Available online at www.sciencedirect.com
ScienceDirect
Polymer 48 (2007) 2263–2279
polymer
www.elsevier.com/locate/polymer

Mechanism of ε-caprolactone polymerization and ε-caprolactone/trimethylene carbonate copolymerization carried out with $Zr(Acac)_4$

Piotr Dobrzynski*

Centre of Polymer and Carbon Materials, Polish Academy of Sciences, 34, Curie-Sklodowska Street, 41-800 Zabrze, Poland

Received 18 October 2006; received in revised form 8 January 2007; accepted 2 February 2007
Available online 7 February 2007

Abstract

The paper presents the mechanism of the polymerization of ε-caprolactone with the use of $Zr(Acac)_4$. At the first stage of the initiation of the polymerization, a reaction consisting of proton transfer from caprolactone to acetylacetonate ligand and then ligand exchange reaction with release of free acetylacetone (HAcac) occur. Complex **1**, arisen as a product of this reaction, is the actual initiator of the observed polymerization. During the conducted polymerization the molar mass increase is directly proportional to monomer conversion degree. On the basis of observed phenomenon, the polymerization of cyclic trimethylene carbonate (TMC) applying ε-caprolactone as a co-initiator is possible. Complex **1** arose in the initial phase of this reaction as well, being an equally efficient initiator for TMC polymerization. Using $Zr(Acac)_4$ as an initiator for an ε-caprolactone/TMC copolymerization resulted in obtaining a series of copolymers with varied, predicted composition and high molar mass values.

Keywords: ε-Caprolactone; Trimethylene carbonate; Zirconium

1. Introduction

Poly-ε-caprolactone and its copolymers with high-molecular weight are very promising bioresorbable materials for biomedical application. The most convenient method for obtaining these polyesters with proper molecular mass and purity grade seems to be ring opening polymerization (ROP) of cyclic ε-caprolactone or their copolymerization with other lactones or lactides [1–4]. According to the used kind of initiator, the polymerization proceeds by different major reaction mechanisms: anionic [5,6], cationic [7,8] and the coordination-insertion ROP mechanisms [9–11]. The choice of proper initiator for the polymerization reactions is an important issue. Usually the typical polymerization of lactides and lactones is carried out in the presence of tin compounds such stannous octoate, aluminum and transition metal halides, alkoxides or organo-complexes [12]. Unfortunately, because of the known toxicity of tin, aluminum and heavy metals compounds [13,14] and the fact that it is practically impossible to totally eliminate them from the synthesized material [15] the obtained polyesters are not often completely biocompatible.

Biomedical application of ε-caprolactone homopolymer is much restricted by the long time of degradation but caprolactone copolymers are most interesting for distinctive degradation properties [16]. Special attention for many applications has been paid to copolymers containing carbonate groups because of their features: flexibility and reduced acidity of hydrodegradation products. These special materials with high flexibility can be obtained as a result of ε-caprolactone copolymerization with cyclic carbonates, generally with trimethylene carbonate [17–19].

Zirconium(IV) acetylacetonate, relatively inexpensive, alkane- and arene-soluble, water free compound, is a very useful initiator of lactide polymerization and copolymerization [20], lactides with lactone copolymerization reactions [21–23], or lactides with cyclic carbonates [24,25]. The obtained on

* Fax: +48 32 2712969.
E-mail address: piotrdb@cchp-pan.zabrze.pl

0032-3861/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2007.02.005

this way bioresorbable materials, may be found useful in controlled drug-releasing processes [26] forming scaffolds for tissue cultures [27] or biodegradable implants for surgical use [28]. Employing this initiator and properly exploiting its ability to generate strong intermolecular transesterification, it is possible to obtain copolymers with any desired composition and pre-planned chain microstructure in one-pot-type reactions. Other zirconium(IV) compounds such as zirconium(IV) *n*-propoxide [9] and zirconocene [29] have also been successfully used in polymerization processes of this type. An essential property of a majority of zirconium compounds, such as $Zr(Acac)_4$, is its relatively low toxicity. They are generally inert in human metabolic processes and are eliminated from the body with bile or through urinary tract [13,14]. Their low biological toxicity has been confirmed by the prolonged survival of selected cell cultures carried out on lactide/glycolide copolymers obtained with zirconium(IV) acetylacetonate in comparison with a culture on an identical material synthesized with most popular initiator in this type of reactions – $Sn(Oct.)_2$ [30]. Other acetylacetonates such as aluminum [31], zinc [32], iron [33] and tin acetylacetonates [34] can be successfully applied to lactide polymerization and copolymerization with ε-caprolactone as well. So far, the mechanism of the initiation reaction using these compounds in polymerization processes practically has not been investigated, unlike the mechanism of the initiation reaction with alkoxides and tin octoate [35]. As for acetylacetonates, only mechanism of lactide and glycolide polymerization carried out with $Zr(Acac)_4$ has been previously described in detail [36,24]. In the reaction between $Zr(Acac)_4$ and the monomer molecules, lactide deprotonation, proton transfer to acetylacetonate ligand, change of ligands and the release of free acetylacetone occurred. The obtained on this route complexes are the actual initiator in the next lactide polymerization stage. Polylactide chain growth proceeded by an insertion–coordination mechanism. The polymer chain grew on one ligand, which was formed in advance from a deprotonated lactide.

The $Zr(Acac)_4$ ligand's quite liability in proton-transfer reactions was well-know previously, for example in the ligand exchange reaction with free acetylacetone (HAcac) [37], catechols [38] or some phenols [39]. The tetrakis (β-dikenato) complexes, like as $Zr(Acac)_4$, are coordinatively saturated and do not contain any chloride or alkoxy ligands, yet they are catalytically active in many polymerization reactions. Therefore, it must be assumed that, during reaction, the chelate ligands can be replaced by other groups, for example by methyl groups from methylalumoxane (MAO) in olefin polymerization to give an active species with an opening in the coordination sphere for the monomer [40].

Our group has previously conducted processes of polymerization and copolymerization of cyclic compounds initiated with $Zr(Acac)_4$, in which one of the monomers present in the initial mixture was always either lactide or glycolide – a compound relatively easily creating enol forms [41,42], thus able to initiate deprotonation processes. At the initial stage of a conducted copolymerization, one of these comonomers reacted with the initiator, which resulted in arising of an active zirconium complex, the actual initiator for the polymerization, containing a ligand originating from the deprotonated lactide and/or glycolide. A high-molecular polymer could not be obtained this way in processes where no relatively easily deprotonable compound was present, like during TMC copolymerization process conducted at 110 °C [43]. There again, during ε-caprolactone homopolymerization conducted in the same conditions, initiated with $Zr(Acac)_4$, polycaprolactone with high molar mass was obtained, with efficiency up to 100% [21]. Like lactides, most lactones, including ε-caprolactone are characterized with aciditie properties and easily create enolate anions [44]. Taking this fact into account one can presume that the mechanism of initiating the caprolactone polymerization with the use $Zr(Acac)_4$ should proceed analogously to the process of initiating the lactide polymerization reactions with this compound. It is equally important to note that a similar mechanism of a polymerization reaction of ε-caprolactone initiated with rare earth phenyl compounds through a coordination–deprotonation–insertion process, by which the monomer inserts on the metal-O bond of rare earth enolate have been also proposed by other authors [45,46].

The investigation of the mechanism of initiating the ε-caprolactone polymerization with the use of $Zr(Acac)_4$, as well as of possibilities of obtaining TMC/caprolactone copolymers using this initiator has become a major task of the present paper.

2. Experimental section

2.1. Monomers, initiator and solvents

ε-Caprolactone (Fluka) was dried with calcium hydride and distilled under argon before use. Monomer 1,3-trimethylene carbonate (TMC) has been obtained from Boehringer Ingelheim, and used after recrystallizations from dried ethyl acetate. The complex zirconium(IV) acetylacetonates (Aldrich) were recrystallized from dry benzene–acetylacetone mixture and the obtained crystals were washed with cold benzene and dried in vacuum. Anhydrous benzene (Fluka) was dried over CaH_2 before distillation.

2.2. Model ε-caprolactone and TMC polymerization in solution

The solution oligomerization and polymerization were carried out under argon in an exhaustively argon-purged, sealed glass Erlenmayer flask (100 mL), equipped with a magnetic stirrer, as a reaction vessel. ε-Caprolactone or trimethylene carbonate (50 mmol) was weighed into the reaction vessel, and then 50 mL of a dry benzene solution of zirconium(IV) acetylacetonate (1 mmol) was added. The reaction vessel was closed with a glass stopper and immersed in a thermostatically controlled oil bath at 80 °C. In the case of TMC polymerization with ε-caprolactone used as a co-initiator, the reaction process has been slightly altered. At the initial stage of the reaction, $Zr(Acac)_4$ and ε-caprolactone benzene solution

(molar ratio of 1:4) have been blended for 30 min and only then the actual monomer (TMC) has been added to the mixture (TMC/$Zr(Acac)_4$, molar ratio 50:1).

In the kinetic investigations, several samples were taken out via syringe at various times and have been quickly quenched to room temperature. The conversion of monomer and oligomer composition was examined with ^{1}H NMR spectroscopy based on the obtained samples, only after concentrating by evaporation at room temperature under argon. The samples assigned to gel permeation chromatography analysis were treated with acetic acid to extract the initiator. The obtained mixtures were washed with cold water, and the organic phases, including the polymer, were separated and concentrated by evaporation in vacuum.

2.3. TMC/ε-caprolactone copolymerization procedure

The copolymerizations have been conducted in the bulk. In argon atmosphere, TMC and ε-caprolactone monomers with the initiator have been charged into dried glass ampoules which have been then sealed. The ampoules have been conditioned in an oil bath equipped with a periodically working shaker at 110 °C. After the selected reaction time the ampoules have been quickly quenched to room temperature and the obtained polymers have been discharged.

2.4. NMR measurement, determination of composition and microstructure of compounds

The ^{1}H NMR spectra of the complexes, oligomers and polymers were recorded at 300 MHz with a Varian Unity Inowa spectrometer and 5-mm sample tube. Benzene-d_6 or deutered chloroform $CDCl_3$ was used as a solvent, and tetramethylsilane was used as an internal standard. The spectra were obtained at 25 °C, with 32 scans, 3.74 s acquisition time, and a 7 μs pulse width.

The ^{13}C NMR spectra of the obtained compounds and polymers were recorded at 75 MHz with 25,000–30,000 scans, 1.8 s acquisition time, a 7 μs pulse width, and a delay of 4.7 s between pulses.

The ratio of polymerization conversion was determined with ^{1}H NMR spectroscopy. In many cases the assignation of signals in the obtained spectra was conducted, with the aid of HyperNMR 7.0 program included in HyperChem 7.5 software package [47]. The method of simulation and iteration has been used in distribution of the complex spectra on separate signals and calculation of their intensity, by means of the VNMR program included in Varian software package.

The average length of the caproyl and carbonate blocks of ε-caprolactone/trimethylene carbonate (TMC) copolymers was calculated based on the ^{13}C NMR observations according to the method described by Pego et al. [48]. I also determined the randomization ratio of copolymer chains with the following Eq. (1), where degree of randomness of copolymer chains:

$$R = {}^{R}l_{\mathrm{Cap}}/{}^{e}l_{\mathrm{Cap}} = {}^{R}l_{\mathrm{T}}/{}^{e}l_{\mathrm{T}} \tag{1}$$

and ${}^{R}l_{\mathrm{Cap}}$ and ${}^{R}l_{\mathrm{T}}$ are the average lengths of caproyl and TMC blocks, respectively, in chains with completely random contributions of caproyl and carbonate units. They may be estimated with following expressions (2) and (3):

$${}^{R}l_{\mathrm{Cap}} = \left(F_{\mathrm{Cap}}/F_{\mathrm{T}}\right) + 1 \tag{2}$$

and

$${}^{R}l_{\mathrm{T}} = \left(F_{\mathrm{T}}/F_{\mathrm{Cap}}\right) + 1; \tag{3}$$

where F_{Cap}, F_{T} – feed molar fraction of ε-caprolactone or TMC, respectively, and ${}^{e}l_{\mathrm{Cap}}$, ${}^{e}l_{\mathrm{T}}$ are the average length of the caproyl or carbonate microblocks, respectively, calculated with NMR.

In the case when we have the reactivity ratios of copolymerization reaction r_{cap} and r_{TMC} denoted, it is also possible to estimate the number average length of the caproyl l^{r}_{Cap} blocks calculated from Eq. (4) [43]

$$\left(l^{r}_{\mathrm{Cap}}\right)^{2}\frac{1-f_{\mathrm{Cap}}}{f_{\mathrm{Cap}}} - l^{r}_{\mathrm{Cap}}\frac{1}{f_{\mathrm{Cap}}} = r_{\mathrm{Cap}}r_{\mathrm{TMC}} \tag{4}$$

The number average length of the carbonate blocks was calculated from the analogical equation (5) [49].

$$\left(l^{r}_{\mathrm{T}}\right)^{2}\frac{1-f_{\mathrm{T}}}{f_{\mathrm{T}}} - l^{r}_{\mathrm{T}}\frac{1}{f_{\mathrm{T}}} = r_{\mathrm{Cap}}r_{\mathrm{TMC}} \tag{5}$$

where f_{Cap} – feed mole fraction of lactidyl units; f_{T} – feed mole fraction of carbonate units; r_{Cap}, r_{TMC} – ε-caprolactone, TMC reactivity ratio.

2.5. Determination of molecular mass (M_n) and molecular mass distribution (M_w/M_n)

Molecular mass and molecular mass distribution were determined by using a gel permeation chromatography with the Physics SP 8800 apparatus (THF was used as the eluent; the flow rate was 1 mL/min; Styragel columns MIXED-E and Shodex se-61 detector were used) at 25 °C and calibrated by using polystyrene standards. Previous studies proved that polystyrene calibration overestimates the average molecular masses, M_{n}, of many aliphatic polyesters. Thus we corrected them for the poly(ε-caprolactone), re-calculating, based on GPC measurements and universal calibration curve that were set up with viscosimetric relationships for polystyrene (Eq. (6)) [50] and poly(ε-caprolactone) – (Eq. (7)) [51] or for poly(TMC), based on relationships for polystyrene (Eq. (6)) [50] and poly(TMC) – (Eq. (8)) [52].

$$[\eta] = 1.25 \times 10^{-4}\,\mathrm{M}^{0.717} \tag{6}$$

$$[\eta] = 1.09 \times 10^{-3}\,\mathrm{M}^{0.60} \tag{7}$$

$$[\eta] = 2.77 \times 10^{-4}\,\mathrm{M}^{0.677} \tag{8}$$

In the case of measuring poly(ε-caprolactone-*co*-TMC) molecular masses, *I* presents only the results based on

calibration with polystyrene standards due the lack appropriate data.

2.6. Computational methods

Molecular modeling was performed generally with the HyperChem 7.5 program package [47] and ArgusLab 4.01 program [53] run on a personal computer with Widows 98 operation system. The optimization of the complex geometry was calculated with semi empirical PM3(tm) method, which proved useful to reproduce experimental geometries of stable, closed-shell zirconium complexes [54]. Another reason for which this method had been selected is because preliminary geometry calculations of $Zr(Acac)_4$ carried out with popular methods for organometallic compounds – ZINDO/1 and PM3(tm) – proved that the PM3(tm) was more accurate, compared to the data [55] obtained with three-dimensional X-ray measurement (see Table 1, Fig. 1). All energies were minimized to RMS gradient less than 0.1 kJ/Å mol applying the Polak–Ribiere minimization algorithm. Each of these starting geometries was preoptimized by molecular mechanics (MM+). To investigate the stability and simulate the dynamic behavior of the complexes Molecular Dynamics functions were used too (starting temperature 250 K, simulation temperature 350 K, heat time – 3 ps, temperature step 1 K).

2.7. Calculation of copolymerization parameters

Copolymerization parameters were obtained by using the integrated form of the Skeist's copolymerization equation [56] Eq. (9)

$$\frac{M}{M_0} = \left(\frac{f}{f_0}\right)^{\alpha}\left(\frac{1-f}{1-f_0}\right)^{\beta}\left(\frac{f_0-\delta}{f-\delta}\right)^{\gamma} \tag{9}$$

where the constants α, β, γ and δ values are, respectively:

$$\alpha = \frac{r_{TMC}}{1-r_{TMC}};\ \beta = \frac{r_{Cap}}{1-r_{Cap}};\ \gamma = \frac{1-r_{Cap}r_{TMC}}{(1-r_{Cap})(1-r_{TMC})};\ \text{and}$$

$$\delta = \frac{1-r_{TMC}}{2-r_{Cap}-r_{TMC}};$$

$1-M/M_0$ refers to copolymerization conversion, f to ε-caprolactone fraction, f_0 to the initial caprolactone fraction and r_{Cap}, r_{TMC} to the reactivity ratios. Eq. (9) relates the overall monomer conversion to the fraction of ε-caprolactone monomer in the mixture according to the ultimate copolymerization model. The use of this equation for estimating reactivity ratios r_{Cap} and r_{TMC} is not only restricted to low conversion while determining the copolymerization parameters [57]. For calculations, the method of Least Squares model was used, which is able to predict reactivity ratios using monomer conversion and monomer fraction – data obtained with NMR spectroscopy. The usefulness of this method was previously confirmed by Van den Brink et al. [58].

Table 1
Averaged bond distances (Å) for the acetylacetonate rings in $Zr(Acac)_4$ molecules

Bound type	X-ray data	PM3(tm) data[a]	ZINDO/1 data[a]
Zr–O	2.20	2.24	2.43
O–C	1.27	1.28	1.32
C–CH_3	1.52	1.51	1.51
C–CH	1.40	1.40	1.40

[a] Results obtained with the HyperChem 7.5 package.

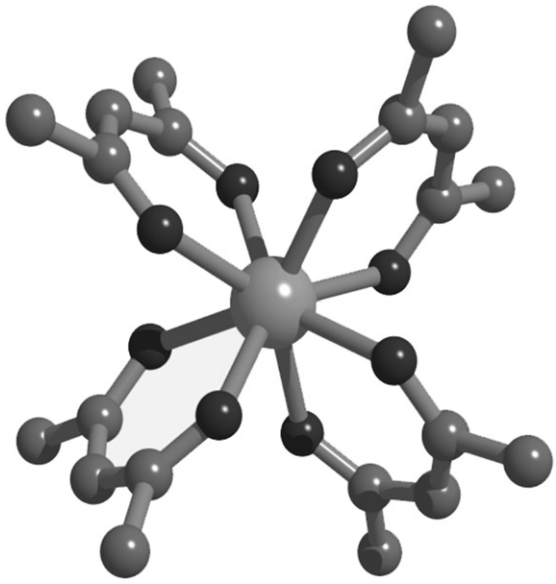


Fig. 1. Optimized geometries of complex [$Zr(Acac)_4$] performed with the HyperChem 7.5 package (semiempirical PM3(tm) method).

The appropriate calculations have been performed by means of KyPlot 2.0 program by Yoshioka [59] with PC computer (OS – Windows 98). During the process of obtained experiment data fitting into the function (9) nonlinear regression method was applied with the use of Least Squares optimization method. The used optimization parameters had the following values: sample point calculation step was automatic, convergence tolerance $= 10^{-5}$, ΔX for derivatives $= 10^{-6}$. The accuracy of the performed optimization was characterized by the following parameters: Var (Error) = 0.001, Coefficient of Determination = 0.987, Multiple Correlation Coefficient = 0.994.

3. Results and discussion

3.1. Structure of the complexes obtained from the reaction between $Zr(Acac)_4$ and ε-caprolactone

To state whether the expected mechanism of ε-caprolactone polymerization initiated with $Zr(Acac)_4$ proceeds analogously to the mechanism of initiation of lactide polymerization, it was necessary to investigate any possibilities of arising a labile complex containing a ligand originating from the deprotonated caprolactone, which would happen as a result of a reaction between the lactone and a $Zr(Acac)_4$. Thus at the first stage of the research I conducted a series of model reactions, in

anhydrous benzene solution at 80 °C. Under the reaction conditions, $Zr(Acac)_4$ was stable in the solvent and did not undergo any modifications for over 12 h. This phenomenon has been stated on the basis of observation of NMR and FTIR spectra.

To obtain zirconium complexes of the same structure that those arising at the initial phase of initiation of the examined polymerization (not containing ε-caprolactone oligomers) I used significant molar surplus of $Zr(Acac)_4$ to ε-caprolactone in the initial monomers mixture. Consequently, the products did not contain oligomers already with the ratio value of 2:1. The conclusion has been drawn on the basis of absence of α1, α2 i ε1 signals in the spectra (Fig. 2A), which can be assigned to the caproyl chain protons. However, the ε signal, not present in the previous ε-caprolactone monomer spectra appeared. It has been attached to the proton of the C═C*H*, group which arose as a result of ε-caprolactone deprotonation. It also entailed arising of some complexes containing an enolate ligand, and free acetylacetonate (in the both, enol and ketone forms) was present in the solvent. The presence of partial amount of released HAcac has also been stated in the obtained samples, after distilling of the solvent. It is marked by ^{1}H NMR signals characteristic for the enol (Table 3, Fig. 2; signals 3, 6) and ketone (signals 4 and 5) forms of this compound. ^{1}H NMR analysis of the obtained samples was conducted basically in $CDCl_3$ solution. As it was impossible to distinguish the signals of the C*H* group acetylacetonate ligands from the C*H* signal of the free acetylacetonate, we did some additional measurement conducted in benzene-d_6. Thanks to a thorough analysis of those spectra, as well as those determined for complexes obtained with ε-caprolactone stoichiometric surplus, we were able to attach the signals to appropriate groups in the synthesized complex, arising as a result of a reaction (Fig. 3, Table 2, complex **1**). A presumed process of a ligand exchange reaction is illustrated by Scheme 1.

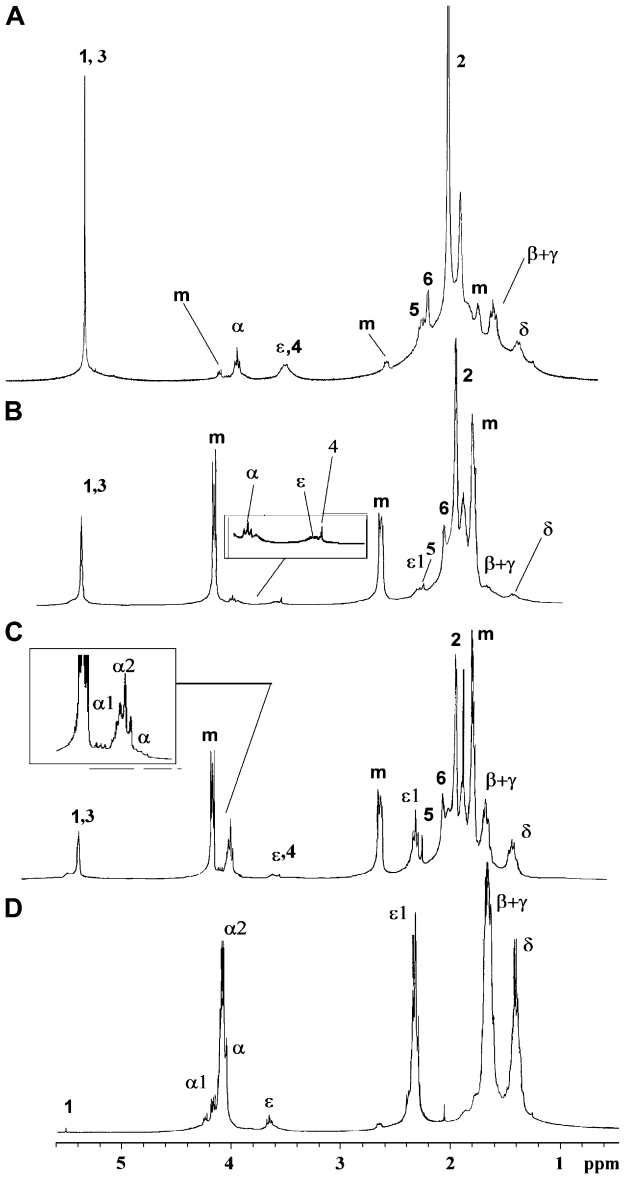


Fig. 2. ^{1}H NMR spectra (in $CDCl_3$) of complexes obtained in the following processes carried out in benzene at 80 °C: (A) with $Zr(Acac)_4$/ε-caprolactone molar ratio of 2:1; and with molar ratio of 1:10 after: (B) 1 h; (C) 3 h; (D) 8 h, after thorough drying in vacuum.

ε-Caprolactone is coordinated by the carbonyl oxygen to the central zirconium atom, forming a labile nine coordinate adduct. The caprolactone deprotonation and transfer of a proton to Acac ligand cause a ligand exchange reaction at a further stage of the process, as a result of which a stable eight-coordinate complex arises, containing a ligand originating from the deprotonated caprolactone (complex **1**). Free HAcac acetylacetonate is released (the solvent contained mostly its enol form) (Scheme 2).

I could not determine the geometry of this complex by means of X-ray examination as the final complex could not be totally separated from the unreacted $Zr(Acac)_4$ and obtaining a monocrystal of this compound of appropriate size was practically impossible. Therefore I used the molecular

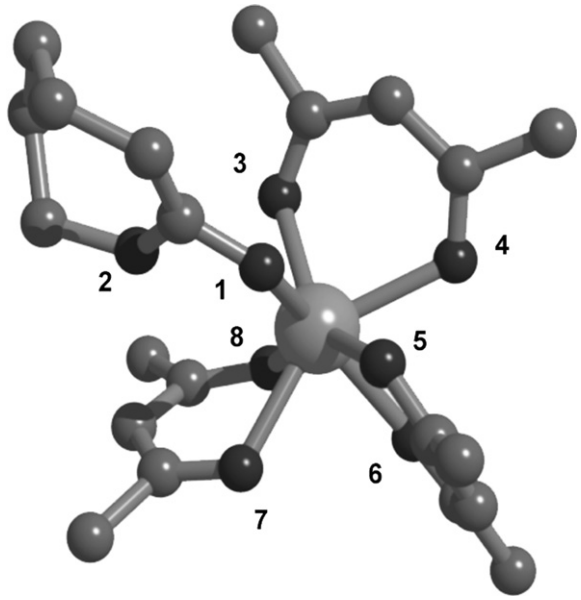


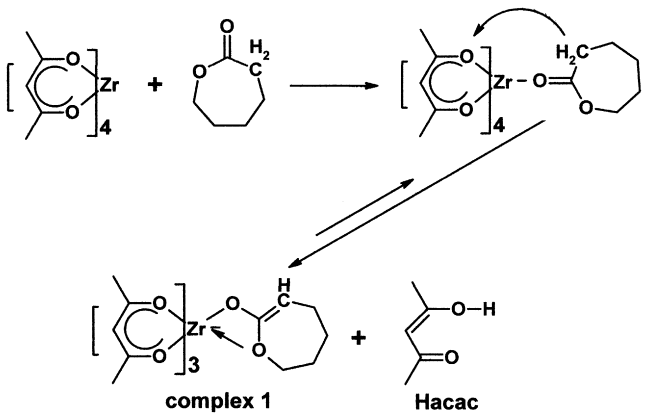
Fig. 3. Optimized geometries of complex (**1**) [$Zr(Acac)_3$(deprotonated ε-caprolactone)] performed with the HyperChem 7.5 package (semiempirical PM3(tm) method).

Table 2
Averaged distances (Å) between selected atoms of obtained zirconium complexes, performed with the HyperChem 7.5 package (semiempirical PM3(tm) method)

No. of complex	Bound type	PM3(tm) data	Data after molecular dynamic calculation
1	Zr–O(1) (carbonyl in depr. ε-caprolactone)	2.11	2.09
	Zr–O(2) (acyl, in depr. ε-caprolactone)	2.90	2.99
	Zr–O(3–8) (in Acac) – average	2.23	2.28
	C–O(1) (carbonyl, in depr. ε-caprolactone ring)	1.32	1.32
	C–O(2) (acyl, in depr. ε-caprolactone ring)	1.39	1.39
	CH_2–O(2) (in depr. ε-caprolactone ring)	1.42	1.43
	CH–C (in depr. ε-caprolactone ring)	1.35	1.35
	CH_2–CH_2 (in depr. ε-caprolactone ring)	1.52	1.53
2	Zr–O(1) (carbonyl in depr. ε-caprolactone)	2.08	2.04
	Zr–O(2) (acyl, in depr. ε-caprolactone)	2.93	3.03
	Zr–O(3–6) (in Acac) – average	2.22	2.24
	Zr–O(7) (in the oligomer chain)	2.47	2.72
	C–O(1) (carbonyl, in depr. ε-caprolactone ring)	1.32	1.34
	C–O(2) (acyl, in depr. ε-caprolactone ring)	1.39	1.39
	CH_2–O(2) (in depr. ε-caprolactone ring)	1.42	1.42
	CH–C (in depr. ε-caprolactone ring)	1.35	1.35
	CH_2–CH_2 (in depr. ε-caprolactone ring)	1.52	1.52

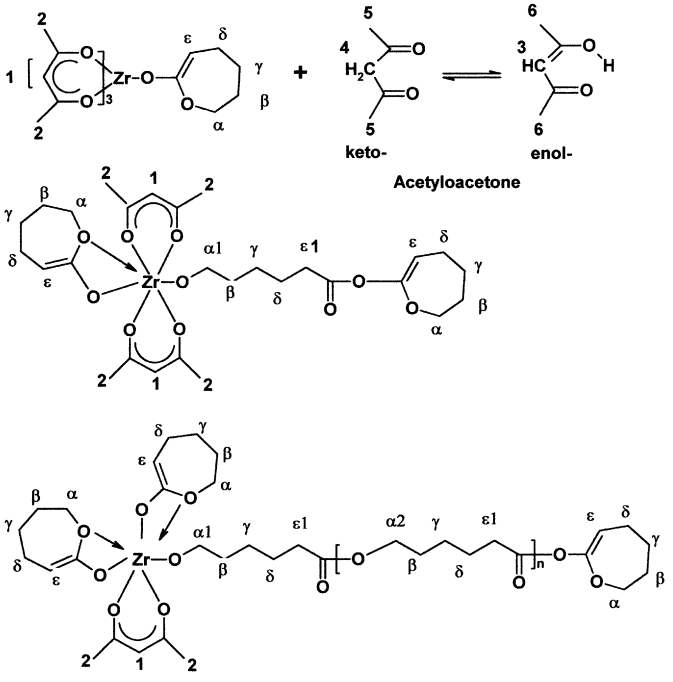
Atom numbering is as shown in Figs. 3 and 4.

modeling method to determine its microstructure. The obtained results are depicted by Fig. 3 and Table 2. The complex that arose as a result of a reaction of exchange of one of the ligands, containing three acetylacetonate ligands and one deprotonated ε-caprolactone ligand retained the initial square antiprizmatic geometry of the zirconium acetylacetonate complex. The coordination number 8 was retained, and the change in average value of Zr–O bond length of the remaining three acetylacetonate ligands was insignificant (Table 1, row 1 and Table 2, row 3). The ligand from deprotonated ε-caprolactone was attached to the central metal trough the carbonyl and acyl oxygens. The length of the Zr–O(1) (carbonyl) bond was noticeably shorter and that of Zr–O(2) (acyl) was significantly longer than Zr–O distance of Acac. ligands (Table 2). In modeled dynamic conditions (HyperChem Molecular Dynamics function) this complex is stable and the attached caprolactone ring does not tend to open. Only the distances between the central atom and the acyl oxygen of the ring of the deprotonated caprolactone enlarge as well as, to an extent, average lengths of Zr–O bonds in the acetylacetonate ligands, which can explain a tendency for exchanging these ligands, demonstrated in the experiments (see also Table 2).



Scheme 1. Reaction of $Zr(Acac)_4$ with ε-caprolactone.

With a view to examine the initial stage of caprolactone polymerization, the process of forming the active initiating complex and the beginning phase of the caproyl chain propagation I investigated the reaction of 10 mmol of ε-caprolatone with mmol of $Zr(Acac)_4$, regularly registering the changes occurring in the reaction mixture. The obtained results are illustrated in Fig. 2; B–D and Table 4. After 1 h of conducting the reaction, when about 13% of the total ε-caprolactone content reacted, the obtained mixture has been subjected to the NMR analysis. The obtained spectrograms, apart from the signals originating from the unreacted caprolactone (Fig. 2B,



Scheme 2. The complexes obtained from the reaction between $Zr(Acac)_4$ and ε-caprolactone.

Table 3
Chemical shifts in the ^{1}H NMR spectra signals (in $CDCl_3$), origin of signals – as shown in Schemes 2 and 4

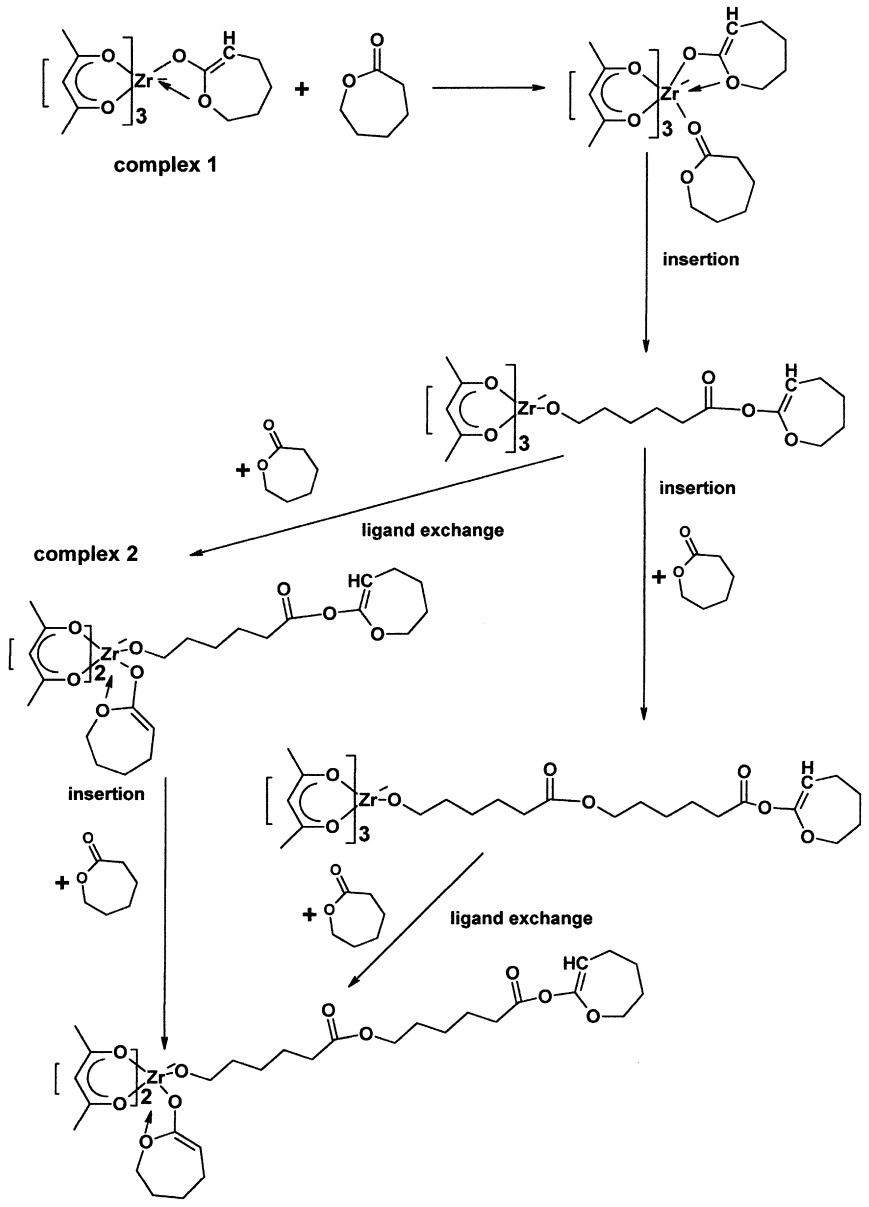
Signal	Origin	δ (ppm)
	Acetylacetonate ligands and acetylacetone (HAcac)	
1	C*H* in $Zr(Acac)_4$	5.51
2	CH_3 in $Zr(Acac)_4$	1.93
3	C*H* in enol isomer HAcac	5.50
4	CH_2 in keto isomer HAcac	3.61
5	CH_3 in keto isomer HAcac	2.22
6	CH_3 in enol isomer HAcac	2.04
	ε-Caprolactone and caproyl sequences	
α	CH_2O in deprotonated ε-caprolactone	4.05
ε	CH═(CO) in deprotonated ε-caprolactone	3.63
ε1	CH_2(CO) in caproyl chain	2.33
β + γ	$CH_2CH_2CH_2CH_2$ in deprotonated ε-caprolactone and in caproyl chain	1.65
δ	$COCH_2CH_2$ in caproyl chain	1.40
α1	Zr–O–CH_2 in the beginning of chain	4.16
α2	(CO)O–CH_2 in caproyl chain	4.08
m	CH_2 in unreacted ε-caprolactone monomer	4.26 2.66 1.77
	Trimethylene carbonate and carbonates sequences	
TMC1	OCH_2 unreacted TMC	4.47
TMC2	CH_2–CH_2–CH_2 unreacted TMC	2.08
a2	CH_2–O–(CO)–$O(CH_2)_3O$(CO)– in chain (sequences T – T)	4.23
a1	CH_2–O–(CO)–$O(CH_2)_5$(CO)– in chain (sequences T-Cap)	~4.15
a	Zr–OCH_2 in the beginning of chain	3.86
c	–OCH_2 on the end of chain	3.74
b	CH_2–CH_2–CH_2 in chain	2.17

Table 3 signal m) and arising free acetylacetonate (signals 3–6) other more interesting signals have been observed (Fig. 2B, Table 3, signals α, ε, δ i β + γ) which were attached to CH_2 and C*H* groups of the arising complex **1**. While no other signals, which would be evidence of the beginning of the caproyl chain propagation process appeared. Calculations of the intensity of particular signals prove that in most of the arisen complexes one acetylacetonate ligand has been exchanged at this stage of the reaction (Table 4, row 1). After following 2 h the conversion degree of the monomer reached 40%, so the synthesized complexes contained, on average summary, 3–4 caproyl and deprotonated caprolactone molecules (Table 4, row 2). The observed concentration of ligands in the reaction mixture decreased significantly. About a half of the initial content of those ligands have been released as free acetylacetonate and exchanged for the ligands of the deprotonated caprolactone (Fig. 2C, signals 1, 2, Table 4, row 2, ratio 2/α) At the same time I observed that the α multiplet band broadened from 4.0 to ca. 4.16 ppm, which is connected with the beginning of the oligomer chain propagation process. This band included the α1 arising at this stage of the reaction, originating form the first O–CH_2 group of the propagating caproyl chain, and α2 attached to the remaining O–CH_2 groups of this chain. I have also noted significant yet unexpected increase in the intensivity of the signals connected with the remaining CH_2 groups of the caproyl chain (ε1, β + γ i δ signals). The predicted mechanism of caproyl chain propagation is shown in Scheme 3. Complex **1**, formed by the way of ligand exchange reaction, was the actual initiator for the examined polymerization. The next caprolactone molecule, coordinating to the central atom of the arisen complex, through a donor free electron pair of the carbonyl oxygen formed an intermediate nine-coordinated adduct. Further chain propagation proceeded according to a well-known and commonly accepted insertion–coordination mechanism. As a result, a caproyl chain ending with deprotonated caprolactone ring attached to the central atom through an acyl oxygen–zirconium bond was formed. The whole process could be repeated when the next ε-caprolactone molecule was coordinated to the complex created in this way. During the coordination of the next caprolactone molecule the reaction competing with the main chain growth reaction was the ligand exchange of the next acetylacetonate ligand (Scheme 3). This reaction, proceeding parallel to an already initiated reaction of chain propagation, induces further loss of acetylacetonate group content in the reaction mixture. The structure of complex **2**, which basically entered into the composition of the reaction mixture obtained at this stage, is illustrated in Fig. 4 and Table 2. This complex contains a heptacoordinate zirconium center attached to two bidentate acetylacetonate ligands, one deprotonated ε-caprolactone ligand through the carbonyl oxygen and caproyl chain ended with deprotonated ε-caprolactone ring through acyl oxygen. The

Table 4
Oligomerisation of ε-caprolactone initiated with $Zr(Acac)_4$[a]

Time [h]	Conv [%]	α/ε	α1/α	$[\alpha 1/\alpha]_N^K$	Av. DP α2/α1	sig2/α	$[sig2/\alpha]_N$
1	13	2.2	–	–	–	7.9	$[9]_3$
3	43	2.1	0.5	$[0.5]_2^1$ $[1.0]_2^2$	3.2	3.5	$[9]_3$ $[3]_2$
6	74	~1.9	~0.3	$[0.25]_4^1$ $[0.5]_4^2$ $[0.75]_4^3$	4.5	0	Lack of Acac ligands
of8	97	~1.9	~0.35	$[0.25]_4^1$ $[0.5]_4^2$ $[0.75]_4^3$	~8	0	lack of Acac ligands

Conv – caprolactone conversion, α/ε, α1/α, sig2/α – ratio of the adequate signals intensity, Av. DP – average number of caproyl sequenes in the chain calculated with signals ratio α2/α1; $[\alpha 1/\alpha]_N^K$ – theoretical value of the signals ratio for complex with; N – number of exchanged ligands, K – number of propagation chains, $[sig2/\alpha]_N$ – theoretical value of the signals ratio for complex with; N – number of remained acetylacetonates ligands.
[a] Carried out in benzene at 80 °C, with *M*/*I* molar ratio of 10:1.



Scheme 3. Mechanism of caproyl chain propagation.

closest examples of complex **2** structure in the literature are the mixed ligand complexes $Zr(Acac)_3NO_3$ [60] or $Zr(Acac)_3(OC_6H_4NO_2)$ [39]. The coordination geometry of this type of complexes is best described as a distorted square-face-capped trigonal prism, with O(7) as a first acyl oxygen of caproyl oligomer chain in the capping position for complex **2**. The Zr–O(7) bond in this complex is noticeably longer than the Zr–O bonds of the remaining acetylacetonate ligands, as well as the Zr–O(1) bond of the deprotonated ε-caprolactone's ligand (Table 2, complex **2**). This complex seemed less stable than complex **1** because of the coordination unsaturation. The chain caproyl ligand was also more labile than all remaining complex ligand, it was coordinate to the central atom through only one Zr–O bond. This suggested that chain growth was more likely to occur on the one ligand already containing chain structure. The measurement of the intensity of NMR spectrum signals (α1/α signals ratio) has proven that the complexes formed after 3 h of conducting the reaction contain one caproyl chain (Table 4, row 2). After 6 h of the reaction, while 74% of the initial caprolactone counted have converted, most of the acetylacetonated ligands have been exchanged and the chain propagation proceeded generally still on one active group (Table 4, row 3). However, the calculated α1/α quotient was still slightly larger than the theoretical one of the complex with one propagation center, which suggests that there is a probability of the propagation process occurring on the other ligands too.

This reaction between ε-caprolactone and $Zr(Acac)_4$ has been then continued for the following 2 h. After this time, virtually total conversion of both substrates was observed (Table 4, row 4). The ^1H NMR spectra of the obtained compound after evaporating the solvent is illustrated in Fig. 2D. The obtained complexes contained neither signals characteristic for acetylacetonate ligands. That proves that the ligand exchange

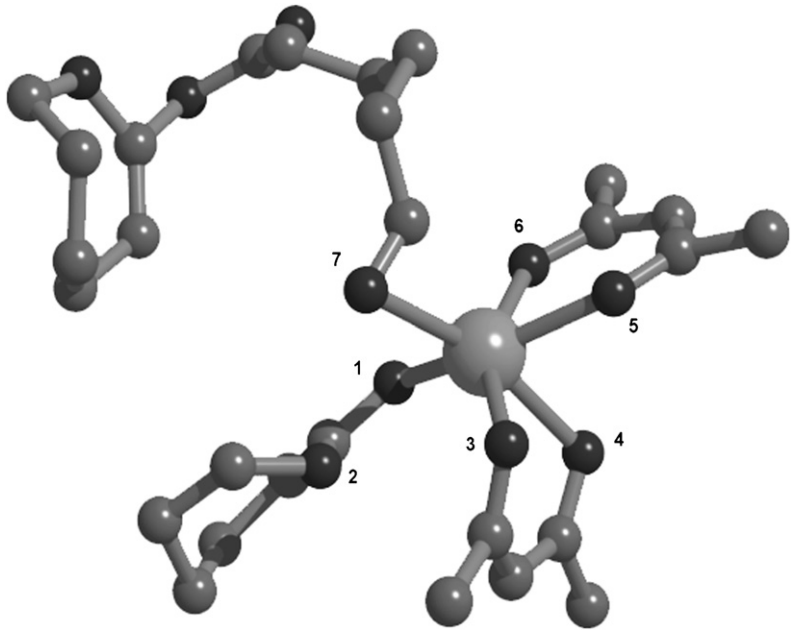


Fig. 4. Optimized geometries of complex (**2**) [Zr(Acac)$_2$(deprotonated ε-caprolactone) (caproyl ending with deprotonated ε-caprolactone)] performed with the HyperChem 7.5 package (semiempirical PM3(tm) method).

reaction proceeded constantly during the chain oligomerization process. The all chelates ligands of the initial Zr(Acac)$_4$ have been exchanged and the oligomer chain that arose did not contain any groups which could originate from those ligands (Table 4, row 4). Major signals visible in the spectrum image are bands connected with certain groups of the propagating oligomer chain: O–CH_2 – α2 signal, CH_2–CO – ε1 and broad, coupled signals of CH_2 groups in the caproyl chain, containing the CH_2 signals of the cyclic ligands of the deprotonated caprolactone (δ, $\beta + \gamma$). The presence of those ligands is proved by α i ε signals, still visible in the spectra, albeit weak.

Laboratory investigation revealed that the complexes obtained by the way of the described reaction, containing caproyl chain and devoid of acetylacetonate ligands, emerged moisture-sensitive, unlike other previously known lactide/zirconium(IV) compounds [30], or complex **1**, stabilized with the chelate bond of the acetylacetonate ligands. On the grounds of the NMR analysis of the spectra of hydrolysis products we could presume that this reaction creates an aliphatic hydroxy acids, ε-caprolactone and possibly the derivatives of the agglomerated zirconium hydroxide (obviously invisible in the ^{1}H and ^{13}C NMR spectra). An analogous phenomenon of easily proceeding hydrolysis of unsaturated zirconium complexes has been also observed for Zr(OBut.)$_4$ [61] which contains unsaturated four-coordinate metal centers, which make them extremely moisture-sensitive, contrary to the complexes of similar microstructure with the bidentate donor functionalised ligand; 1-methoxy-2methyl-2propanolate – six-coordinate, mononuclear complexes characterized with much less moisture-sensitivity [62].

On the basis of the obtained results I can draw a conclusion that the initial phase of ε-caprolactone polymerization initiated with Zr(Acac)$_4$, proceeds similarly to an analogous reaction with lactones [24,36]. At this stage, due to the process of acetylacetonate ligand exchange, a complex containing the ligand originating from the deprotonated caprolactone arises in the molecule, connected with the central atom through the Zr–O bond. This is the actual initiator for the polymerization. However, the difference in the rates of concurrent reactions (oligomer chain propagation and ligand exchange) is less for the polymerization of ε-caprolactone. For this reason, during the reaction process, some complexes devoid of acetylacetonate chelate ligands with relatively short caproyl chain arise. As for lactide oligomerization, such complexes could be obtained only provided the reaction was conducted at high temperature (over 140 °C). Increasing the temperature of the initiation process of lactide polymerization reduced the difference between the chain propagation rate and ligand exchange rate.

3.2. ε-Caprolactone homopolymerization

To examine the process of actual polymerization of ε-caprolactone and to verify whether the chain propagation proceeds on only one active center (as the calculations employing molecular modeling suggested), I conducted a model polymerization of this lactone. The samples destined for molar mass analysis were drawn periodically, acidified and then hydrolyzed. The arising zirconium compounds was separated from the organic part.

The polymerization process is illustrated in Figs. 5 and 6. After 20 min of conducting the reaction, when the monomer conversion valued about 10%, low concentration of acetylacetonate groups in the reaction mixture was observed. The ^{1}H NMR at this stage was very similar to that presented in Fig. 2C. Apart from the caprolactone monomer signals, ε and α signals, assigned to the ligands of the deprotonated caprolactone, as well as weak α1 and α2 signals appeared, certifying that the caproyl chain propagation process commenced. With high stoichiometric surplus of caprolactone to the

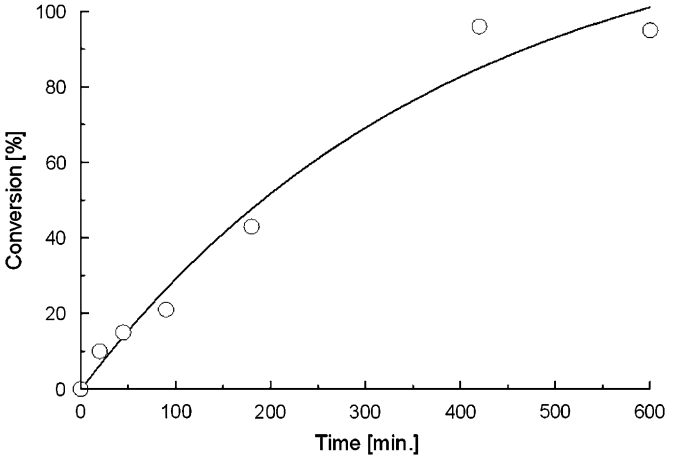


Fig. 5. Conversion of ε-caprolactone as a function of polymerization time, process carried out in benzene at 80 °C, with *M*/*I* molar ratio of 50:1.

initiating zirconium complex during the polymerization process, the ligand exchange stage proceeded relatively fast. The influence of changes in the structure of initiating complex on the process of caproyl chain propagation was unnoticeable.

Over less than 7 h, the monomer conversion value reached over 90% (Fig. 5). Average molar masses of the obtained polycaprolactone were slightly higher than the theoretical ones (ca. 8–10%), calculated for one propagation center (Fig. 6) and were characterized with monomodal distribution at every stage of the reaction. The little difference in the mass values was probably caused by errors in GPC measurements and inaccuracy of the used method of correction of styrene standards. The results indicate that the polycaprolactone chain propagation proceeded practically rather on one active center and a linear increase of the average mass with the conversion is observed, which would be a sign of a live polymerization. On the other hand, taking into account the fact of rapid acetylacetonate ligand exchange process, as well as earlier reports indicating that in the case of this kind of polymerization initiated with zirconium [9] or titanium propoxides [63] the process of chain propagation proceeded on four active groups, we cannot exclude the possibility of more than one active alkoxide group

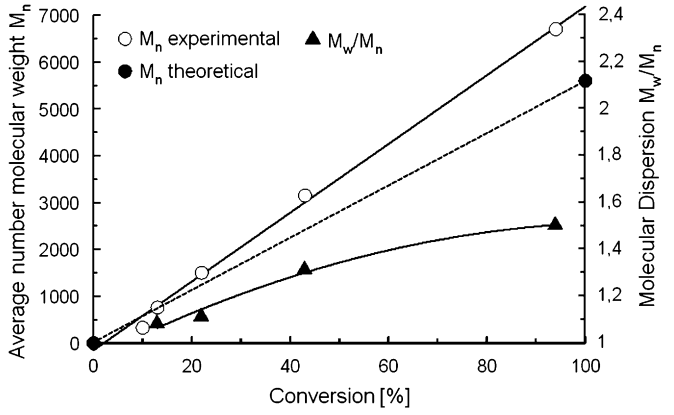


Fig. 6. Relationship between number average molecular weight M_n, molecular weight dispersion M_w/M_n and the degree of ε-caprolactone conversion, polymerization carried out in benzene at 80 °C, with *M*/*I* molar ratio of 50:1.

arisen during the course of the polymerization, that takes part in the process. Probably, similarly to the case of ε-caprolactone polymerization conducted with the use titanium phenoxide [63], an initiator with similar microstructure as the zirconium complex arising in the investigated process, a slight evolution of average number of active alkoxide groups per initiator may occur along with the increase of monomer conversion degree. While applying titanium phenoxide, the number valued over 1.5. Average number of active groups in the discussed process of caprolactone polymerization with the use of $Zr(acac)_4$ cannot significantly exceed 1 though, as it is proven with the research on the dependance of the molar mass on conversion, the GPC chromatography results where bimodal molar mass distribution was not observed at any stage of the polymerization process, as well as the analysis of the results of the previously described caprolactone oligomerization – all of which has been provided above. Observed, slow increase of molar mass dispersion values with the polymerization duration is thus probably connected with the phenomenon of transesterification, generally with intramolecular transesterification. The transesterification processes occur simultaneously with the main process of polymer chain propagation. In the case of using zirconium initiator, it is basically intermolecular transesterification, consisting of the active end of the chain attacking the ester bounds of another molecule. It has a major influence on the final microstructure of the chain. The course of the transesterification process of this type has been described in detail in previous papers concerning the copolymerization processes initiated with $Zr(Acac)_4$ [20–25]. Molar mass dispersion was much lower for ε-caprolactone polymerization than in the previously investigated L-lactide polymerization, conducted with the same initiator in very similar reaction conditions [36]. A cause to that phenomenon is a much less difference between the rate of the ligand exchange reaction and the chain propagation rate in the case of caprolactone polymerization, compared to a noticeable difference between these values during the lactide polymerization. In the obtained oligomers, after evaporating the solvent, I did not observe any signal which could possibly originate from the C*H* and CH_3 of an acetylacetonate derivative. This certifies that no such group exists at the end of the chain, and which is also proved by the suggested mechanism of initiation of this polymerization.

3.3. TMC homopolymerization

3.3.1. Polymerization initiated with $Zr(Acac)_4$

For further verification of the suggested initiation mechanism, I made an attempt to form analogous zirconium complexes, containing a TMC ligand, and to conduct TMC polymerization initiated with $Zr(Acac)_4$ – a monomer which should not be deprotonated in the reaction conditions identical as the previously conducted and described caprolactone polymerization. In this case, if the polymerization of this monomer occurred, its course would be different than the suggested mechanism of initiating the ε-caprolactone polymerization.

After 12 h of heating the benzene solution of equimolar mixture of TMC and zirconium acetylacetonate, alongside with a

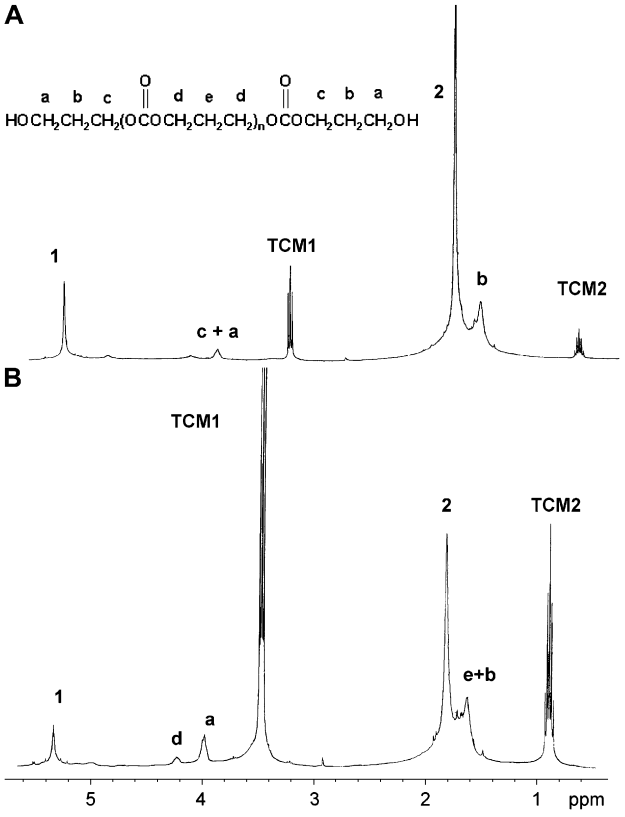


Fig. 7. ^{1}H NMR spectra (in d_6-benzene) of samples obtained with the following processes carried out in benzene at 80 °C: (A) with equimolar amount of TMC and Zr(Acac)$_4$, (B) with molar ratio of TMC/Zr(Acac)$_4$ as 5:1.

solution of 5 mmol of TMC and 1 mmol of Zr(Acac)$_4$, the NMR spectra presented virtually no loss in acetylacetonate groups content (Fig. 7A, B), while no free acetylacetone groups were virtually visible. In both reactions, only about 10%–20% of the initial TMC content has been oligomerized. In the ^{1}H NMR spectra (samples in benzene-d_6 solution), after attaching the signals according to previous description of poly(TMC) spectra [64], I observed the presence of O–CH_2 (3.95 ppm) and

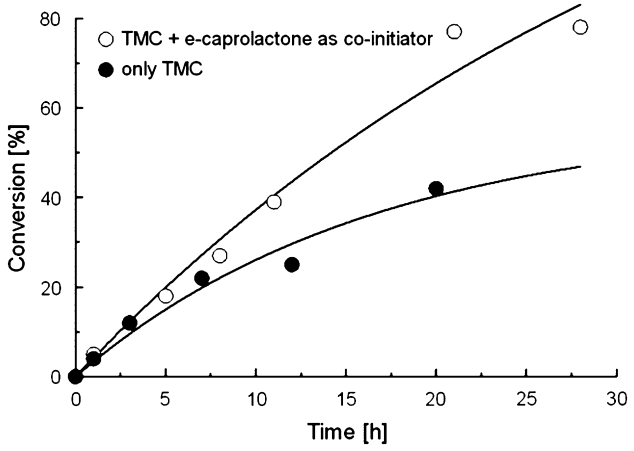


Fig. 8. Conversion of TMC in polymerization initiated with Zr(Acac)$_4$ and carried out in benzene at 80 °C, without ε-caprolactone (TMC/Zr(Acac)$_4$ ratio as 50:1) and with ε-caprolactone as a co-initiator (TMC/Zr(Acac)$_4$/ε-caprolactone ratio as 50:1:4).

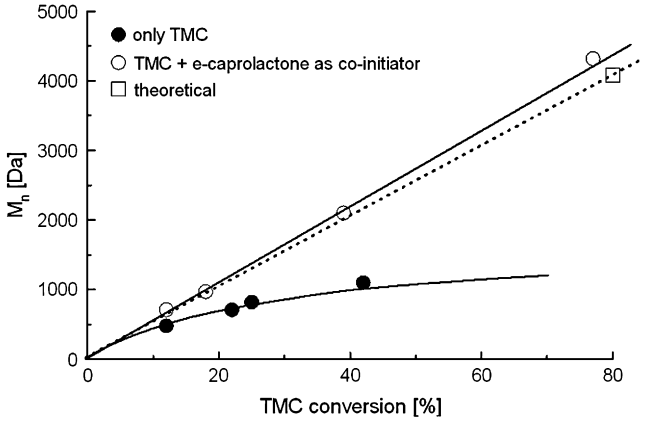


Fig. 9. Relationship between average number molecular weight M_n, and the degree of TMC conversion in polymerization initiated with Zr(Acac)$_4$ and carried out in benzene at 80 °C, without ε-caprolactone (TMC/Zr(Acac)$_4$ ratio as 50:1) and with ε-caprolactone co-initiator (TMC/Zr(Acac)$_4$/ε-caprolactone ratio as 50:1:4).

CH_2–CH_2 (1.63 ppm) groups, originating from the carbonate chain, and weaker signals connected with the HO–CH_2 groups situated at the end of the chain (4.22 ppm). The signals of CH_2 groups of non-converted TMC (signals TMC1, TMC2) were shifted towards lower ppm values, compared to the model (TMC in deutered benzene, 3.71 ppm and 1.20 ppm). The shift value depended on the Zr(Acac)$_4$ content and certified that strong adducts of ε-caprolactone with the central atom of the complex were arising. An attempt of model polymerization of 50 mmol of TMC by the use of 1 mmol of Zr(Acac)$_4$ proved the phenomenon of TMC oligomerization. The course of this reaction is illustrated in Figs. 8 and 9. After approximately 5 h, the reaction

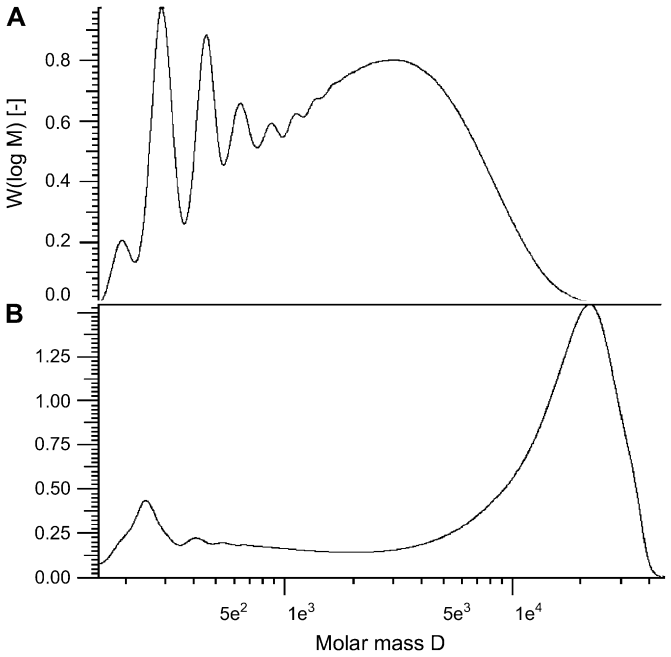
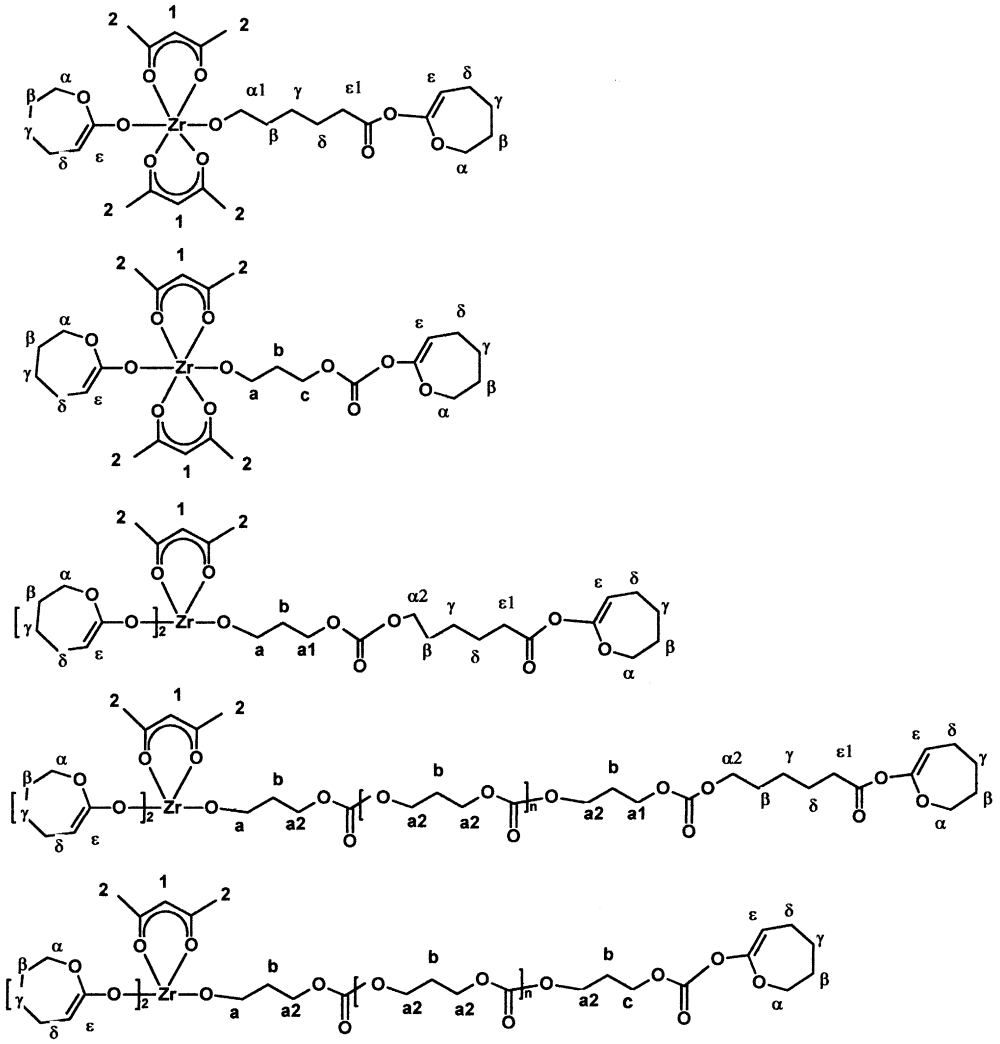


Fig. 10. GPC chromatograms of samples obtained in polymerization of TMC initiated with Zr(Acac)$_4$ and carried out in benzene at 80 °C (A) without ε-caprolactone, after 20 h, TMC/Zr(Acac)$_4$ ratio as 50: 1; (B) with ε-caprolactone co-initiator, after 22 h, TMC/Zr(Acac)$_4$/ε-caprolactone ratio as 50:1:4.

rate would gradually decrease. According to the calculations based on the ^{1}H NMR spectrum of the reaction products (Fig. 8, Fig. 11A), monomer conversion valued ca. 40%. During the investigated reaction, practically only TMC oligomerization took place. As the GPC analysis reveals (Fig. 10A), the final product to this reaction was a mixture of low-molecular products, with number average molar mass of ca. 700–800 Da. Linear increase in molar mass was not observed (Fig. 9), most probably due to reactions of finalizing the propagation and cyclization of the chain. The reaction process was similar to the previously described TMC polymerization conducted without using catalysts, only with the presence of residual water [65]. On the basis of these results, we can conclude that under the conditions of the conducted reaction, zirconium acetylacetonate did not directly participate in the process of initiating the TMC polymerization, and that the observed phenomenon of oligomerization of this monomer proceeded rather spontaneously.

3.3.2. Polymerization initiated with Zr(Acac)$_4$ and carried out with ε-caprolactone presents as co-initiator

While attempting to conduct the TMC polymerization, the Zr(Acac)$_4$ complex emerged stable and did not initiate polymerization of this monomer because of its saturation and resistant bonds of acetylacetonate chelate ligands. Thus to initiate the process, it was necessary to add an agent reacting with Zr(Acac)$_4$ at the first stage of reaction initiation to form a more labile complex. For this reason I re-conducted the TMC polymerization reaction initiated by Zr(Acac)$_4$, adding a small amount of ε-caprolactone as a co-initiator (with molar ratio of TMC/Zr(Acac)$_4$/ε-caprolactone as 50:1:4). The course of this polymerization is illustrated in Figs. 8 and 9. The sequences of arising chain are presented in Scheme 4. The ^{1}H NMR spectra of these complexes are illustrated in Fig. 11. In the sample drawn after 1 h of conducting the reaction, zirconium complex containing ligands of the deprotonated ε-caprolactone was present (Fig. 11B, Table 3; signals α. ε, δ, β + γ), according to previous predictions. At the same time, a couple of signals connected with the presence of caproyl chain were visible (signals α1, α2, ε1). At this stage, an amount of unreacted caprolactone (signal m) and unconverted monomer – TMC (signals TMC1, TMC2) was still present in the reaction mixture. Very weak signals connected with CH_2 groups of the first segment of the arising carbonate chain (signals a, c) could also be observed in this spectrum.



Scheme 4. The oligomers obtained from TMC polymerization conducted with Zr(Acac)$_4$ and ε-caprolactone co-initiator.

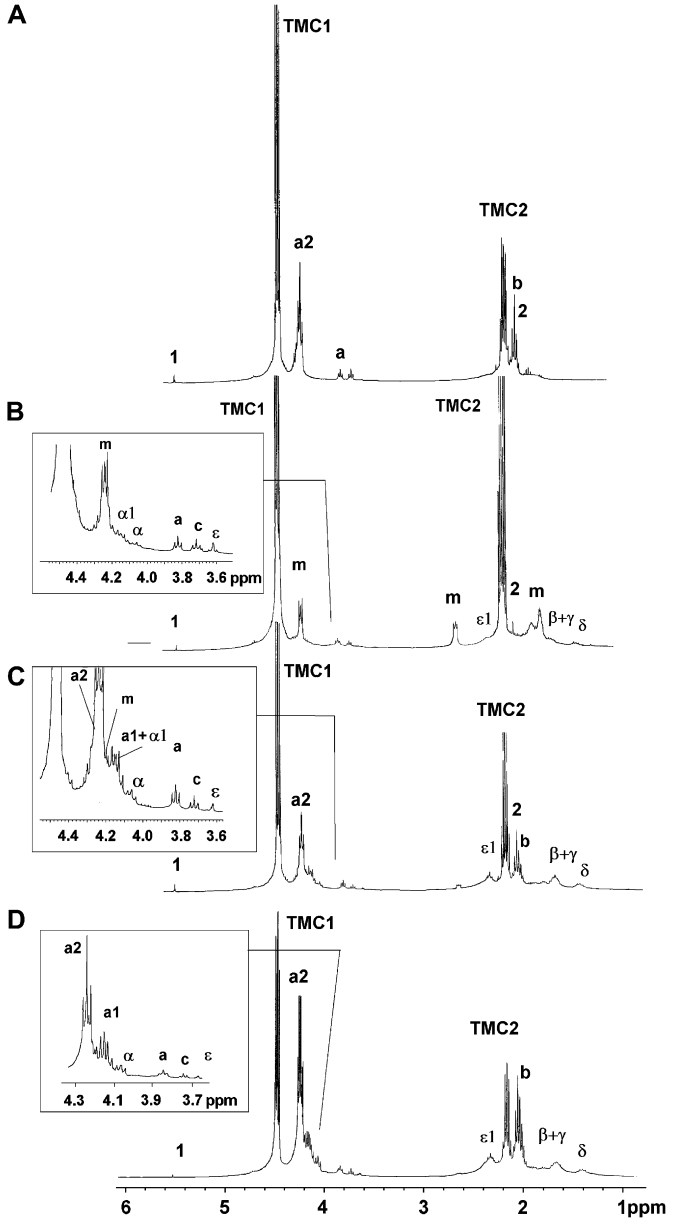


Fig. 11. ^{1}H NMR spectra (in $CDCl_3$) of PTMC obtained in polymerization of TMC carried out in benzene at 80 °C, with $Zr(Acac)_4$ and molar ratio *M*/*I* of 50:1; (A) polymerization without ε-caprolactone co-initiator, after 20 h; and with ε-caprolactone as co-initiator (ratio *I*/ε-caprolactone as 1:4) after (B) 1 h (C) 11 h, (D) 22 h.

After 11 h of conducting the reaction (Fig. 11C), the ε-caprolactone has been virtually totally converted. However, not all of acetylacetonate ligands of the initiating complex have been exchanged, as the signals of C*H* of these ligands were visible 1. This observation has been proved with NMR analysis conducted in deutered benzene solution. The propagating oligomer chains must have therefore contained caproyl sequences, whose α2 signals could not be visible due to their being overlapped by strong a2 signal. Strong a2 and b signals certified the carbonate chain propagation. Also signals originating by the end groups of this chain (signals a, c) were observed. The increase of intensity of signal a (beginning of the carbonate chain) compared to the signal c also proved that the chain propagation proceeded according to the insertion mechanism. At the first stage of the process, the beginning of the propagating chain consisted mainly of the caproyl sequence. Only a small number of carbonate chains appeared, so the intensity of signals a and c, connected with the beginning and the end of this sequence was then very similar at this stage. In the following phase, as a result of insertion of next other TMC molecules attached in between the Zr–O–CH_2 caproyl bond, an increase if intensity of signal a (connected with the presence of carbonate sequence at the beginning of the arising oligomer chain) was observed. Most probably, the broad, complex signal spanning from 4.11 to 4.20 ppm contains the a1 signal (coupled with α1 and α2 signal), proving the existence of the created T–Cap sequence (where Cap stands for caproyl sequence $-O-(CH_2)_5CO-$, T for carbonate sequence $-O-(CH_2)_3-O-CO-$) in the chain of the arising polymer. After over 20 h, TMC conversion valued ca. 65% (Fig. 8). Very weak signal of 1C*H* of the acetylacetonate ligand was still visible in the ^{1}H NMR spectrum of the product (Fig. 11D). Apart from the increase in intensity of signals a2 and b, characteristic for poly(TMC) most of the signals described before could also be observed in the spectrum.

The reaction of TMC polymerization with ε-caprolactone used as a co-initiator proceeded much slowly in comparison with ε-caprolactone homopolymerization. However, the reaction rate did not tend to decrease at any stage of the process. Thus, the molecular mass gain was directly proportional and the obtained molar masses were very close to the estimated values, theoretically obtained with the assumption of existence of one propagation center (Fig. 9). The mass distribution was monomodal. Molar mass dispersion value M_w/M_n of the obtained polycarbonate did not exceed 1.5 (Fig. 10).

The presented data prove that the complexes arising at the first stage of the conducted process, containing the ligand originating from the deprotonated caprolactone, were the actual initiator for the investigated polymerization, the further course of which proceeded according to the insertion–coordination mechanism.

3.4. TMC/ε-caprolactone copolymerization

The results of the research into ε-caprolactone hompolymerization and TMC polymerization with a small amount of caprolactone with the use of $Zr(Acac)_4$ suggest that this compound should be an equally high-efficient initiator for the copolymerization of both monomers. To prove this thesis, I conducted a series of reactions of TMC/caprolactone copolymerization, aiming to obtain high-molecular copolymers with diverse composition. The obtained results are illustrated in Table 5. Characteristic NMR spectra of the obtained copolymers are presented in Figs. 12 and 13. To attach the signals to proper groups of the copolymer chain, I used the assignation proposed in previous papers [18,19,48,66]. Besides the initial composition of the reaction mixture, I obtained high-efficient copolymers with totally random chain microstructure. Average

Table 5
Copolymerization of ε-caprolactone with TMC initiated by $Zr(Acac)_4$[a]

No	${}^0f_{TMC}$ [% mol]	F_{TMC} [% mol]	Time [h]	C [%]	${}^el_{TMC}$	${}^el_{cap}$	${}^rl_{TMC}$	${}^rl_{cap}$	R	M_n [kDa]	D
1	15	16	24	99	1.1	5.8	1.3	6.8	1.1	100	1.9
2	30	31	24	~100	1.2	2.5	1.6	3.6	1.2	129	1.9
3	50	50	24	~100	1.5	1.5	1.7	1.7	1.3	60	2.2
3	70	71	36	98	3.0	1.2	3.1	1.3	1.2	70	2.1
4	85	82	48	98	5.0	1.2	5.9	1.3	1.1	29	2.2

${}^0f_{TMC}$ – Initial feed molar fraction of TMC, F_{TMC} – feed molar fraction of TMC, C – total conversion of copolymerization, ${}^el_{cap}$ – average length of caproyl microblock calculated with NMR, ${}^rl_{LL}$ – theoretical average length of caproyl microblock calculated according to Eq. (4), ${}^el_T$ – average length of carbonate microblock calculated with NMR, ${}^rl_T$ – theoretical average length of carbonate microblock calculated according to Eq. (5), R-randomness of chain calculated according to Eq. (1), M_n – number average molecular weight, D – molecular weight dispersion.

[a] Copolymerization carried out in bulk at 110 °C, initiator/comonomers molar ratio of 1:800.

microblock lengths were lower than the theoretical ones, resulting from the reactivity ratios of both comonomers. The most probable reason to this effect must have been the intermolecular transesterification processes, taking place simultaneously with the major reaction of chain propagation. Interestingly enough, the chain randomization degree (R) was noticeably higher than 1, especially for the copolymer obtained by the way of the equimolar mixture reaction (Table 5, entry 3). This indicates that a major part of the chain of this copolymer has alternating structure and the quantity of –Cap–T– sequences is larger than expected according to the Bernoulli statistics. Most of the obtained copolymers were characterized with high molar mass, similar to the theoretical estimated value. Only in the case of the copolymer containing over 80% mol of carbonate sequences, its molar mass was significantly lower. A reason for this phenomenon is the presence of large amount of carbonate sequences, well-known as ready to thermal degradation [67], and also a longer time required for total comonomers conversion in this sample.

To investigate the course of TMC/ε-caprolactone copolymerization and to determine its coefficients, a reaction of equimolar mixture of TMC and ε-caprolactone has been carried out (Table 6). The composition and structure of the arising copolymer, as well as the conversion degree of the comonomers, have been determined on the basis of NMR analysis (in chloroform or DMSO solution).

Within 6–7 h, virtually total conversion of both comonomers has been observed (Fig. 14). Caprolactone proved more reactive (Fig. 15, Table 6, entries 1–3), but the differences between the reactivity of the comonomers were less than in the case of TMC/glycolide [24] or TMC/lactide [25] copolymerization. The determined reactivity coefficients valued, respectively: $r_{cap} = 1.5$ i $r_{TMC} = 0.3$. Strong transesterification processes, occurring at every stage of the investigated reaction, caused the contraction of average microblock length. High ratio of chain randomness, much over 1, was connected with arising of longer chain sequences of alternate character, which I had observed since the beginning of the reaction. This phenomenon, after taking into account the copolymerization coefficients, suggested that it was most probably caused by intermolecular transesterification processes. As I have obtained alternate sequences of –T–Cap–T–Cap– type, the

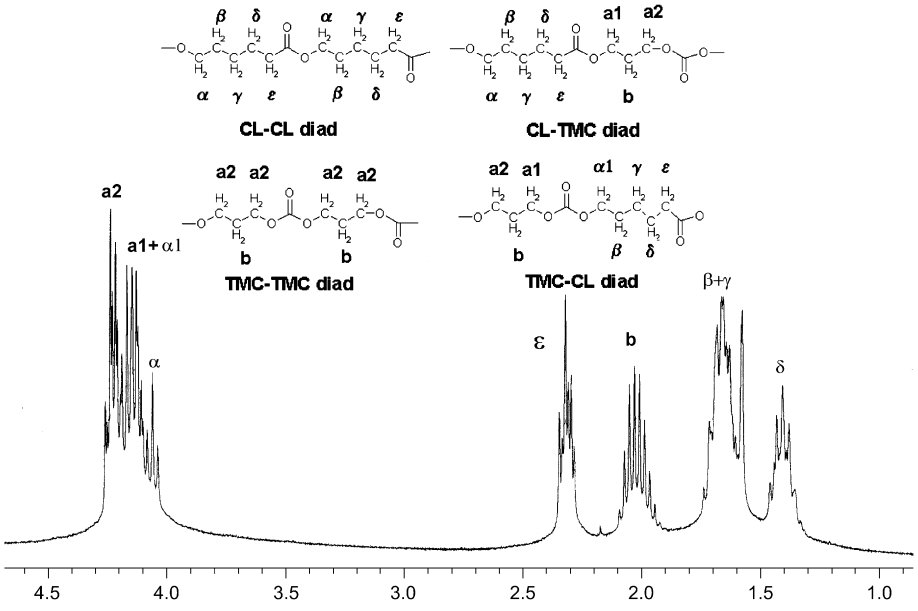


Fig. 12. ^1H NMR (in $CDCl_3$) spectrum of equimolar ε-caprolactone/TMC copolymer.

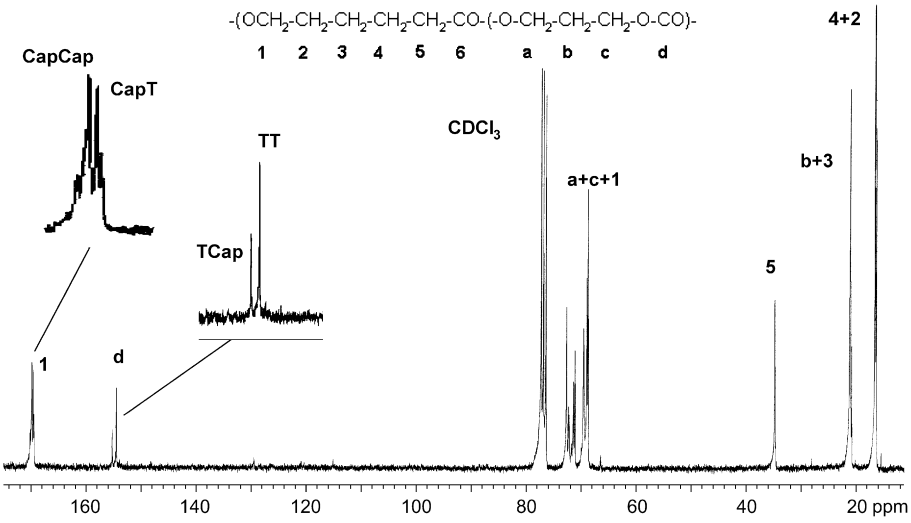


Fig. 13. ^{13}C NMR (in $CDCl_3$) spectrum of equimolar ε-caprolactone/TMC copolymer.

Table 6
Copolymerization of equimolar mixture of ε-caprolactone with TMC initiated by $Zr(Acac)_4$[a]

No	Time [h]	C_{Cap} [%]	C_T [%]	C	${}^0f_{cap}$	F_{cap}	${}^el_T$	${}^el_{Cap}$	${}^rl_T$	${}^rl_{Cap}$	R	M_n	D
1	1	61	33	47	36	65	1.2	2.2	1.7	3.1	1.6	28	1.7
2	2	88	50	69	19	62	1.1	1.8	1.8	2.9	1.4	53	1.9
3	3	98	78	89	8	55	1.3	1.6	2.0	2.4	1.4	60	1.9
4	5	~100	98	99	~0	51	1.5	1.5	2.2	2.3	1.4	67	2.0
5	24	~100	~100	~100	–	50	1.4	1.4	2.2	2.2	1.4	58	2.2

${}^0f_{Cap}$ – Initial feed molar fraction of ε-caprolactone, F_{cap} – feed molar fraction of ε-caprolactone, C_{Cap} C_T – conversion of ε-caprolactone, TMC; C – total conversion of copolymerization, ${}^el_{cap}$ – average length of caproyl microblock calculated with NMR, ${}^rl_{Cap}$ – theoretical average length of caproyl microblock calculated according to Eq. (4), ${}^el_T$ – average length of carbonate microblock calculated with NMR, ${}^rl_T$ – theoretical average length of carbonate microblock calculated according to Eq. (5), R-randomness of chain calculated according to Eq. (1), M_n – number average molecular weight, D – molecular weight dispersion.

[a] Copolymerization carried out in bulk at 110 °C, initiator/comonomers molar ratio of 1:800.

intermolecular transesterification processes must have consisted mainly of the attack of the active carbonate end of the propagating chain of one molecule on the ester bond ending the caproyl sequences of the other one; and/or of the attack of active caproyl end of the chain on the ester bonds ending the carbonate sequences of the other copolymer chain. These processes are illustrated in Scheme 5. During the copolymerization process, the effects of thermal degradation were also

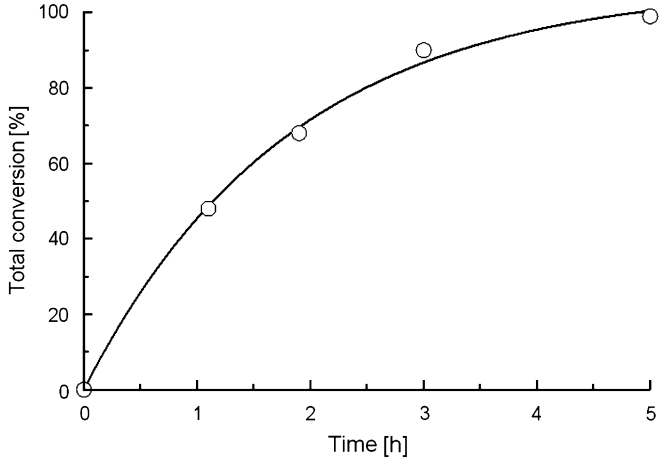


Fig. 14. Total conversion of monomers in copolymerization with M/I ratio as 800:1 of equimolar mixture of TMC with ε-caprolactone initiated with $Zr(Acac)_4$ and carried out in bulk at 110 °C.

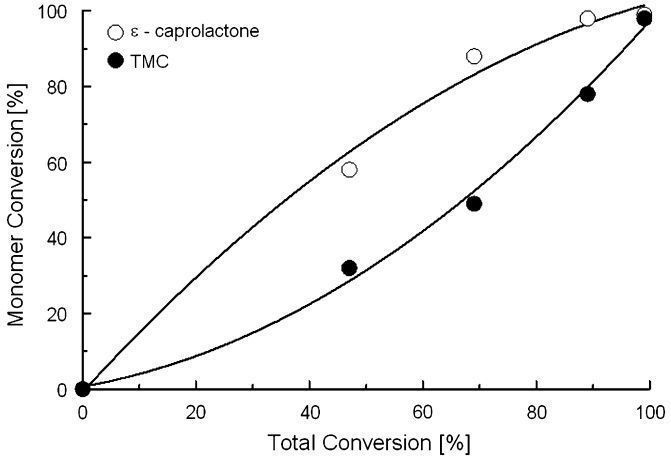
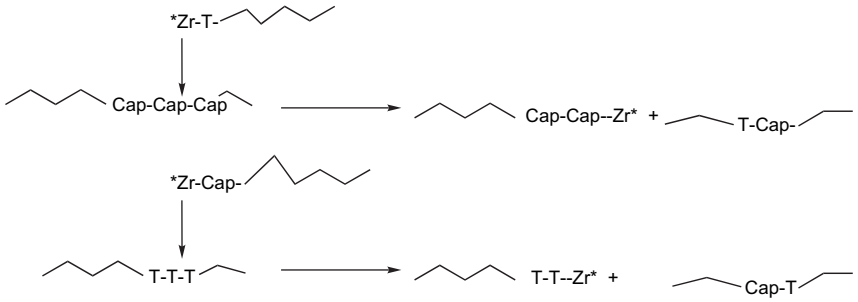


Fig. 15. Dependence of the ε-caprolactone and TMC conversion on the total conversion of the copolymerization. The starting ε-caprolactone/TMC molar ratio was of 1:1, M/I ratio as 800:1, carried out in bulk at 110 °C.



Scheme 5. Process of intermolecular transesterification.

visible, decreasing the average molar mass of the obtained copolymers (Table 6, entries 4 and 5).

References

[1] Loefgren A, Albertsson AC, Dubois P, Jerome R. J Macromol Sci Rev Macromol Chem Phys 1995;C35:379–418.
[2] Duda A, Florjańczyk Z, Hofman A, Słomkowski S, Penczek S. Macromolecules 1990;23:1640–6.
[3] Penczek S. J Polym Sci Part A 2000;38:1919–33.
[4] Kubisa P, Penczek S. Prog Polym Sci 1999;24:1409–37.
[5] Hofman A, Słomkowski S, Penczek S. Makromol Chem 1984;185:91–101.
[6] Bero M, Adamus G, Kasperczyk J, Janeczek H. Polym Bull 1993;31:9–14.
[7] Kricheldorf HR, Dunsing R. Makromol Chem 1986;187:1611–23.
[8] Hofman A, Szymanski R, Słomkowski S, Penczek S. Makromol Chem 1984;185:655–67.
[9] Kricheldorf HR, Berl M, Scharnagl N. Macromolecules 1988;21:286–93.
[10] Bero M, Kasperczyk J, Adamus G. Makromol Chem 1991;192:1777–87.
[11] Ph Dubois, Barakat RJ, Jerome R, Teyssie Ph. Macromolecules 1993;26:4407–12.
[12] Stridsberg KM, Ryner M, Albertsson A. Adv Polym Sci 2002;157:41–65.
[13] IPC INTOX Databank 1996, http://www.intox.org.
[14] Levis RJ, editor. Sax's dangerous properties of industrial materials. 8th ed. New York: Van Nostrand Reinhold; 1992.
[15] Schwach G, Coudane J, Engel R, Vert M. J Polym Sci Part A Polym Chem 1997;35:3431–40.
[16] Li S, Dobrzynski P, Kasperczyk J, Bero M, Braud Ch, Vert M. Biomacromolecules 2005;6:489–97.
[17] Rokicki G. Prog Polym Sci 2000;25:259–342.
[18] Pego AP, Grijpma DW, Feijen J. Polymer 2003;14:6495–504.
[19] Ling J, Zhu W, Shen Z. Macromolecules 2004;37:758–63.
[20] Dobrzynski P, Kasperczyk J, Bero M, Janeczek H. Macromolecules 2001;34:5090–8.
[21] Dobrzynski P. J Polym Sci Part A Polym Chem 2002;40:1379–94.
[22] Dobrzynski P. J Polym Sci Part A Polym Chem 2002;40:3129–43.
[23] Dobrzynski P, Li S, Kasperczyk J, Bero M, Gasc F, Vert M. Biomacromolecules 2005;6:483–8.
[24] Dobrzynski P, Kasperczyk J. J Polym Sci Part A 2006;44:98–114.
[25] Dobrzynski P, Kasperczyk J. J Polym Sci Part A 2006;44:3184–201.
[26] Kryczka T, Marciniec B, Popielarz-Brzezinska M, Bero M, Kasperczyk J, Dobrzynski P, et al. J Control Release 2003;89:447–56.
[27] Pamula E, Błażewicz M, Czajkowska B, Dobrzynski P, Bero M, Kasperczyk J. Ann Transplant 2004;9(Suppl. 1A):64–7.
[28] Chłopek J, Kmita G, Dobrzynski P, Bero M. Eng Biomater 2002;23–25:88–90.
[29] Hayakawa M, Mitami M, Yamada T, Makaiyama T. Macromol Chem Phys 1997;198:1305–17.
[30] Czajkowska B, Dobrzynski P, Bero M. J Biomed Mater Res Part A 2005;75:591–7.
[31] Bero M, Kasperczyk J, Adamus G. Makromol Chem 1993;194:907–12.
[32] Bero M, Kasperczyk J, Jedlinski Z. Makromol Chem 1990;191:2287–96.
[33] Dobrzynski P, Kasperczyk J, Janeczek H, Bero M. Polymer 2002;43:2595–601.
[34] Nijenhuis AJ, Grijpma DW, Penings AJ. Macromolecules 1992;25:6419–24.
[35] Dechy-Cabaret O, Martin-Vaca B, Bourissou D. Chem Rev 2004;104:6147–76.
[36] Dobrzynski P. J Polym Sci Part A 2004;42:1886–900.
[37] Jung WS, Ishizaki H, Tomiyasu H. J Chem Soc Dalton Trans 1995;1077–81.
[38] Chi Y, Lan J, Ching W, Peng S, Lee G. J Chem Soc Dalton Trans 2000;2923–7.
[39] Evans WJ, Ansari MA, Ziller JW. Polyhedron 1998;17:299–304.
[40] Janiak Ch, Lange K, Scharmann TG. Appl Organometal Chem 2000;14:316–24.
[41] Bhaw-Luximon A, Jhurry D, Spassky N, Pensec S, Belleney J. Polymer 2001;42:9651–6.
[42] Kricheldorf HR, Kreiser-Saunders J. Makromol Chem 1990;191:1057.
[43] Dobrzynski P, Pastusiak M, Bero M. J Polym Sci Part A 2005;9:1913–22.
[44] Karty JM, Janaway GA, Brauman JI. J Am Chem Soc 2002;124:5213–21.
[45] Deng X, Yuan M, Xiong C, Li X. J Appl Polym Sci 1999;73:1401–8.
[46] Yuan M, Li X, Xiong C, Deng X. Eur Polym J 1999;35:2131–8.
[47] Hypercube, Inc. 2003, http://www.hyper.com/products/Professional/index.htm.
[48] Pego AP, Zhong Z, Dijkstra PJ, Grijpma DW, Feijen J. Macromol Chem Phys 2003;204:747–54.
[49] Koening J. Chemical microstructure of polymer chains. New York: Wiley-Interscience; 1980.
[50] van Dijk JAP, Smit JAM, Kohn FG, Feijen I. J Polym Sci Polym Chem Ed 1983;21:197–208.
[51] Heuschen J, Jerome R, Teyssie P. Macromolecules 1981;14:242–6.
[52] Kricheldorf HR, Stricker A, Lossin M. J Polym Sci Part A 1999;37:2179–89.
[53] Thompson MA. ArgusLab 4.0.1, 2004 Planaria Software LLC, http://www.arguslab.com.
[54] Borve KJ, Jensen VR, Karlsen T, Stovneng JA, Swang O. J Mol Model 1997;3:193–202.
[55] Silverton JV, Hoard JL. Inorg Chem 1963;2:243–9.
[56] Meyer VE, Lowry GG. J Polym Sci Part A Gen Pap 1965;3:2843–51.
[57] Montgomerry DR, Fry CE. J Polym Sci Part C Polym Symp 1968;25:59–64.
[58] Van de Bring M, Van Herk A, German A. J Polym Sci Part A Polym Chem 1999;37:3793–803.

[59] Yoshioka K. Comput Stat 2002;17:425–37.
[60] Muller EG, Day VW, Fay RC. J Am Chem Soc 1976;98:2165–72.
[61] Takahashi Y, Kawae T, Nasu N. J Cryst Growth 1986;74:409–14.
[62] Williams PA, Roberts JL, Jones AC, Chalker PR, Bickley JF, Steiner A, et al. J Mater Chem 2002;12:165–7.
[63] Cayuela J, Bounor-Legare V, Cassagnau Ph, Michel A. Macromolecules 2006;39:1338–46.
[64] Shen Y, Shen Z, Zhang Y, Hang Q. J Polym Sci Part A 1997;35: 1339–52.
[65] Sepulchre M, Dourges M, Neblai M. Macromol Chem Phys 2000;201: 1405–14.
[66] Kricheldorf HR, Rost S. Macromolecules 2005;38:8220–6.
[67] Martele Y, Van Speybroeck V, Waroquier M, Schacht E. e-Polymers, http://www.e-polymers.org, 2002;49.