyrene standards).

Recently,[2,3] lactides were polymerized in a living manner in toluene or xylene as a solvent and with aluminum triisopropoxide [Al(O-*iso*-Pr)$_3$] or Bu$_2$Sn(OMe)$_2$ as an initiator. In addition, the copolymerization of mixtures of ϵ-caprolactone and D,L- or L,L-lactide initiated by aluminum isopropoxide was reported.[4] As a result of the monomer reactivity, tapered copolymers were obtained, particularly when D,L-lactide is the comonomer (rather than L,L-lactide).

Polymer Synthesis. In preliminary experiments, we polymerized both monomers in toluene solution at 90 °C and made the following observations (cf. Table 1): (i) Except for the homopolymerization of DTC with Bu$_2$Sn(OMe)$_2$, the polymer yields are around 90%. The low polymer yield (45%) in the system DTC/Bu$_2$Sn(OMe)$_2$ is due to the high content of cyclic oligomers.[1] (ii) The molecular weights of the polymer samples are close to each other, except for the polymer obtained with Zn(Et)$_2$ as initiator,[1] and close to the calculated value. (iii) Under the reaction conditions, no racemization of the lactic acid (LA) moiety occurs. [100% optically pure poly(LLA) shows a value of $[\alpha]^{20}_{D} = -156 \pm 2°$ ($c = 0.01$ g/mL $CHCl_3$).[5]]

The copolymerization of equimolar amounts of LLA and DTC in toluene solution at 90 °C (cf. Table 2) results in copolymers with a composition that differs considerably from the composition in the feed. However, the best results were obtained with Et$_2$Zn as initiator with regard to the polymer yield and to its composition. All other initiators do not incorporate DTC to the expected extent.

Since the results obtained in solution polymerization are not satisfactory, polymerization experiments in the melt were performed (cf. Table 3). From these results it was concluded that initiators based on Al are not suitable for the copolymerization since the yields are very low and the composition of the polymer is far from that of the feed. Et$_2$Zn gives good results only at temperatures between 100 and 130 °C. At lower temperatures, LLA is polymerized, but the polymerization of DTC is rather slow. Similar results were obtained with Bu$_2$Sn(OMe)$_2$. As a conclusion, poly(LLA-*stat*-DTC) copolymers are obtained in good yield and with

Table 5. Copolymerization of Equimolar Amounts of DTC and LLA in the Melt with Et_2Zn as Initiator[a] at 105 °C: Copolymer Composition, Polymer Yield, and Molecular Weight as a Function of Time

time, h:min	$\frac{100 \times [LLA]}{[DTC] + [LLA]}$ mol %	yield, wt %	M_{obs}[b]
0:02	93	27.8	23 750
0:04	87	43.4	25 000
0:20	84	51.5	27 500
1:00	70	56.6	28 000
2:00	69	60.2	27 900
4:00	55	65.0	28 300
10:00	54	69.2	29 200
22:00	53	73.7	31 600
60:00	50	74.5	32 000

[a] Molar ratio ($[DTC]_0 + [LLA_0]/[I] = 146$. [b] $1.4 < M_w/M_n < 1.9$ (from GPC, based on polystyrene standards).

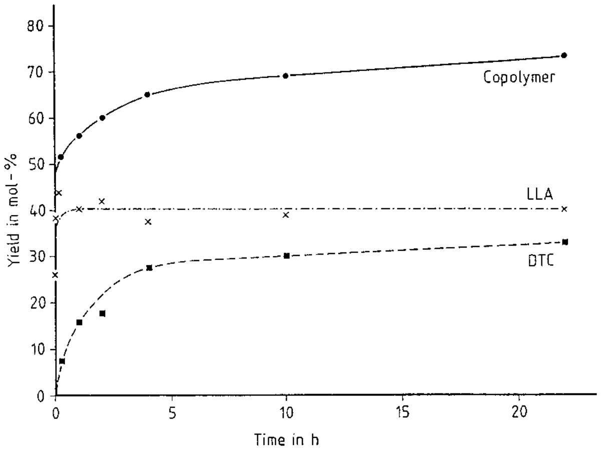


Figure 1. Polymerization of equimolar amounts of LLA and DTC in the melt at 105 °C with diethylzinc as initiator. Dependence of the monomer conversion on polymerization time.

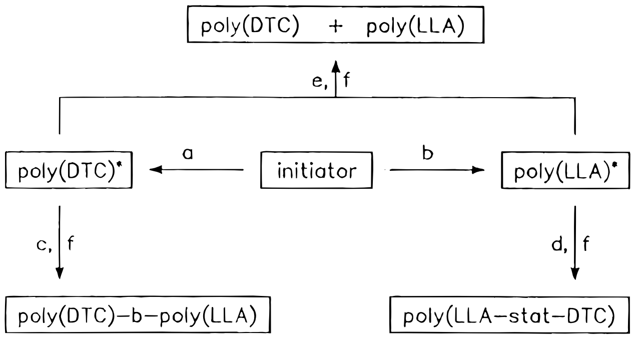
controlled composition when Et_2Zn and $Bu_2Sn(OMe)_2$ are used as initiators under well-defined polymerization conditions.

For further mechanistic investigation of the polymerization, the system LLA/DTC/Et_2Zn was chosen, while for investigations of the copolymer microstructure, both systems—LLA/DTC/Et_2Zn and LLA/DTC/$Bu_2Sn(OMe)_2$—were compared by means of ^{13}C NMR analysis. To establish the changes in thermal properties of the copolymers with their composition, a series of nine copolymers was prepared with Et_2Zn as initiator (cf. Table 4). The results reveal that, under the reaction conditions, copolymer yields of 76−79 wt % were obtained, with a composition close to that of the feed and with comparable molecular weights.

Mechanistic Aspects. In order to obtain deeper insight into the mechanism of copolymerization with Et_2Zn, a time/conversion plot of the melt copolymerization was developed (cf. Table 5 and Figure 1). These results show that first, in a fast reaction, LLA is polymerized, and later DTC is consumed in a slow reaction. Still, the result is a copolymer with random distribution of the monomer units.

The question arises of what happens when the monomers are added consecutively to the initiator. For experimental reasons, the polymerization was performed in toluene. When first LLA was polymerized (cf. Table 1) and then DTC was added and the reaction continued for 8 h, a copolymer was isolated in 75% yield, which shows a statistical diad distribution (cf. Scheme 1). When first DTC was polymerized (cf. Table 1) and then LLA was added and the reaction continued (8 h, 90 °C), an A-B block copolymer was isolated (cf. Scheme 1). Finally, mixing of living poly(LLA) and living poly(DTC) (cf. Table 1) yielded a polymer which consists of a blend of the two components (cf. Scheme 1). Separation of the blend components was successfully accomplished by fractional solubilization in THF (poly(DTC) is soluble and poly(LLA) is insoluble in THF).

Scheme 1[a]



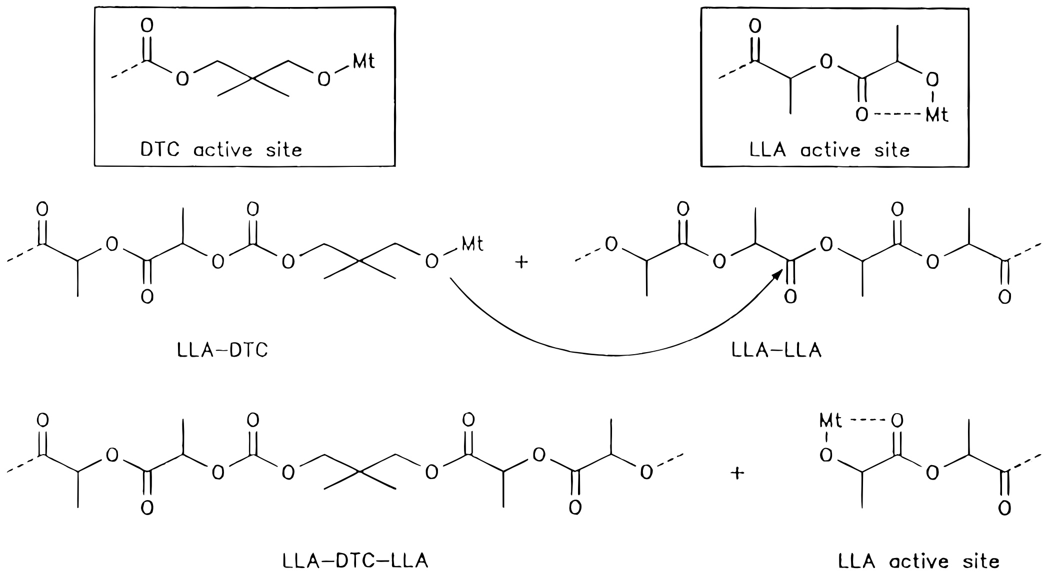
[a] Conditions: (a) DTC/toluene, 20 °C, 10 h; (b) LLA/toluene, 90 °C, 8 h; (c) LLA, 90 °C, 8 h; (d) DTC, 20 °C, 8 h; (e) 80 °C, 1 h; (f) H_3PO_4/MeOH.

The mechanistic conclusions from these experiments are the following: (i) With Zn in the active site, transesterification between two living polymer chains of poly(DTC)* and poly(LLA)* does not occur. (ii) Poly(DTC)* with Zn in the active site initiates the polymerization of LLA with formation of a block copolymer. (iii) Poly(LLA)* with Zn in the active site reacts with DTC, resulting in a statistical copolymer, however.

The last, somehow peculiar, result is explained in the following way. The active site of poly(LLA) is highly stabilized by an intramolecular five-membered ring (cf. Scheme 2) and by the −I effect of the adjacent carbonyl group. Thus, only strong electrophilic species such as LLA will react in a fast reaction with this active site. Once LLA is consumed, the weaker electrophile DTC reacts only slowly with the LLA active site at the chain end. After site transformation, the resulting DTC active site has a reduced ability of stabilization (intramolecular stabilization would lead to an unfavorable eight-membered ring) and is, therefore, highly reactive. The strongest electrophile in the system, however, is not the DTC monomer but the ester groups of the LLA-LLA diad. Thus, by intermolecular reaction of the DTC active site with a lactate group of another chain, the active LLA site is regenerated, and a LLA-DTC-LLA triad is formed (cf. Scheme 2). Formally, an insertion of DTC into an LLA-LLA diad has occurred. Repetition of this process leads to an increase of heterodiads on the expense of LLA homodiads. Toward completion of DTC conversion, DTC-DTC diads are formed as well as DTC-LA-DTC triads (LA = lactate); the latter result from formal insertion of DTC into a lactide repeating unit of a DTC-LLA diad.

^{13}C NMR analysis (see later) as a function of conversion supports this mechanism. First LLA-LLA-LLA triads are formed, and then triads with an LLA/DTC ratio of 2 appear (DTC-LLA-LLA, LLA-LLA-DTC, LLA-DTC-LLA), followed by triads with an LLA/DTC ratio of 1/2 (DTC-DTC-LLA, LLA-DTC-DTC, DTC-LLA-DTC), and finally DTC-DTC-DTC triads as well as DTC-LA-DTC triads appear. Once all monomer is consumed, i.e.,

Scheme 2. Polymerization of a Mixture of LLA and DTC: Mechanism of Randomization



the concentration of monomers is below its critical concentration, the microstructure of the copolymer does not change anymore, indicating the absence of intermolecular transesterification reactions under the given reaction conditions.

Spectroscopic Characterization of the Copolymers. ^{13}C NMR spectroscopy is a strong analytical tool for the determination of the diad and triad distribution of copolymers. To identify the homodiads, ^{13}C NMR spectra of the homopolymers and of a block copolymer were analyzed. As expected, poly(DTC)-*block*-poly(LLA) shows only signals corresponding to the sum of signals obtained for the homopolymers (Figure 2a), while poly(LLA-*stat*-DTC) shows for each type of carbon atom the resonance lines due to their presence in different triads (Figure 2b). For statistical copolymers with two repeating units, 2^3 triads can be theoretically expected (Chart 1).

Taking into consideration that, at high DTC concentrations, a lactide repeating unit is cleaved with formation of lactate (LA), additional triads should be observed. Beside the DTC-LA-DTC triad, however, the other theoretically possible triads include LLA-LA sequences, which cannot be distinguished from LLA-LLA sequences.

The complete assignment of the resonance lines in a ^{13}C NMR spectrum to the eight triads comprising LLA and DTC repeating units and the DTC-LA-DTC triad was achieved in several steps. (i) First, the resonance lines of the homotriads were assigned by comparison with the spectra of homo and block copolymers. (ii) The chemical shifts of the carbon atoms of the reference triads were taken as the base values for the calculation of the chemical shifts of mixed triads. The increments corresponding to the structural elements missing in the reference compound were then added to the base values, while those of structural elements present in the reference but absent in the mixed triads were substracted.[6,7] Finally, the calculated values for the chemical shifts were attributed to the respective experimental resonance line. (iii) Evaluation of ^{13}C NMR spectra with different ratios of repeating units LLA/DTC of 4, 1, and 0.25 were used to verify the assignment of certain triads by means of the intensity of the experimental resonance lines. (iv) Last but not least, the occurrence of racemization was excluded by comparison with spectra of samples containing D,L-lactide repeating units.

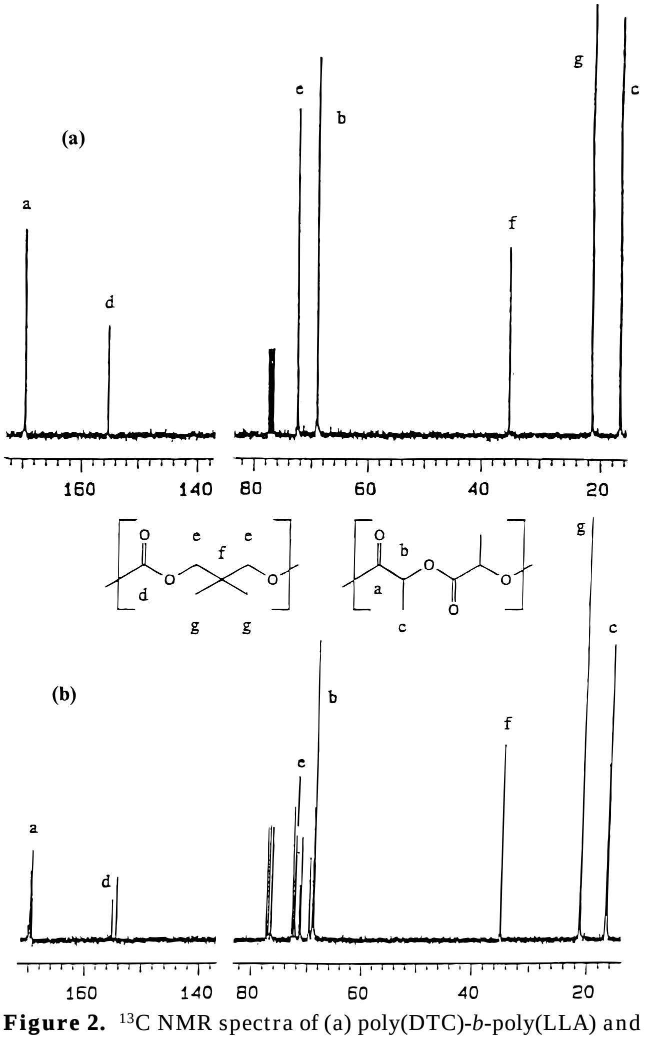
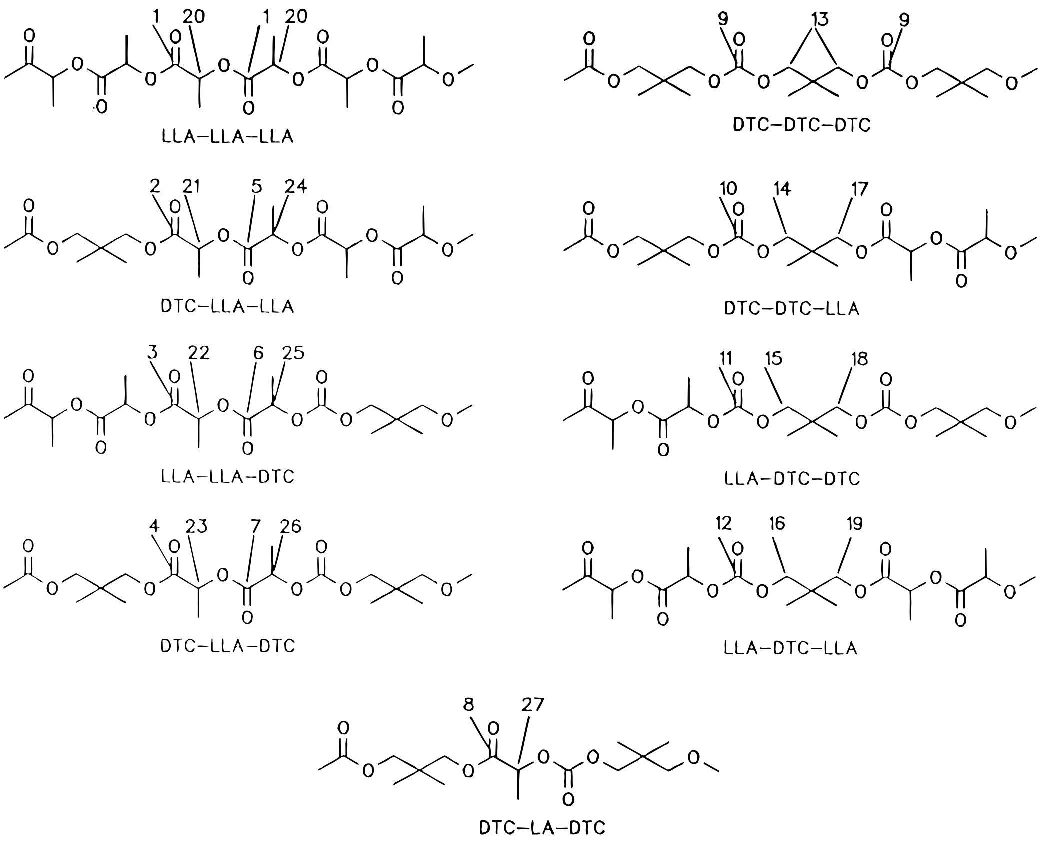


Figure 2. ^{13}C NMR spectra of (a) poly(DTC)-*b*-poly(LLA) and (b) poly(LLA-stat-DTC).

Figures 3 and 4 show the carbonyl, methylene, and methine regions of LLA/DTC and DLLA/DTC copolymers initiated with Et_2Zn and $Bu_2Sn(OMe)_2$ and the assignment to the different triads. The chemical shifts centered at 169 and 153 ppm in Figure 3 are assigned to the ester and carbonate carbonyl carbon atoms,

Chart 1. Theoretically Expected Triads in the Random LLA/DTC Copolymers[a]



[a] The numbers refer to the resonance lines in ^{13}C NMR spectra of Figures 3–5.

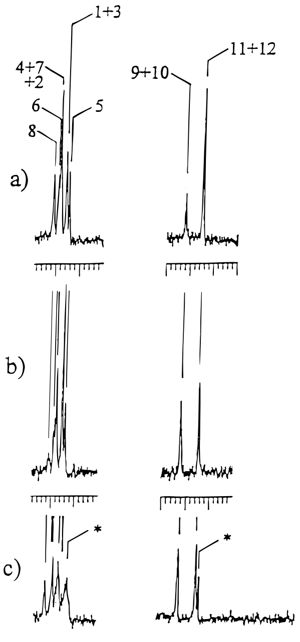
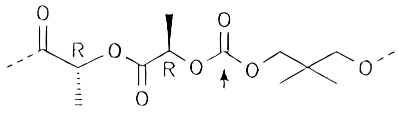
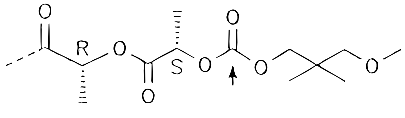


Figure 3. Carbonyl region of the ^{13}C NMR spectra of LLA-DTC and DLLA-DTC copolymers. (a) Copolymer of LLA/DTC (1/1) obtained with $Bu_2Sn(OMe)_2$ as initiator; (b) copolymer of LLA/DTC (1/1) obtained with Et_2Zn as initiator; (c) copolymer of DLLA/DTC (1/1) obtained with Et_2Zn as initiator. Asterisk indicates additional signal due to DLLA repeating units.

respectively. The ^{13}C NMR spectrum of the polymer containing D,L-lactide repeating units shows a characteristic chemical shift not only for the ester carbonyl carbon atom but also for the carbonate carbonyl carbon atom. The latter resonance line is due to the opposite stereogenic center in *β*-position to the carbonate carbonyl carbon atom:



δ = 154.55 ppm



δ = 154.42 ppm

In the spectra of LLA/DTC copolymers, no resonance lines of D,L-lactide repeating units are detected; hence, racemization during polymerization was excluded.

An evaluation of ^{13}C NMR spectra by the line intensities is acceptable if the substituents at the carbon atom under consideration are identical; in this case, the relaxation time and nuclear Overhauser effect are virtually identical for the two species under well-defined measuring conditions. A comparison of the spectra of LLA/DTC copolymers prepared with Et_2Zn and $Bu_2Sn(OMe)_2$ as initiator reveals a higher concentration of DTC-LA-DTC triads (signal 8) for $Bu_2Sn(OMe)_2$, corresponding to a higher transesterification activity; in addition, the intensity of signal 9 (corresponding to a DTC-DTC-DTC triad) is much lower for the Sn-based initiator. It should be noticed also that the intensity of DTC-LA-DTC triads is higher when D,L-lactide is present in the mononer mixture (cf. Figure 3b and c); i.e., an ester linkage with participation of one D-lactate unit is

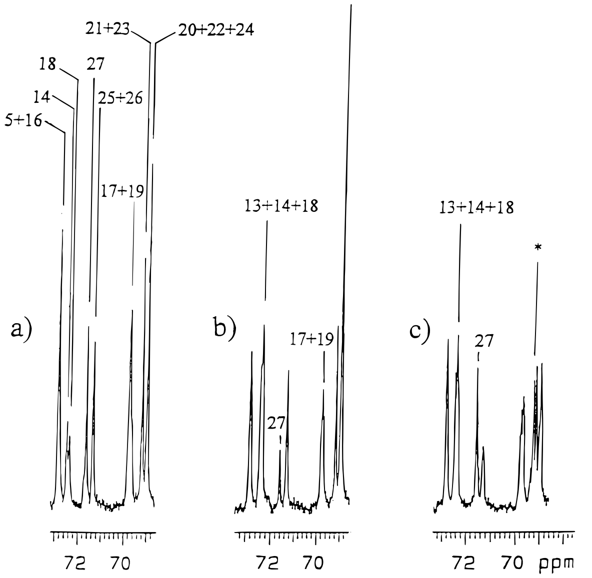


Figure 4. Methylene and methine region of the ^{13}C NMR spectra of LLA-DTC and DLLA-DTC copolymers. (a) Copolymer of LLA/DTC (1/1) obtained with $Bu_2Sn(OMe)_2$ as initiator; (b) copolymer of LLA/DTC (1/1) obtained with Et_2Zn as initiator; (c) copolymer of DLLA/DTC (1/1) obtained with Et_2Zn as initiator. Asterisk indicates additional signal due to DLLA repeating units.

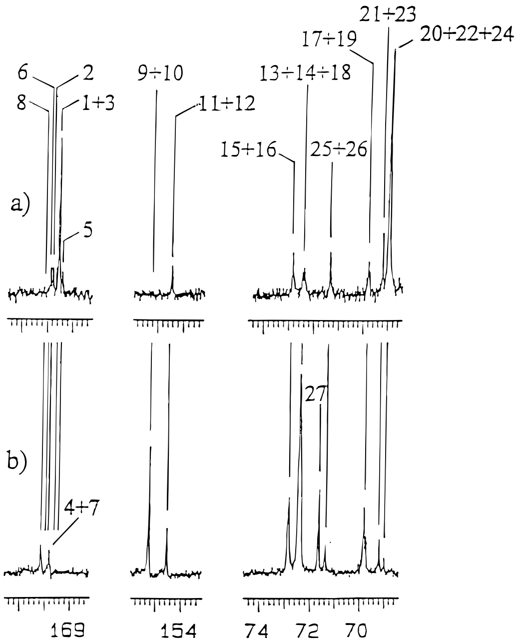


Figure 5. Part of the ^{13}C NMR spectra of LLA-DTC copolymers prepared with Et_2Zn as initiator. Molar ratio (a) 4 and (b) 0.25.

more easily cleved than an ester linkage between two L-lactate units.

In Figure 4, the global assignment of methylene and methine carbon atoms for ^{13}C NMR spectra recorded in the attached proton test (ATP mode) is given. The best information on the triad distribution is expected from the analysis of the CH_2 region; the large frequency range in which methylene groups appear is proof for the high magnetic sensitivity of this group to its particular neighborhood. The methine region shows very low sensitivity; as a consequence, only two different chemical shifts are observed. However, racemization should be observed in the methine region, since the spectrum containing D,L-lactide repeating units shows a distinct resonance line (Figure 4c). A comparison of the triad distribution in samples prepared with Sn and Zn in the active site confirms the results of the analysis of the carbonyl region; a high concentration of DTC-LA-DTC triads in samples prepared with $Bu_2Sn(OMe)_2$ and a relatively high concentration of DTC-DTC-DTC triads in samples prepared with Et_2Zn are an argument for the higher transesterification activity of the Sn-based initiator as compared to the Zn-based initiator. The absence of DTC-DTC-DTC triads (Figure 4a, signal 13) leads to a distinction between the DTC-DTC-LLA triad (signal 14) and the LLA-DTC-DTC triad (signal 18).

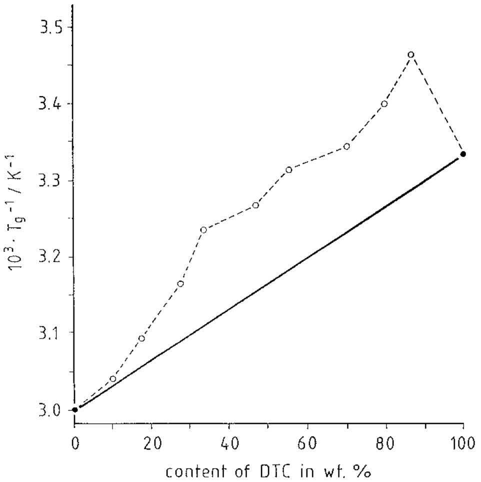


Figure 6. Glass transition temperature (T_g) of statistical LLA-DTC copolymers as a function of copolymer composition, represented according to the Fox relation (eq 1).

^{13}C NMR spectra of samples prepared with different LLA/DTC ratios, e.g., LLA/DTC = 4 and 0.25, and Et_2Zn as initiator show opposite intensities of resonance lines of particular triads. Thus, for polymer samples with a low DTC content, the probability of diads containing two DTC moieties is extremely low; the opposite is true for samples with low LLA content. Beside this trivial result which, however, proves the correctness of the assignment, additional information is obtained for resonance lines which overlap in polymer samples with a ratio of repeating units equal to 1. For example, in Figure 3a, the resonance lines 2, 4, 6, and 7 overlap. However, in Figure 5a, due to the absence of the DTC-LLA-DTC triad (absence of resonance lines 4 and 7), the resonance lines 2 and 6, corresponding to the DTC-LLA-LLA and LLA-LLA-DTC triads, can be clearly identified.

Thermal Properties of Poly(LLA-*stat*-DTC). The homopolymers of DTC and LLA are both highly crystalline materials. The crystallinity of poly(LLA), however, is crucially dependent on the molecular weight and the prehistory of the material.[8] The melting point varies from 160 to 192 °C, the glass transition temperature is in the range of 54 to 61 °C, and the crystallinity reaches values up to 89%. The crystallinity of poly(DTC) is also highly dependent on its prehistory; e.g., on first heating of foils cast from methylene chloride, the material shows two melting transitions at 86 and 121.5 °C, while on the second heating, only one melting point at 123.5 °C and a glass transition temperature (T_g) at 27 °C were found.[9]

Poly(DTC)-*b*-poly(LLA), with a molar ratio of LLA/DTC of 55/45 and a molecular weight of 28 000 (according to GPC measurements and with polystyrene standards), shows two melting transitions: on first heating, melting points at 101 and 166 °C are observed; on second heating, melting points are at 106 and 163 °C. The lower melting point was assigned to the poly(DTC) and the higher melting point to the poly(LLA) microphase.

The random copolymers prepared in this work, comprising a large range of composition from 89/11 to 12/88 for the molar ratio LLA/DTC (cf. Table 4), were analyzed by means of differential scanning calorimetry (DSC) after precipitation from a CH_2Cl_2 solution into methanol, 2 weeks storage, and drying at high vacuum at room temperature. All copolymers are amorphous, since neither in the first nor in the second heating cycle were melting points detected. A representation of $1/T_g$ vs w_2 according to the Fox relation (eq 1),

$$1/T_g = 1/T_{g1} + w_2(1/T_{g2} - 1/T_{g1}) \tag{1}$$

where w_1 and w_2 represent the weight fractions and T_{g1} and T_{g2} the glass transition temperatures of the homopolymers poly(LLA) and poly(DTC), reveals that the experimental values (cf. Figure 6, dotted line) are shifted toward temperatures lower than those predicted by the Fox equation (cf. Figure 6, solid line). It should be noted that, at DTC contents of the copolymer higher than 50 mol %, the glass transition temperature is below 37 °C (body temperature). This fact may have some importance for biomedical applications, since mechanical properties are changing drastically above T_g, and also the rate of hydrolysis is expected to be significantly increased at temperatures above the glass transition temperature.

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