Controlled homo- and copolymerization of ε-caprolactone and D,L-lactide in the presence of Ti^{IV} complexes

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Titanium complexes with dialkanolamine (**1**, **2**) and salen ligands (**3**), as well as titanium alkoxide containing two fragments of an unsaturated alcohol (*cis*-but-2-ene-1,4-diol) as σ-ligands (**4**), were studied in the anionic ring-opening bulk polymerization of ε-caprolactone (CL) at 80—130 °C. All the catalysts involved initiate controlled polymerization and afford polyesters with a number-average molecular weight up to M_n = 20 000 g mol^{-1}, which can be regulated by adjusting the [monomer] : [catalyst] ratio. Among the catalysts studied, complex **2** is most efficient in CL polymerization and affords polyesters with the narrowest molecular weight distribution ($M_w/M_n < 1.2$). In addition, complex **2** initiates the controlled polymerization of D,L-lactide (LA) and is effective in the synthesis of random and block copolymers of CL and LA.

Key words: biodegradable polymers, ε-caprolactone, D,L-lactide, titanium complexes, controlled polymerization, ring-opening polymerization.

In the last few years, considerably growing interest has been shown in the synthesis of biodegradable and biocompatible homo- and copolymers from such monomers as lactones (ε-caprolactone (CL), δ-valerolactone), D,L- and L-lactides, glycolide, *etc.*[1—5] First and foremost, this is due to the ability of the above compounds to be degraded by microorganisms and undergo hydrolysis in physiological media to hydroxy carboxylic acids, which are nontoxic to a human body. All this makes such polymers very promising for many applications in medicine (as implantates, suture materials, and orthopedic fixation devices), in pharmacology (as controlled drug delivery systems) as well as for the manufacture of various materials for engineering purposes.[6—9] However, homopolymers of this series are known to have many drawbacks. For instance, polylactide and polyglycolide are characterized by good mechanical properties but poor elasticity, while elastic and permeable polylactones have poor mechanical properties.[10—13] By producing compositionally different copolymers from the aforementioned monomers, one can easily regulate their properties.[14—17] Particular attention is given to the synthesis of biodegradable (co)polyesters containing terminal functional groups because they can be used as building blocks for the construction of more complex macromolecular structures (stars, combs, and brushes).[18—26]

Many currently known catalytic systems are capable of initiating the polymerization of cyclic esters. First of all, these are alkoxides and various metal complexes, the metals being Sn,[27—31] Al,[32—38] Bi,[39] Zn,[14,40—43] rare earth metals,[44—47] and Group IV metals.[17—18,48—55] However, most of the proposed compounds have a number of drawbacks. For instance, organotin (Sn^{II}, Sn^{IV}) compounds commercially used for the preparation of polyesters (PE) are cytotoxic. Metal complexes with various chelating ligands[47,55] are often accessible through multistep syntheses, so they are rather expensive. At the same time, reactions initiated by metal alkoxides[32—34,48—50] yield polymers with broad molecular weight distributions.

Current investigations are spending much effort on the polymerizations of lactones and lactide in the presence of titanium complexes, primarily because they are nontoxic and allow the synthesis of PE with controlled molecular weights and narrow molecular weight distributions (MWD).[49,53—57] Moreover, it has been found earlier that the use of complexes containing bulky bridging ligands minimizes the risk of such side reactions as intra- and intermolecular transesterification.[32,37,55]

Here we studied the controlled anionic ring-opening polymerizations of CL and D,L-lactide (LA) in the presence of titanium complexes with dialkanolamine (**1**, **2**) and salen ligands (**3**) and in the presence of titanium alkoxide with two σ-ligands (**4**) that are the fragments of an unsaturated alcohol (*cis*-but-2-ene-1,4-diol). We chose the above initiators because they are preparatively avail-

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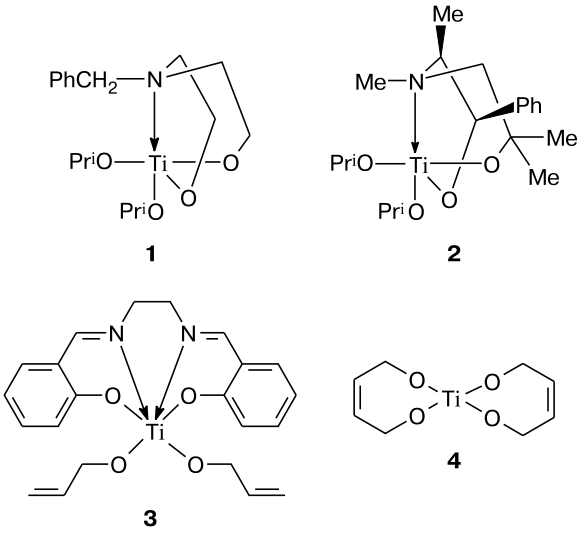
able, well soluble in organic solvents and monomers, stable at high temperatures,[58,59] and nontoxic. We also looked into the possibility of employing catalysts **3** and **4** for the synthesis of functionalized PE containing a reactive terminal and internal double bond, respectively, in the polymer chain. Such functionalized PE can be used to obtain more complex biodegradable macromolecular structures (block or graft copolymers).[60]

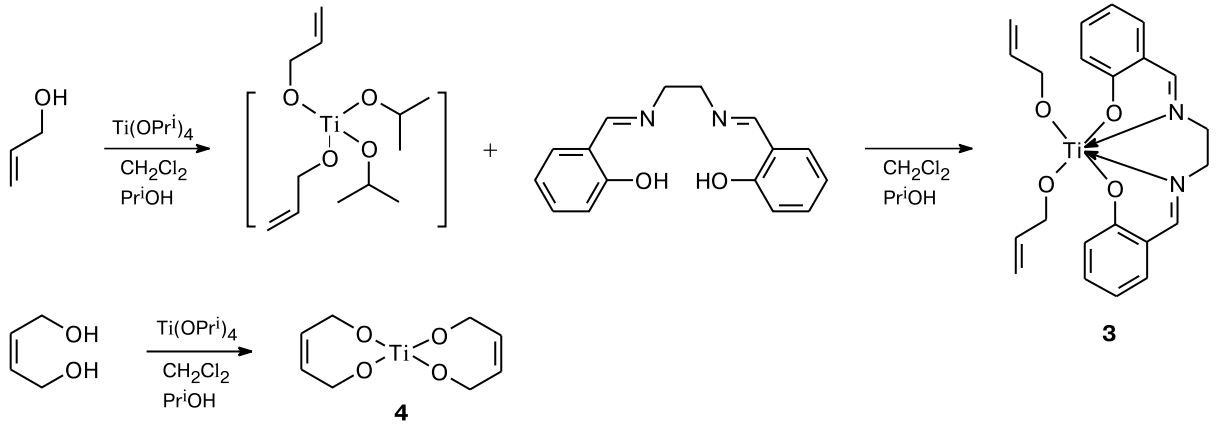


Results and Discussion

Synthesis of titanium complexes. Complexes **1**—**4** were prepared by transalkoxylation of $Ti(OPr^i)_4$ in the presence of appropriate alcohols (Scheme 1). Complexes **1** and **2** were synthesized as described earlier.[58,61] Complex **3** was obtained by a sequence of two reactions. The first reaction of $Ti(OPr^i)_4$ with allyl alcohol gave $(H_2C{=}CHCH_2O)_2$-$Ti(OPr^i)_2$, which was *in situ* involved in a reaction with a solution of the ligand $SalenH_2$ in CH_2Cl_2. This approach allows control of the reaction[62—64] and easier isolation of its products.[65] Structures **3** and **4** were determined by ^1H and ^{13}C NMR spectroscopy; their molecular formulas, by elemental analysis.

Polymerization of ε-caprolactone. The bulk polymerization of CL was studied in the presence of all the titanium complexes under discussion (**1**—**4**) at 80—130 °C and the [monomer] : [catalyst] ratio = 300 : 1. Note that complexes **1** and **2** showed low activity in stereospecific polymerization of styrene (<9% yields of the polymers for 4 h). The resulting polystyrenes are characterized by relatively high syndiotacticity (60—80%) and molecular weights (M_w > 100 000 g mol^{-1}).[59] It can be seen in Table 1 and Fig. 1 that complexes **1** and **2** containing the OPr^i groups at the Ti atom show high and virtually equal catalytic activity in the polymerization of CL: the complete conversion of the monomer (96—97%) is achieved in less than 1 and 1.5 h, respectively. Both the catalytic complexes initiate controlled polymerization of CL: the first-order plots are linear, all the straight lines passing through the origin (see Fig. 1, *a*). The experimental values of the number-average molecular weight (M_n) increase with the monomer conversion and agree well with the values calculated under the assumption that a catalyst molecule generates two polymer chains (see Fig. 1, *b*, Table 1, and Scheme 2). It should be noted that the MWD of the PE obtained in the presence of complex **2** containing bulky phenyl and methyl substituents in the ligand are narrower (M_w/M_n < 1.2 up to the 80% conversion of the monomer) than the MWD of the polymers synthesized with complex **1** as a catalyst. The insignificant broadening of the MWD to 1.5 in late polymerization steps can be attributed to intra- and intermolecular transesterifications as side reactions occurring under monomer-starved conditions. The number-average functionality (F_n) of the PE obtained in the presence of complex **2** is 98—100% (with respect to the calculated value); *i.e.*, all macromolecules contain isopropoxy head and hydroxy end groups. This provides evidence that the polymerization occurs by insertion of mono-

Scheme 1



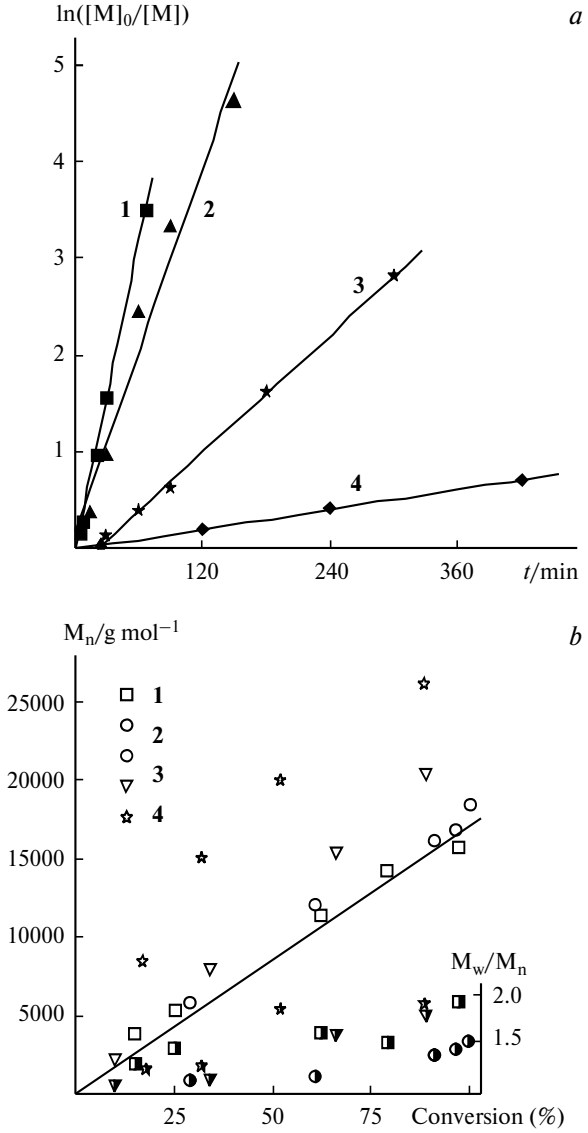


Fig. 1. Plots of $\ln([M]_0/[M])$ *vs.* the time (*a*) and the plots of M_n and M_w/M_n *vs.* the conversion of the monomer (*b*) for the bulk polymerization of CL in the presence of complexes **1**—**4** at 80 (**1**, **2**, **4**) and 130 °C (**3**); [CL] : [catalyst] = 300 : 1. The straight line in Fig. 1, *b* corresponds to the theoretically calculated molecular weight.

Table 1. Anionic ring-opening bulk polymerization of ε-caprolactone in the presence of the Ti^{IV} complexes[a]

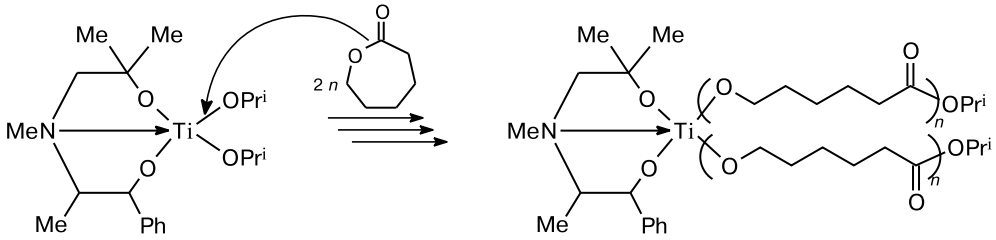
Catalyst	*T*/°C	*t*/h	Conversion (%)	M_n[b] (calc)	M_n[c] (GPC)	M_w/M_n	F_n[d] (%)
				/g mol^{-1}			
1	80	0.3	62	10650	11450	1.63	86
	80	1	97	16630	15800	1.94	81
2	80	0.5	61	10450	12150	1.18	100
	80	1.5	96	16450	16900	1.46	98
3	80	24	0	—	—	—	—
	130	1	32	5550	8150	1.15	44
	130	3	80	13750	20500	1.84	10
4	80	4	34	11650	15055	1.21	84
	80	24	88.5	30250	26100	1.87	93

[a] [CL] : [catalyst] = 300 : 1.
[b] $M_n(\text{calc}) = ([CL]/n[\text{catalyst}]) \cdot 114 \cdot (\text{conversion of the monomer})$, where n is the number of active Ti—O bonds in the complex.
[c] Determined by gel permeation chromatography using polystyrene standards and corrected for a factor of 0.52.[66]
[d] The number-average functionality calculated from the ^{1}H NMR spectra as a signal intensity ratio for the protons of the head and end groups, respectively.

mer molecules only into the Ti—OPr^i bonds of the complex (see Scheme 2). The effects of the temperature and the concentrations of complexes **1** and **2** on the polymerization as well as on the molecular weight characteristics of poly(CL) have been studied in detail earlier.[66]

A titanium complex containing the unsubstituted salen ligand and two fragments of an unsaturated alcohol (**3**) was also studied in ring-opening polymerization of CL. Note that complex **3** is virtually insoluble in the monomer at 80—100 °C, so no polymerization occurs under these conditions. When the reaction temperature was raised to 130 °C, a high monomer conversion (80%) was achieved in 3 h (see Table 1). Although the M_n values of the resulting PE increase linearly with the monomer conversion to M_n = 20 500 g mol^{-1}, the experimental M_n values are higher than the calculated ones, which can be explained by aggregation of the complex. The molecular weight distribution of the polyesters obtained remains narrow ($M_w/M_n \leq 1.2$) up to a monomer conversion of ~50% and

Scheme 2



then broadens to $M_w/M_n \leq 1.8$ (see Fig. 1, *b*). However, the number-average functionality of the PE obtained in the presence of complex **3** does not exceed 45%, which can be attributed to partial hydrolysis of the catalyst by residual amounts of water in the system or to side reactions of the allyl group at high polymerization temperatures.[38]

With complex **4** as an initiator, the resulting polyesters are characterized by increasing M_n values (up to 25 000 g mol^{-1}) with conversion, narrow MWD ($M_w/M_n \leq 1.4$), and high content of the double bonds in the polymer chain ($F_n \geq 85\%$; see Table 1, Fig. 1). However, as with the polymerization initiated by complex **3**, the experimental M_n values are higher than the theoretical ones, which can be explained by aggregation of the complex.

As shown in Fig. 1, the first-order plots are linear for all the catalysts under discussion, which suggests a constant concentration of active species throughout the polymerization. The polymerizations catalyzed by complexes **3** and **4** proceed more slowly than those catalyzed by complexes **1** and **2**; in addition, the former have an induction period of 15 to 60 min (see Fig. 1). Based on the results obtained, we chose complex **2** as the most active catalyst in the polymerization of CL for detailed investigations of the polymerization of D,L-lactide and its copolymerization with CL.

A typical ^{1}H NMR spectrum of poly(CL) obtained in the presence of complex **2** at 80 °C is shown in Fig. 2. The ^{1}H NMR spectrum features well-resolved signals for the methylene protons present in the main chain: —CH_2CO— (δ 2.3, C(5)); —CH_2O— (δ 4.0, C(1)); —CH_2— (δ 1.4, C(3); δ 1.6, C(2+4)). In addition, the spectrum contains signals for the hydroxymethylene end group (δ 3.64, C(8), —C$\underline{H}_2$OH) and the isopropoxy head group (δ 1.22, C(7), Me; δ 4.99, C(6), —CHO—).

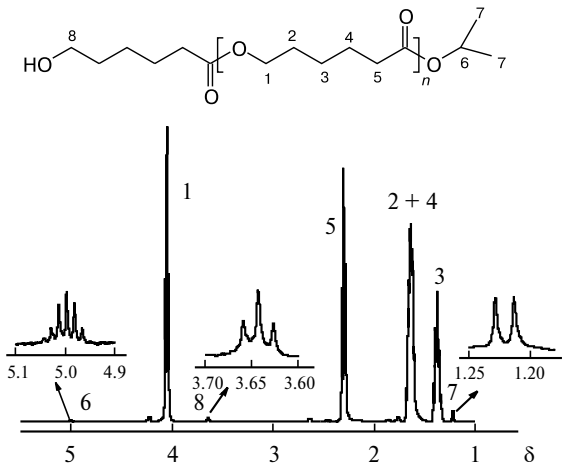


Fig. 2. ^{1}H NMR spectrum of the poly(CL) obtained in the presence of complex **2** at 80 °C; [CL] : [**2**] = 300 : 1.

Polymerization of D,L-lactide. Ring-opening bulk polymerization of LA in the presence of complex **2** (as the most active catalyst for the polymerization of CL) was carried out at 130 °C. The polymerization rate is high: the complete conversion of the monomer is achieved in less than 1.5 h (Fig. 3, *a*). The induction period is absent; the monomer consumption in a first-order reaction coordinates increases linearly with time, which suggests that the polymerization proceeds in a controlled fashion. The M_n values (coming up to 21 000 g mol^{-1}) of the resulting poly(LA) plotted versus the monomer conversion fall on a straight line and agree well with the M_n values calculated under the assumption that a catalyst molecule generates two polymer chains (Fig. 3, *b*). The molecular weight distribution is quite narrow (~1.3) up to a monomer conversion of ~80%.

It can be seen in Fig. 4 that the gel permeation chromatograms are shifted to the higher molecular weights region with increasing monomer conversion, which sug-

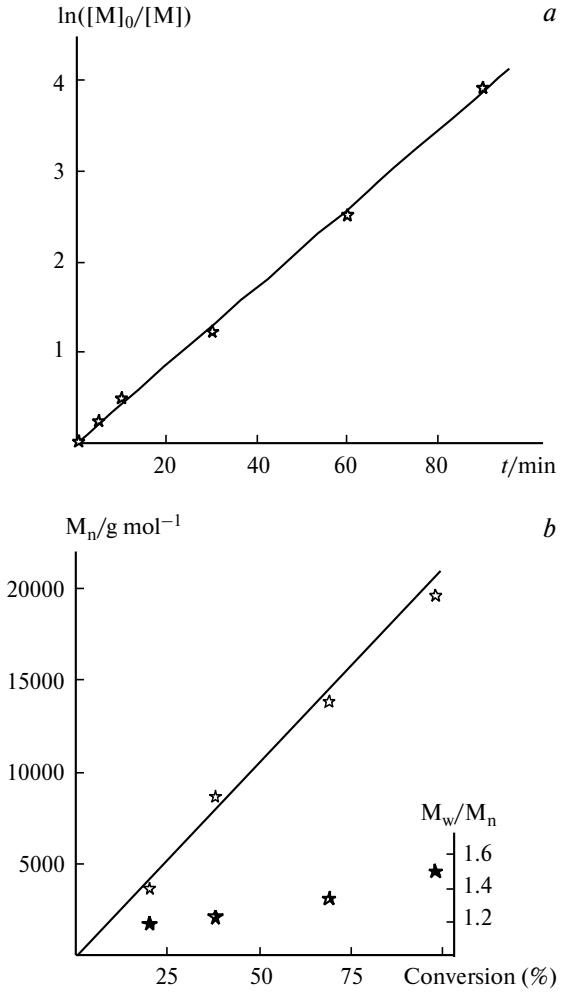


Fig. 3. Plot of $\ln([M]_0/[M])$ *vs.* the time (*a*) and the plots of M_n and M_w/M_n *vs.* the conversion of the monomer (*b*) in the polymerization of D,L-lactide at 130 °C; [LA] : [**2**] = 300 : 1. The straight line in Fig. 3, *b* corresponds to the calculated M_n value.

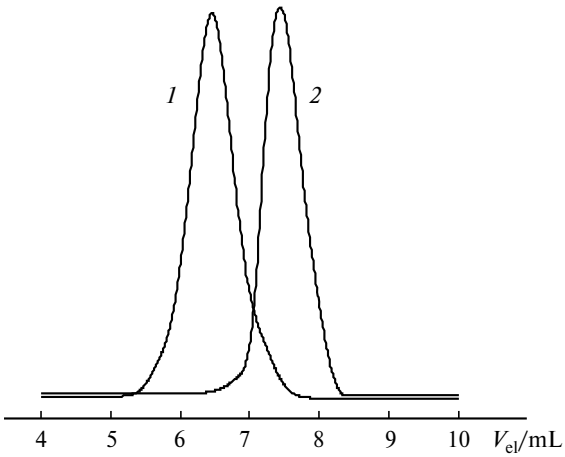


Fig. 4. Gel permeation chromatograms of the poly(LA) obtained by the polymerization of D,L-lactide in the presence of catalyst **2** at 130 °C; [LA] : [**2**] = 300 : 1. Peak *1* refers to the 98% conversion; M_n = 21 600 g mol^{-1}, M_w/M_n = 1.5. Peak *2* refers to the 20% conversion; M_n = 3600 g mol^{-1}, M_w/M_n = 1.19.

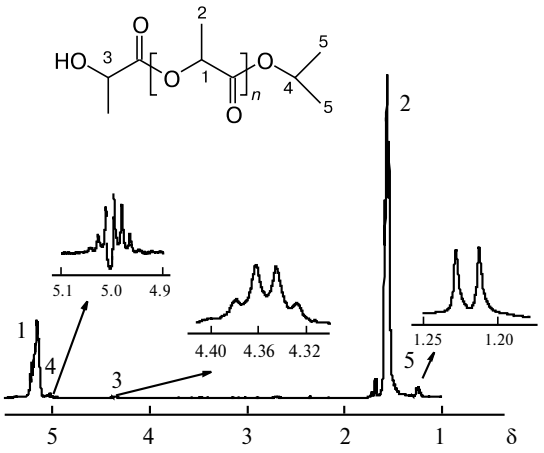


Fig. 5. ^{1}H NMR spectrum of the poly(LA) obtained in the presence of complex **2** at 130 °C; [LA] : [**2**] = 300 : 1.

gests the absence of side processes. Along with the MWD data, this provides additional evidence for the controlled polymerization of D,L-lactide in the presence of complex **2** at 130 °C.

The ^{1}H NMR spectrum of poly(LA) obtained with complex **2** as a catalyst shows well-resolved signals for the methine (δ 5.14—5.2, C(1), MeC<u>H</u>O—) and methyl protons (δ 1.5, C(2)) of the main chain and weaker signals for the hydroxymethine end group (δ 4.35, C(3), —C<u>H</u>(Me)OH) and the isopropoxy head group (δ 1.22, C(5), Me; δ 5.0, C(4), (Me)C<u>H</u>O—) (Fig. 5). The spectrum contains no other signals.

The ^{1}H NMR spectra suggest that the polymerization of LA follows the coordination-insertion mechanism involving the insertion of monomer molecules only into Ti—OPr^i bonds, while the Ti—O bonds of the ligand remain inert.

Synthesis of copolymers of ε-caprolactone with D,L-lactide. Since complex **2** proved to be an effective initiator of the controlled bulk polymerization of both CL and LA, we found it interesting to study its activity in the synthesis of biodegradable copolymers. As shown in Table 2, the synthesis of random copolymers proceeds much more slowly (the conversions of CL and LA in 24 h are 63 and 91%, respectively) than the homopolymerization of either monomer (the complete conversion takes less than 1 h for CL and about 10 h for LA; see Fig. 1, *a* and Fig. 3, *a*), in agreement with known data.[17,33,67] Interestingly, the copolymer is enriched in the "less reactive" monomer (D,L-lactide), especially in early polymerization steps. The M_n values of the resulting copolymers increase to 33 600 g mol^{-1} with an increase in the conversions of the monomers, though the MWD somewhat broadens (M_w/M_n ~1.9) (see Table 2). Despite the relatively wide MWD, the data obtained suggest that the copolymerization of CL with LA in the presence of catalyst **2** proceeds in a living fashion similarly to the homopolymerization of either monomer.

We estimated the catalytic efficiency of complex **2** in the synthesis of block copolymers of CL and LA. As can be seen in Table 2, a block copolymer is formed at a substantially higher rate than a random copolymer: the high conversions of the monomers are achieved in ~3 h. The polymerization of the second monomer (LA) added to the PE

Table 2. Bulk copolymerization of ε-caprolactone with D,L-lactide in the presence of complex **2** at 130 °C[a]

Polymer	*t*/h	Conversion of CL/LA[b] (%)	CL/LA[b]	M_n[c] (GPC)	M_w/M_n[c]
Random copolymer	6.5	16/39	29/71	13700	1.47
	10	29/41	51/49	22500	1.65
	24	63/91	41/59	33600	1.88
Block copolymer	0.5	100/0	—	23800	1.28
	3	100/78	58/42	37900	1.54

[a] [CL+LA] : [**2**] = 600 : 1, [CL] : [LA] = 1 : 1.
[b] The conversion of the monomer and the content of the CL and LA units in the copolymer, calculated from the ^{1}H NMR spectra.
[c] Determined by gel permeation chromatography using polystyrene standards.

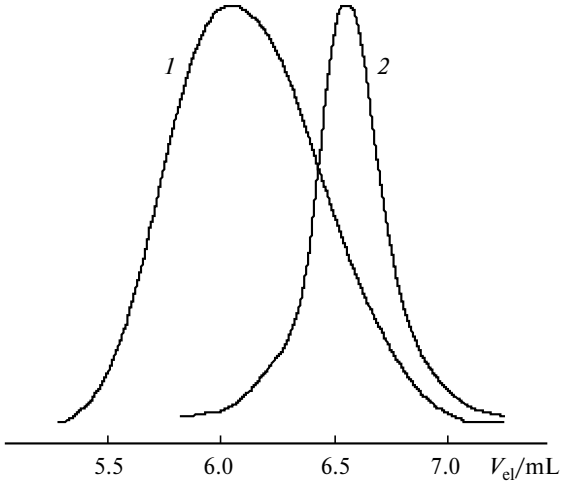


Fig. 6. Gel permeation chromatograms of the poly(CL)—*block*-poly(LA) (*1*) and poly(CL) (*2*) obtained in the presence of catalyst **2** at 130 °C; [CL] : [**2**] = [LA] : [**2**] = 300 : 1. Peak *1* refers to the 78% conversion; M_n = 37 900 g mol^{-1}, M_w/M_n = 1.54. Peak *2* refers to the 100% conversion; M_n = 23 800 g mol^{-1}, M_w/M_n = 1.28.

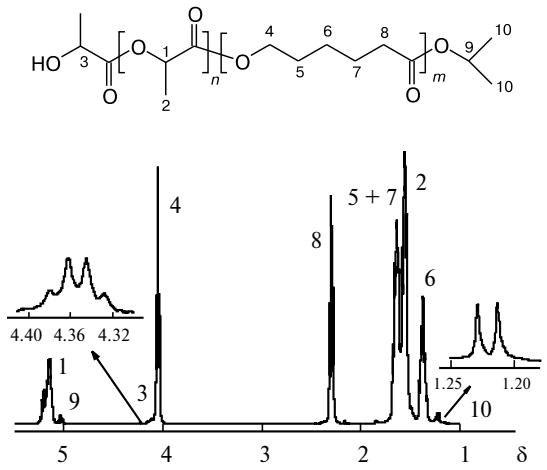


Fig. 7. ^{1}H NMR spectrum of the poly(CL)—*block*-poly(LA) obtained in the presence of complex **2** at 130 °C; [CL+LA] : [**2**] = = 600 : 1, [CL] : [LA] = 1 : 1.

produced by the polymerization of the first monomer (CL) doubles the molecular weight (up to M_n = 38 000 g mol^{-1}): the gel permeation chromatogram is shifted to the higher molecular weights, and the MWD broadens only slightly (from M_w/M_n = 1.28 to M_w/M_n = 1.54) (Fig. 6). This provides evidence for the formation of the block copolymer poly(CL)—*block*-poly(LA) in the presence of complex **2**.

The data presented above suggest the high catalytic efficiency of complex **2** in the synthesis of biodegradable block copolymers. Like random polymerization, the block copolymerization proceeds in a living fashion; this allows one to easily change the length of each block in the copolymer and, accordingly, regulate the properties of materials on their basis.

A typical ^{1}H NMR spectrum of the block copolymer poly(CL)—*block*-poly(LA) is shown in Fig. 7. The spectrum contains well-resolved signals for the methylene protons in the main chain of the poly(ε-caprolactone) block (δ 2.3, C(8), —CH_2CO—; δ 4.0, C(4), —CH_2O—; δ 1.4, C(6); δ 1.6 C(5+7), —CH_2—) and signals for the methine and methyl protons of the poly(D,L-lactide) block (δ 5.14—5.2, C(1), —(Me)C<u>H</u>O—; δ 1.5, C(2), Me). The spectrum also exhibits signals for the methine protons of the hydroxymethine end group (δ 4.36, C(3), —C<u>H</u>(Me)OH) and those for the methine and methyl protons of the isopropoxy head group (δ 1.22, C(10), Me; δ 5.0, C(9), Me_2C<u>H</u>O—). Note that the spectrum does not contain the characteristic signal at δ 3.6—3.7 for the hydroxymethylene end group of poly(CL), which also confirms the formation of the block copolymer poly(CL)—*block*-poly(LA).

To summarize, titanium complexes **1** and **2** with dialkanolamine ligands are more active in the polymerization of ε-caprolactone than complexes **3** and **4**, while the latter allow the synthesis of polyesters containing both internal and terminal double bonds in the polymer chain. Such functionalized polymers can subsequently be used for the assembly of more complex biodegradable macromolecular structures. Complex **2** initiates the controlled ring-opening bulk polymerization of D,L-lactide at 130 °C and is effective in the synthesis of random (M_n = = 34 000 g mol^{-1}; M_w/M_n ~1.9) and block copolymers (M_n = 36 000 g mol^{-1}; M_w/M_n ~1.5) from ε-caprolactone and D,L-lactide. The formation of random and block copolymers proceeds in a living fashion, which allows one to easily change the length of each block and regulate the properties of copolymers.

Experimental

All manipulations dealing with the preparation of compounds to the synthesis, as well as homo- and copolymerizations, were carried out in dry glassware evacuated three times and filled with argon. The starting materials were purified according to common procedures and recommendations. Toluene (reagent grade) was treated with conc. H_2SO_4, washed with aqueous $NaHCO_3$ (or NaOH) and distilled water to a neutral reaction, dried with $CaCl_2$, refluxed, and distilled with metallic sodium. Then it was refluxed with Na/benzophenone to a blue color and distilled into a Schlenk reactor. The NMR solvent (99.8% $CDCl_3$, Ruth) was distilled with CaH_2 prior to use. ε-Caprolactone (97%, Aldrich) was dried with CaH_2 and distilled *in vacuo*. D,L-Lactide (98%, Aldrich) was twice recrystallized from toluene and dried *in vacuo* at 45—50 °C for 5 h. Dichloromethane was refluxed and distilled with CaH_2. *cis*-But-2-ene-1,4-diol (Aldrich) and allyl alcohol (Aldrich) were purified by distillation *in vacuo*. The ligand $SalenH_2$ was prepared according to a known procedure.[68]

The number-average (M_n) and weight-average (M_w) molecular weights and the polydispersity of the (co)polymers obtained were determined by gel permeation chromatography on an

Agilent 1200 instrument equipped with a Nucleogel GPC LM-5, 300/7.7 column and two detectors (a differential refractometer and a diode matrix detector). Tetrahydrofuran was used as a solvent (elution rate 1 mL min^{-1}, 30 °C). The M_n and M_w/M_n values of the polymers were calculated using polystyrene standards with $M_w/M_n \leq 1.05$ (Polymer Labs, Germany). ^1H NMR spectra of solutions of polymers in $CDCl_3$ (C ~0.015 g mL^{-1}) were recorded on a Bruker AC-400 instrument (400 MHz) at 25 °C. ^1H and ^{13}C NMR spectra of titanium complexes were recorded on a Bruker Avance-400 spectrometer (400.130 and 100.613 MHz, respectively) at ~20 °C. Deuterated chloroform was used as both a solvent and an internal standard (owing to its residual protons); chemical shifts δ are referenced to Me_4Si. Elemental analysis was carried out on a Heraeus Vario Elementar microanalyzer.

Synthesis of titanium complexes. Complexes **1** (see Ref. 58) and **2** (see Ref. 62) were prepared as described earlier.

Complex 3. Freshly distilled allyl alcohol (0.16 mL, 2.27 mmol) was added at ~20 °C to a solution of $Ti(OPr^i)_4$ (0.33 mL, 1.13 mmol) in CH_2Cl_2 (20 mL). The reaction mixture was stirred for 6 h, whereupon a solution of $SalenH_2$ (0.31 g, 1.13 mmol) in CH_2Cl_2 (20 mL) was added. After 16 h, volatile components were removed *in vacuo*. The residue was washed with diethyl ether and dried to give a yellowish powder of complex **3** (0.37 g, 77%). ^1H NMR ($CDCl_3$), δ: 8.34 (s, 2 H, NCH=); 7.47—7.35 (m, 4 H, Arom); 6.95—6.86 (m, 2 H, Arom); 6.84—6.76 (m, 2 H, Arom); 5.64—5.55 (m, 2 H, 2 CH=); 4.78—4.67 (m, 4 H, 2 CH_2=); 4.28—4.32 (m, 4 H, 2 OCH_2); 3.95 (br.s, 4 H, NCH_2). ^{13}C NMR ($CDCl_3$), δ: 162.74 (NCH=); 139.33 (=CH); 165.11, 135.58, 133.62, 122.24, 118.64, 117.76 (Arom); 112.23 (=CH_2); 73.47 (OCH_2); 58.61 (NCH_2). Found (%): C, 61.46; H, 5.48; N, 6.62. $C_{22}H_{24}N_2O_4Ti$. Calculated (%): C, 61.69; H, 5.65; N, 6.54.

Complex 4. Titanium tetraisopropoxide (5.40 mL, 18.05 mmol) was added at ~20 °C to a solution of *cis*-$HOCH_2CH$=$CHCH_2OH$ (2.97 mL, 36.10 mmol) in CH_2Cl_2 (50 mL). The reaction mixture was stirred for 16 h and concentrated *in vacuo*. The residue was washed with toluene and dried to give a white powder of complex **4** (3.41 g, 86 %). ^1H NMR ($CDCl_3$), δ: 5.78 (br.s, 4 H, 4 CH=); 5.01—4.84 (m, 8 H, CH_2). ^{13}C NMR ($CDCl_3$), δ: 133.34 (br.s, CH=); 67.57 (br.s, CH_2). Found (%): C, 43.16; H, 5.08. $C_8H_{12}O_4Ti$. Calculated (%): C, 43.67; H, 5.50.

Polymerization. Bulk (co)polymerizations of CL and LA were carried out in Schlenk reactors equipped with magnetic stirring bars. Prior to polymerization, the reactors were evacuated and filled with argon. For kinetic studies of the polymerization, the reaction mixtures were regularly sampled throughout the reaction. The samples were promptly cooled to ~20 °C to stop the polymerization. The conversion of the monomer was determined from ^1H NMR spectra.

Polymerization of CL (general procedure). A reactor was charged with a 0.1 *M* solution of the catalyst in toluene (1.57 mL, $1.57 \cdot 10^{-4}$ mol). The solvent was removed *in vacuo* at ~20 °C for 5 min, whereupon CL (5 mL, 0.047 mol) was added. The reactor was heated on an oil bath at 80 or 130 °C.

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