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ORIGINAL PAPER

The influence of hydroxylic compounds on cationic polymerization of ε-caprolactone mediated by iron (III) chloride in tetrahydrofuran solution

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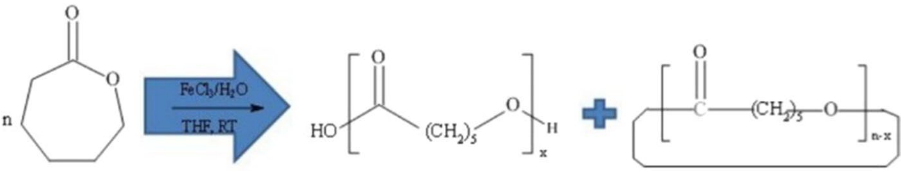
Abstract

Cationic polymerization of ε-caprolactone (CL) mediated by anhydrous iron (III) chloride ($FeCl_3$) or $FeCl_3/nH_2O$ systems (where $n=2$, 4, 6 and 8) was investigated. Reaction proceeded in tetrahydrofuran solution at room temperature. Analysis of polymers by MALDI-TOF technique revealed in both cases the formation of linear $HO{+}CO-(CH_2)_5-O{+}_nH$ as well as cyclic PCLs macromolecules. It was proposed, that in the presence of anhydrous $FeCl_3$ polymerization occurs by active chain end (ACE) mechanism accompanied by inter- and intramolecular transesterification, the latter leads to the formation of cyclic macromolecules. However, in the systems containing water two mechanisms operate simultaneously, i.e. ACE ones and activated monomer (AM) mechanism mediated witch $FeCl_3$ (catalyst)/H_2O (initiator) system, which prevails and results exclusively in linear macromolecules. Unexpectedly, methanol and dipropylene glycol used as hydroxylic additives to $FeCl_3/6H_2O$ system were inert in the polymerization. Moreover, synthesized polymers appeared to be polymodal. The results obtained differ strongly from reported previously. The course of the studied processes was discussed. Molar masses and dispersities of polymers were determined by means of size exclusion chromatography (SEC). ^{13}C nuclear magnetic resonance (NMR) was also used for analysis of the polymers. Thermal properties of the polymers obtained were also examined. Wide angle X-ray scattering was used to characterize phase composition of PCL.

Graphical abstract



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Keywords Cationic polymerization · ε-caprolactone · ACE mechanism · Iron (III) chloride · MALDI-TOF

Introduction

Poly (ε-caprolactone) (PCL) is one of the most important synthetic polymers due to wide possibilities of applying, mainly to fabrication of fibriles and for potential medical applications. PCL has uses in different fields such as scaffolds in the tissue engineering [1–4], in long-term drug delivery systems [5–7], in microelectronics [8], as adhesives [9] and in packaging [10]. It is semicrystalline polymer [11], which advantage is ease utilization by biodegradation [1–10]. PCL is synthesized by polycondensation of 6-hydroxycaproic acid [12] as well as ring-opening polymerization (ROP) of CL, i.e. anionic, cationic and coordinative ones [13]. The main classes of initiators used are alkali-based compounds (e.g. potassium hydroxide [14], potassium *t*-butoxide [14, 15], potassium hydride [14], lithium diisopropyl amide [16, 17] or phenyllithium [18]), alkaline, earth-based compounds (e.g. magnesium alkoxide complexes [19–21], calcium ammoniate [22–24] or strontium ammoniate isopropoxide [25], poor metal-based compounds (e.g. aluminium [26–48] or tin-based compounds [49–62], transition metal-based compounds (e.g. zinc mono- and di-alkoxides [63], zirconium (IV) acetylacetonate [94], iron (III) alkoxide complexes [64] and titanium complexes based on catechol ligands [65] or bisphenolate ligands[66], and rare earth metal-based compounds (e.g. scandium, yttrium, lanthanium, neodymium, cerium, gadolinium, and lutetium triflates [67–75] as catalysts with ethanol, butanol, and other hydroxylic compounds as initiators). Even organic compounds as aza-compounds [76, 77], phosphazene bases [78, 79] and various carboxylic acids, as lactic acid, tartaric acid in the presence of benzyl alcohol [80, 81] as well as enzymatic systems [82–87] can initiate the ROP of CL. However, at present metal-based compounds have been studied the most. Recently [88], simple hydrated iron group chlorides, i.e. $FeCl_3/6H_2O$, $FeCl_3/4H_2O$ and $RuCl_3/H_2O$ were used for cationic CL polymerization in bulk or toluene solution. Mechanism of this process was determined as activated monomer (AM) ones, in which metal chloride, as Lewis acid, is catalyst and H_2O or H_2O/ROH are initiators. In this paper we reported new data concerning polymerization of CL mediated by anhydrous or hydrated $FeCl_3$ in tetrahydrofuran (THF) solutions at room temperature. We changed toluene to polar THF in order to observe its influence on polymerization. The aim of this wok was determination of water effect on the process performed at various $FeCl_3/H_2O$ ratios. The effect of ROH added was also discused. Several mechanisms of processes were proposed basing of polymers analysis by MALDI-TOF and NMR techniques. Moreover, thermal properties of the prepared polymers were also examined.

Experimental

Materials

ε-Caprolactone (CL) was purchased from Aldrich, dried and distilled prior to use. Methanol and dipropylene glycol (DPG) (ALDRICH) were used after drying by molecular sieves. Water was distilled twice before use. Anhydrous $FeCl_3$ and $FeCl_3{\cdot}6H_2O$ were purchased from Aldrich and used as received. Anhydrous tetrahydrofuran (THF) (Acros Organics) was distilled over K/Na alloy prior to use. All materials were storage in glass ampoules equipped with Teflon valves under argon atmosphere at room temperature.

Polymerization procedure

All experiments were carried out at $[CL]_o = 5.0$ and $[FeCl]_o = 0.01$ mol/dm^3 in the presence of various amounts of H_2O and also MeOH or DPG as additives in some cases. For example, anhydrous $FeCl_3$ (0.0324 g, 0.19 mmol) was introduced into a glass reactor (50 cm^3) with two Teflon valves, filled by dry argon and THF (9.0 cm^3) was then added. Next, H_2O (0.021 g, 1.17 mmol) was added by microsyringe and mixed vigorously by magnetic stirred for 10 min at room temperature. Finally, CL (11.0 g, 0.877 mol) was slowly added to the system and mixed for 10 h. Arise in viscosity was observed and finally the stirring ceased. After the specified time, i.e. 170 h the reaction mixture was quenched by small amount of wet THF. The polymer was precipitated by pouring the mixture in cold *n*-hexane, filtered and further dried in vacuum at 60 °C for 20 h.

Measurements

100 MHz ^{13}C nuclear magnetic resonance (NMR) spectra were recorded in $CDCl_3$ at 25 °C on a BrukerAvance 400 pulsed spectrometer equipped with 5 mm broad-band probe and applying Waltz16 decoupling sequence. Chemical shifts were referenced to an internal standard (TMS). To reveal microstructural details of the polymer main chain high quality spectrum must be recorded with 3000 scans being satisfactory amount, however to observe the signals of the polymer chain ends more than 10,000 scans was necessary.

Molar masses and dispersities of polymers were determined by means of size exclusion chromatography (SEC) on a Shimadzu Prominance UFLC instrument at 40 °C on a Shodex 300 mm × 8 mm OHpac column using tetrahydrofuran as a solvent. PSs were used as calibration standards.

Molar masses and dispersities were also determined by SEC with a Viscotek GPC Max VE 2001 and a Viscotek TDA 305 triple detection (refractometer, viscosimeter, and low angle laser light scattering). The OmniSec 5.12 was used for data processing. The apparatus was used in the triple detection mode, and absolute molecular weights and dispersities obtained with calibration with a polystyrene standard.

Matrix-assisted laser desorption/ionization-time of flight (MALDI-TOF) spectra were recorded on a Shimadzu AXIMA Performance instrument with dithranol used as a matrix.

Differential Scanning Calorimetry (DSC) was performed using the Mettler Toledo apparatus. Samples were heated, cooled and reheated with a speed of 10 °C/min, in the temperature range of −100–120 °C. The DSC curves taken for the analysis were obtained from the second run. Temperature calibration was performed with indium (melting temperature = 156.6 °C), heat of fusion ($\Delta H_f = 28.5$ J/g).

Phase composition investigations of materials were performed by powder X-ray diffraction (XRD) method using a Empyrean Panalytical diffractometer and CuKα ($\lambda = 0.1542$ nm) radiation equipped with PIXcel3D detector. The data collection was over the 2-theta range of 5°–100° in of 0.02° steps.

The phase content of each sample was calculated from the XRD scattering profiles with peak deconvolution method using the Origin OriginLab 2020b software. We used the fitting method with Gaussian profiles assumed for all scattering peaks and halos as proposed by Stoclet et al. [89]. The content of each phase (amorphous and crystalline) was calculated based on the area under the diffraction peaks by calculating the ratio from one phase to the total scattering peaks. XRD scans were taken at room temperature.

Spectrophotometer measurements were performed on the FTIR ATR device (Shimadzu IR Prestige) equipped with diamond ATR crystal purified prior to measurement with i-propanol. Data were analyzed using the LabSolutions program.

Results and discussion

Several PCLs were synthesized at the same $[CL]_o/[FeCl_3]_o$ (monomer/catalyst) molar ratio, i.e. 500/1 without additives and with various initiators at different initial concentrations. The chemical structure of the polymers obtained was analyzed by MALDI-TOF spectrometry and ^{13}C NMR spectroscopy. Molar masses and dispersities of polymers were determined by SEC chromatography and, comparatively, in one case also by light scattering (LS) technique.

Structural analysis and mechanistic considerations

Polymerization of CL catalyzed by anhydrous $FeCL_3$

In 2009 Chakraborty et al. [88] reported, that anhydrous $FeCl_3$ alone, as Lewis acid can be used catalytically for the bulk polymerization of CL at 27 °C. The polymer prepared at $[CL]_o/[FeCl_3]_o = 200/1$ ratio has appreciably high $M_n = 19\,400$ (measured by SEC relative to polystyrene standards with Mark-Houwink corrections for M_n in the case of CL polymerizations [90]) in the relation to M_n (calcd) = 22,800. Polymer is unimodal with relatively high dispersity

Table 1 Characterization of products prepared in the polymerization of CL catalyzed by anhydrous $FeCl_3$ in THF at room temperature

No.	$[CL]_o$ mol/dm^3	$[FeCl_3]_o$ mol/dm^3	Yield (%)	M_n (calcd)^b	M_n (SEC)	M_w/M_n (SEC)^b	M_n (LS)	M_w/M_n (LS)
1	2.0	0.1	35.0^a	–	–	–	–	–
2	5.0	0.01	99.5	57,088	(a) 8500 (85%) (b) 2500 (10%) (c) 1000 (5%)	1.12 1.07 1.05	14 500	1.20

^{a}Determined by ^{13}C NMR

^{b} M_n (calcd) = $([M]_o/[Cat]_o/M_{CL} + M_{H2O}$

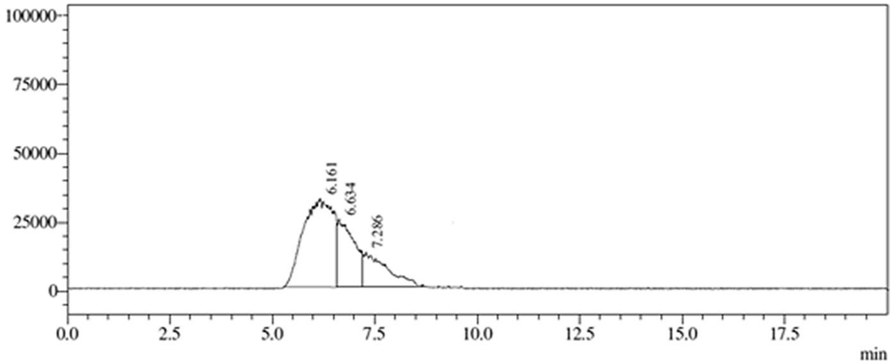


Fig. 1 SEC chromatogram of PCL (2) synthesized by anhydrous $FeCl_3$

($M_w/M_n = 1.87$). After 1 h the yield was 100%. However, the course of the process was not proposed. Therefore, we performed this polymerization at room temperature using THF as a solvent. At $[M]_o = 2.0$ and $[Cat]_o = 0.1$ mol/dm^3 after 150 h only oligomers and unreacted monomer were found solubilized in the reaction mixture. However, at much higher initial concentration of monomer and lower concentration of catalyst trimodal polymer was obtained (Table 1). SEC chromatogram of polymer (2) was shown in Fig. 1.

The chromatogram shows two main polymer's fractions and low molar-mass tail. This phenomenon was unexpected and needs further studies. Comparatively, the result of analysis of this polymer by light scattering was presented below in Fig. 2. This method gives real molar mass values, however, none data concerning modality of polymer.

In order to determine chemical structure of the polymer several techniques, i.e. MALDI-TOF, NMR and FTIR were applied. Figure 3 presents MALDI-TOF spectrum of PCL (2).

MALDI-TOF spectrum reveals two main series of signals. First one containing signals with higher intensity at *m/z* 839.2 to 4284.7 represents polyester

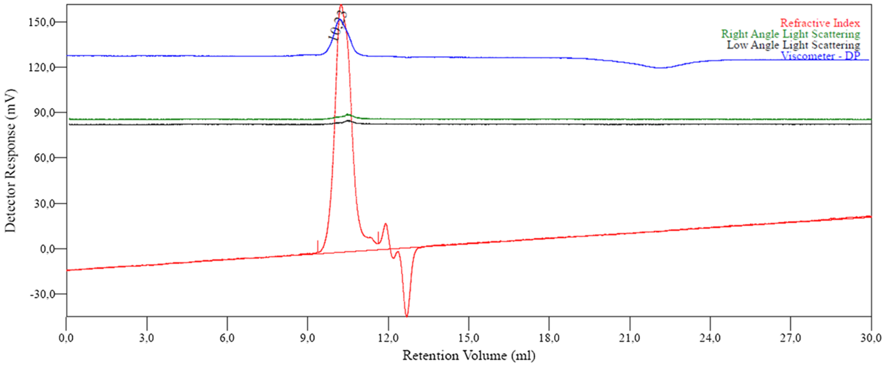


Fig. 2 SEC—MALS analysis of PCL (2)

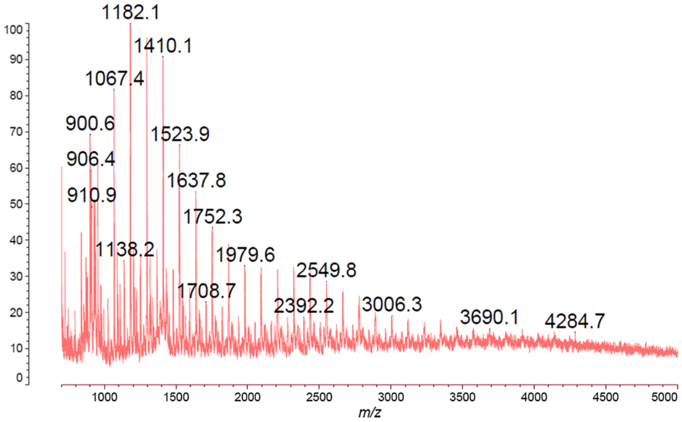


Fig. 3 MALDI-TOF spectrum of PCL (2) prepared with anhydrous $FeCl_3$

macromolecules with carboxyl and hydroxyl end groups. For example, signals at *m/z* 1067.4, 1752.3 and 3006.3 belongs to macromolecules containing 9,15 and 26 mers of CL as well as H and OH derived from initiator. They form adducts with Na^+ ions. ($M_{calcd} = 1068.3$, 1753.1 and 3008.0 respectively). The second series reveals the signals with much lower intensity at *m/z* 795.8–2989.3. They presumably represent cyclic PCL macromolecules, which form adducts with H^+ ions. For example, signals at *m/z* 1138.2, 1708.7 and 2392.2 belong to cycles with 10, 15 and 21 mers od CL ($M_{calcd} = 1142.4$, 1712.9 and 2397.5, respectively).

^{13}C NMR spectrum shows high signals of carbon atoms derived. From CL mers at 24.7, 25.7, 28.5, 34.3, 64.3 and 173.7 ppm and confirm the presence of—$\underline{C}H_2OH$ (62.7 ppm) and—$\underline{C}H_2COOH$ (33.4 ppm) end groups in linear macromolecules of the synthesized polymer (2) (Fig. 4).

Basing on the results obtained we proposed the course of CL polymerization catalyzed by anhydrous $FeCl_3$ (Scheme 1). In the first step exocyclic oxygen atom of

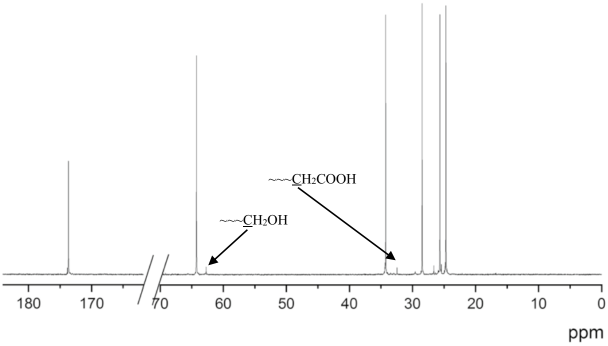
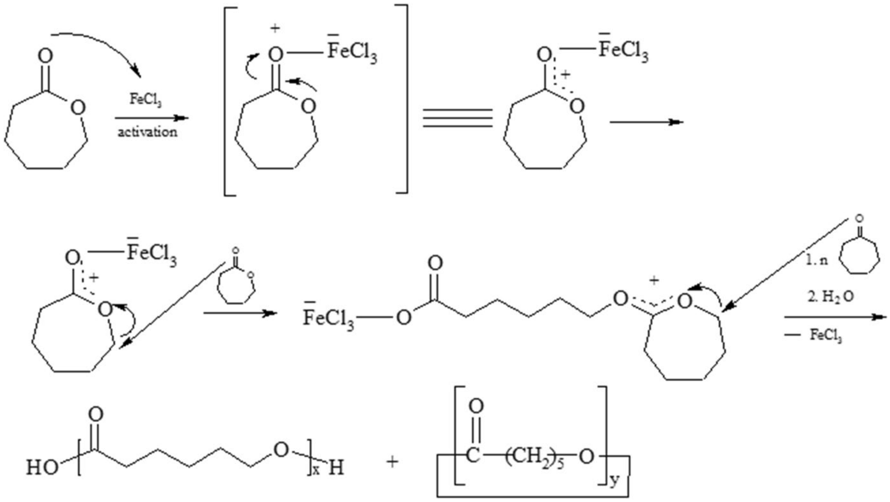


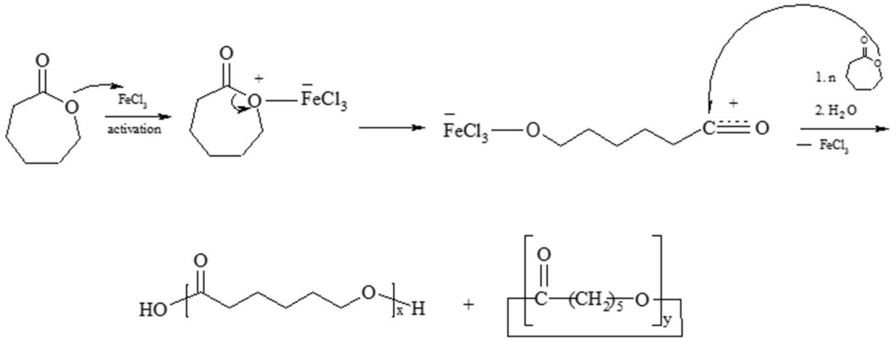
Fig. 4 ^{13}C NMR spectrum of PCL (2) obtained with anhydrous $FeCl_3$



Scheme 1 Active chain end (ACE) mechanism in cationic CL polymerization catalyzed with $FeCl_3$ (propagation proceeds by alkyl-oxygen bond cleavage)

the monomer attacks the catalyst. The propagation proceeds according to the principal mechanism of the cationic ROP of oxygen-containing heterocyclic monomers called active chain end (ACE) mechanism by nucleophilic attack of oxygen atom in monomer on α-carbon atom in tertiary oxonium ion located at the growing chain end. The process occurs by alkyl-oxygen bond cleavage and is accompanied by inter- and intramolecular transesterifications as side transfer reactions. The former leads to linear products and caused increasing of polymer dispersity. The second one occurs by back-biting and/or end-to-end closure resulting in the formation of cyclic macromolecules and great decreasing of molar masses.

We considered also other mechanism of this process, involving attack of the endocyclic oxygen atom of CL on $FeCl_3$ catalyst (Scheme 2) and then on acylium cation. It also results in linear and cyclic macromolecules. However, this mechanism



Scheme 2 Active chain end (ACE) mechanism in cationic CL polymerization catalyzed with $FeCl_3$ (propagation proceeds by acyl-oxygen bond cleavage)

is less probable due to the fact, that the endocyclic oxygen is less nucleophilic, than the exocyclic one [90]. Moreover, in the first case delocalization of the positive charge strongly stabilizes the cation formed, therefore the mechanism on Scheme 1 is preferred.

Polymerization of CL mediated by hydrated $FeCl_3$

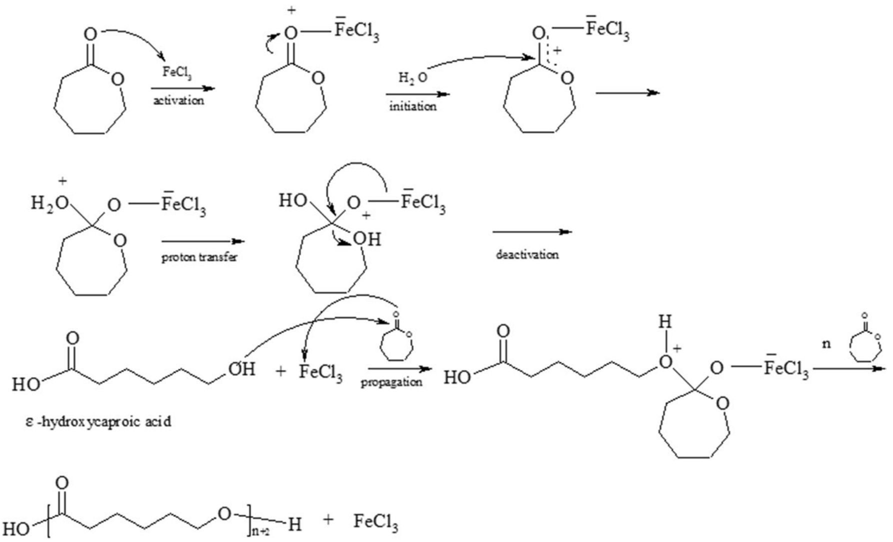
In the second step of the work we studied the polymerization catalyzed by $FeCl_3$ in the presence of water used as initiator. Concentration of water was in the wide range from 0.02 to 0.08 mol/dm^3. The results obtained were collected in Table 2.

Synthesized polymers (3)–(6) were bimodal or trimodal and their molar masses (M_n) estimated by SEC method were lower than calculated ones. In general, disperisities of fractions (a) were relatively high ($M_w /M_n = 1.11–1.52$), whereas those of fractions (b) and (c) were extremely low ($M_w/M_n = 1.01–1.05$). Similar result

Table 2 Characterization of PCLs synthesized in polymerization mediated by $FeCl_3/H_2O$ (catalyst/initiator) system in THF at room temperature; $[CL]_o = 5.0$ mol/dm^3; $[FeCl_3]_o = 0.01$ mol/dm^3

No.	$[I]_o$ mol/dm^3	CL/OH ratio	Yield (%)	M_n (calcd)^a	M_n (SEC)^b	M_w/M_n (SEC)^b
3	0.02	250/1	98.5	28,553	(a) 7700 (60%)	1.11
					(b) 350 (22%)	1.04
					(c) 1400 (18%)	1.13
4	0.04	125/1	99.0	14,285	(a) 3500 (90%)	1.52
					(b) 900 (10%)	1.01
5	0.06	~83/1	99.2	9529	(a) 4100 (93%)	1.37
					(b) 1000 (7%)	1.04
6	0.08	~63/1	98.9	7151	(a) 6800 (60%)	1.12
					(b) 3000(30%)	1.04
					(c) 1400 (10%)	1.05

$^a M_{n\ calcd} = ([M]_o/[I]_o)/M_{CL} + M_{H2O}$

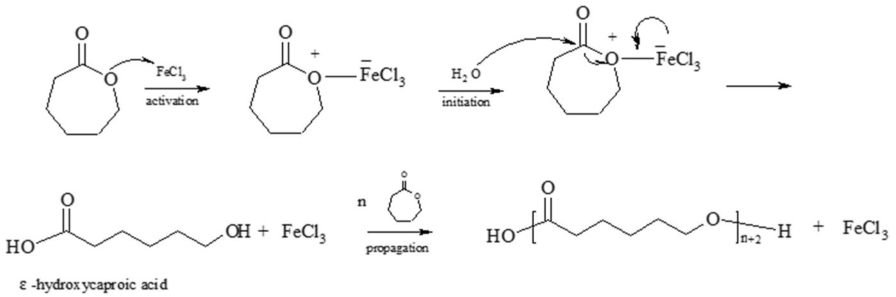


Scheme 3 Activated monomer (AM) mechanism in cationic polymerization of CL mediated with $FeCl_3$/H_2O system (propagation proceeds by acyl-oxygen bond cleavage)

obtained by use of commercial $FeCl_3{\cdot}6H_2O$ from ALDRICH. Comparatively, polymers obtained in [88] by $FeCl_3{\cdot}6H_2O$ were unimodal and had higher M_n and dispersity depending on initial concentration of monomer. Analysis of the polymers (3)–(6) by MALDI-TOF technique indicated the formation of linear and small amount of cyclic macromolecules in all cases, independently of amount of water added. The latter were not observed previously by Chakraborty et al. [88] in the polymerization of CL mediated by $FeCl_3{\cdot}6H_2O$ system at CL/OH ratios equal to 200/1, 167/1, 133/1, 67/1 and 33/1 in bulk or toluene solution at 27 °C. We suggested, that this polymerization proceeds predominantly by activated monomer (AM) mechanism shown on Scheme 3 adapted from [88]. In the first step of the process exocyclic oxygen atom of carbonyl and group in the monomer interacts with metal atom of catalyst and then water attacks carbonyl carbon atom. Then, CL ring opens by acyl-oxygen bond cleavage simultaneously with leasing of $FeCl_3$. The reaction product, i.e. ε-hydroxycaproic acid reacts with complex of CL with activated monomer, which induces further chain growth. However, activated monomer can also react with next H_2O molecules generating new macromolecules.

However, we proposed an alternative version of AM mechanism, in which endocyclic oxygen atom in the monomer molecule interacts with metal atom of the catalyst and water attacks carbonyl carbon atom. These way also leads to the same intermediated product, i.e. *ε*-hydroxycaproic acid (Scheme 4). Similar mechanism was suggested by Basko et al. [91] for polymerization of *β*-butyrolactone performed in CH_2Cl_2 solution at room temperature in the presence of CF_3SO_2H as the catalyst and isopropanol as the initiator.

Formation of cyclic PCL fraction observed in our work was rather unexpected. In order to explain this phenomenon we suggested, that small part of $FeCl_3$ catalyzes



Scheme 4 Cationic polymerization of CL mediated by $FeCl_3/H_2O$ system according to AM mechanism with alternative way of monomer activation (propagation proceeds by acyl-oxygen bond cleavage)

polymerization without participation of water. Consequently, two mechanisms, i.e. AM, which prevails and ACE operate simultaneously in the polymerization mediated by $FeCl_3$/n H_2O systems in THF solution at room temperature. This phenomenon can be explained by the presence of polar solvent, which interacts with water by formation of hydrogen bonds. It decreases the reactivity of water in the initiation step of polymerization.

Polymerization of CL mediated by $FeCl_3$/6 H_2O in the presence of alcohols

It was reported by Chakraborty et al. [88], that in the CL bulk polymerization mediated by $FeCl_3$/6 H_2O addition of alcohol (EtOH, *i*-PrOH, BnOH or glycol at $H_2O/ROH = 6/5$ ratio) enhance the tendency to increase of molar masses ($M_n = 59{,}800–82{,}000$) and produce hydroxy- and alkoxy-end terminal functionalized product, e.g. $\mathrm{BnO}{-}[\mathrm{CO}{-}(\mathrm{CH_2})_5{-}\mathrm{O}]_n{-}\mathrm{H}$ which prevails.

Using toluene as a solvent, M_n of the latter diminishes from 67,200 to 18,200 at the same concentrations of reagents. Comparatively we carried out similar polymerizations in the presence of MeOH or DPG in THF solution (Table 3).

Table 3 Characterization of PCLs prepared by polymerization occurred with $FeCl_3/6H_2O/5MeOH$ or $FeCl_3/6H_2O/5DPG$ in THF solution at room temperature; $[CL]_o = 5.0$ mol/dm^3; $[FeCl_3]_o = 0.01$ mol/dm^3; $[H_2O]_o = 0.06$ mol/dm^3; $[MeOH]_o = 0.05$ mol/dm^3; $[DPG]_o = 0.05$ mol/dm^3

No.	$[I]_o$ mol/dm^3	CL/OH ratio	Yield (%)	M_n (calcd)[a]	M_n (SEC)[b]	M_w/M_n (SEC)[b]
7	H_2O/MeOH (0.11)	45.5/1	96.6	5210	(a) 6500 (62%)	1.13
					(b) 2800(28%)	1.03
					(c) 1100 (10%)	1.04
8	H_2O/DPG (0.11)	45.5/1	99.1	5210	(a) 9100 (50%)	1.12
					(b) 3300 (40%)	1.05
					(c) 900(10%)	1.01

[a] $M_{n\ calcd} = ([M]_o/[I]_o)/M_{CL}\ M_{H2O}$

Unexpectedly, in both studied systems alkoxy-end terminal functionalized products were not detected using MALDI-TOF and NMR techniques. It means, that alcohols used did not react as initiators. Polymerization occurred according to AM and ACE mechanisms resulting mainly in $HO-\left(CO-(CH_2)_5-O-\right)_nH$ macromolecules as well as cyclic macromolecules as side products. Interestingly, in all studied systems several polymer fractions were formed with various yields, molar masses and dispersity. Presumably, polarity of the solvent used influences the formation of ionic centers with various reactivities, which are responsible for such effect. However, this phenomenon is unexpected and needs further studies.

Properties of the obtained polymers

Differential scanning calorimetry (DSC)

One of the techniques for analyzing the thermal behavior of polymers is differential scanning calorimetry (DSC). It enables to description of the polymers structure by determining the temperature and effects associated with physical changes in these materials. The typical DSC curve of PCLs obtained are shown in Fig. 5.

The endothermic peaks at 29.28 °C (2), 33.26 °C (3), 30.07 °C (4), 30.57 °C (5), 29.58 °C (6), 30.00 °C (7), 30.85 °C (8) without mass loss is due to the melting of the crystalline phase of PCL, which gives a ΔH values of 76.20 J g^{-1} for polymer 2; 74.74 J g^{-1} for polymer 3; 77.48 J g^{-1} for polymer 4; 76.63 J g^{-1} for polymer 5; 73.86 J g^{-1} for polymer 6; 72.21 J g^{-1} for polymer 7 and 78.62 J g^{-1} for polymer 8. The similar results indicate that initiators and different initial concentrations used in

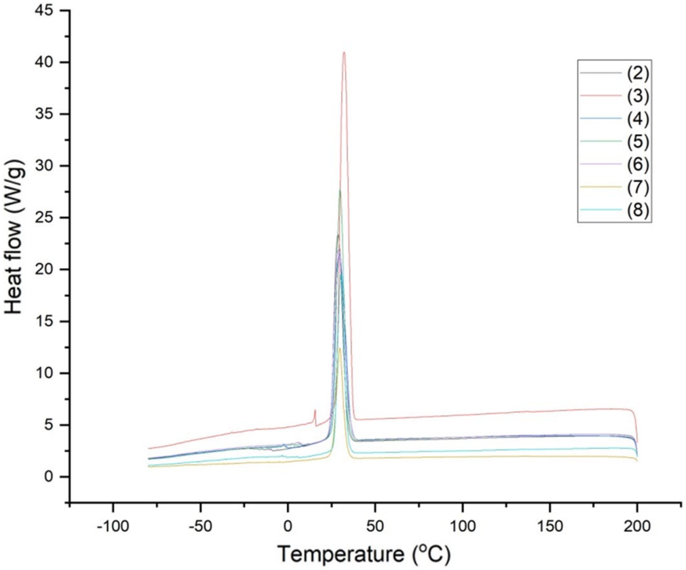


Fig. 5 Thermograms for obtained polymers (2)–(8)

the polymerizations do not affect the thermal properties of the obtained PCLs. The results obtained are consistent with those proposed by Ting Ting Sui et al. [92].

Wide angle X-ray scattering

XRD was used to characterize phase composition of PCL. The amorphous phase content was estimated by the area of the amorphous halo with a peak at a 2θ value of approximately 21°. For all samples the peaks of (110), (111), and (200) orthorhombic crystalline face were found [93]. The calculated crystalline content (%) is shown in Table 4. The samples display an isotropic scattering profile with a diffused amorphous halo and sharp crystalline peaks. Three peaks at 2θ values of 21°, 22° and 24 ° are repeatedly observed in all samples (Fig. 6). All of them are characteristic to crystalline PCL. The diffraction at 21° is attributed to the (110) faces while at 24° to the (200) faces corresponding to the orthorhombic crystal lattice of PCL [89]. A small peak seen at a 2θ value of 22° is associated with the (111) plane of the same unit cell [94]. These states of order are associated with both the LAMELLAR folding and intermolecular spacing specific to each crystal face. Variation of the peak intensities and peak widths among the samples can be seen—the broadening of a crystalline peak manifests either decreasing crystal size or increasing structural disorder within the sample.

The peak ratios of the faces is changing in the range of ($I_{(110)}/\mathrm{I}_{(200)}$) in the studied group. The observed changes deliver information about possible formation of condis crystal mesophase orientation. Condis crystals (conformationally disorder crystals) were described as a type of mesophase in the solid state material with birefringent properties connected to positional and orientation order, and partial or full conformational disorder.

Along with increase in initiator concentration (P3-P6) 3 diffraction peaks were observed for P3, P4 and P6, while P5 XRD pattern revealed presence of 2 main diffraction peaks with side-shoulder. P5 is also the sample characterized with the lowest value of $I_{(110)}/I_{(200)}$ratio. This observation may reflect the lowest content of the mesophase-type orientation in this sample. The calculated crystalline content (%)

Table 4 Phase content based on the quantitative structural analysis obtained by peak deconvolution of the integrated XRD scattering profiles for PCLs (2)-(8)

No.	Peak 1 position [2θ]	Peak 2 position [2θ]	Peak 3 position [2θ]	$\mathrm{I}_{(110)}/\mathrm{I}_{(200)}$	Crystalline content (%)	Amorphous content (%)
2	21.53343	22.13742	23.84436	3.08085	58.35	41.65
3	21.27082	21.90107	23.58175	2.62145	34.18	63.82
4	21.53343	22.13742	23.84436	2.88138	62.28	37.72
5	21.58595	x	23.92314	2.43714	49.75	50.25
6	21.19204	21.79603	23.50297	2.54742	52.00	48.00
7	21.27082		23.58175	2.53888	26.32	73.68
8	21.13952	21.76977	23.45045	2.79518	46.89	53.11

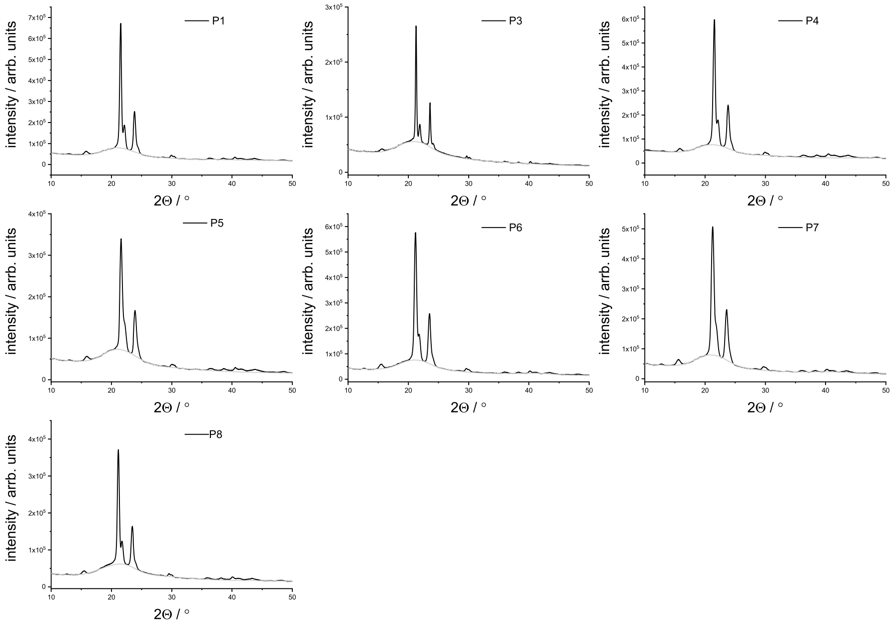


Fig. 6 The integrated XRD profiles of polymers (2)-(8)

was the highest for P4 sample (62.28%), followed by P6 (52.00%), P5 (49.75%) and P3 (34.18%). By looking at this sequence one may indicate that in this series the proneness of the PCL to form crystalic–type package is influenced by the average molecular weight of the polymer. The lowest value of M_n was reported for P4 sample (Table 2), while the highest was calculated for P3 sample (Table 2). Additionally, P4 was characterized with the highest dispersity, which is an indicator of greater extend of variation of macromolecules' length. Additional presence of MeOH (P7) or DPG (P8) led to decrease in crystalline content to 26.32% (P7) and 46.89% (P8). P7's XRD pattern revealed presence of 2 diffraction peaks with side-shoulder part and this sample is characterized with the lower value of $I_{(110)}/I_{(200)}$ ratio. Contrary to the previous series (P3-P6) the increased average molecular weight did not hampered crystalline phase formation. It seems that there are additional forces that favor alignments, which are induced by dipropylene glycol presence.

FTIR analysis

For P2 sample FT-IR spectrum is shown in Fig. 7. The most prominent characteristic absorption peak of PCL, which is linear aliphatic polyesters, is located at 1720–1730 cm^{-1} and corresponds to the carbonyl stretching mode of the ester group [95]. The changes of the shape of this band correlates well with the melting and crystallization processes. Two separated carbonyl bands were prescribed to amorphous (1735 cm^{-1}) and crystalline regions (1725 cm^{-1}) [96]. Their intensities described as absorbances value are helpful in establishment of the relative amount

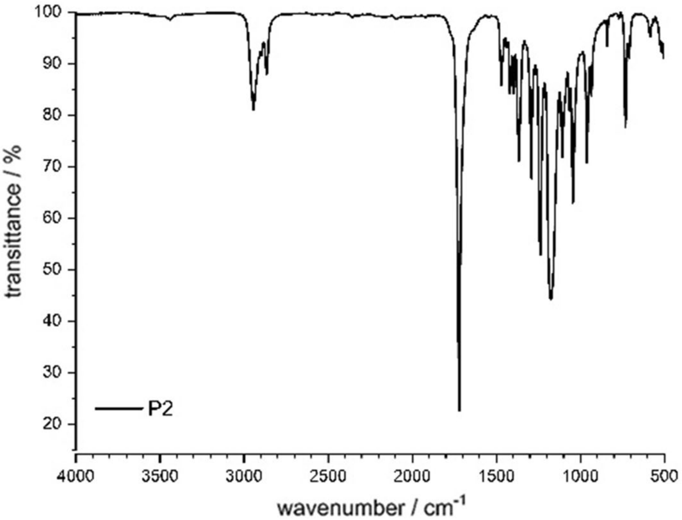


Fig. 7 FTIR spectra of PCL (2)

of crystalline and amorphous fractions [97]. Additional strong band at 1174 cm^{-1} is visible corresponding to stretching vibration mode of C–O–C part [98]. Furthermore, P2 spectrum shows peaks of CH_2 stretching vibrations corresponding to alkyl chain structure [99, 100]. The C-H both symmetric and anti-symmetric stretching are seen with peaks at 2864 and 2945 cm^{-1} respectively. A broad peak around 3425 cm^{-1} is due to the OH stretching of PCL end group.

Conclusions

Both anhydrous and hydrated $FeCl_3$ mediated ε-caprolactone (CL) polymerization in tetrahydrofuran (THF) solution at room temperature. The main features of these processes are:

1. Anhydrous $FeCl_3$ catalyzed CL polymerization proceeding by ACE mechanism leading to linear macromolecules, however, cyclic macromolecules are also formed by intramolecular transesterification.
2. Addition of water as initiator resulted in occurrence of AM mechanism of polymerization, which operates simultaneously with ACE ones at wide range of $FeCl_3$ / H_2O ratio (1/2,1/4,1/6 and 1/8), however, the AM mechanism prevails.
3. Alcohols, i.e. MeOH and DPG use together with water appeared to be completely inactive in the studied process.
4. The polyesters obtained were polymodal and consisted of two or three fractions with various yields, M_n and M_w/M_n.

5. XRD analysis showed the coexistence of two phases, i.e. —crystal and amorphous ones with possible mesophase orientation formation. The calculated crystalline content (%) was the highest for P4 sample due to its lowest average molecular weight.
6. Addition of either MeOH (P7) or DPG (P8) led to decrease in crystalline content to 26.32% (P7) and 46.89% (P8). Still it seems that there are additional forces that favor alignments, which are induced by presence of dipropylene glycol.
7. Unexpectedly, the results obtained in this work differ strongly from these reported previously [88], probably due to the influence of THF used as a polar solvent.

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