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Author: Zbigniew Grobelny, Justyna Jurek-Suliga, Sylwia Golba

Citation style: Grobelny Zbigniew, Jurek-Suliga Justyna, Golba Sylwia. (2020). New way of anionic ring-opening copolymerization of β-butyrolactone and ε-caprolactone : determination of the reaction course. "Journal of Polymer Research" (2020, iss. 12, art. no. 359, s. 1-10), DOI: 0.1007/s10965-020-02333-9

Journal of Polymer Research (2020) 27:359
https://doi.org/10.1007/s10965-020-02333-9

ORIGINAL PAPER

New way of anionic ring-opening copolymerization of β-butyrolactone and ε-caprolactone: determination of the reaction course

Zbigniew Grobelny[1] · **Justyna Jurek-Suliga**[2] · **Sylwia Golba**[2]

Received: 27 May 2020 / Accepted: 23 October 2020

Abstract

Poly(ε-caprolactone)-*block*-poly(β-butyrolactone) copolymers were prepared in two-step synthesis. Firstly, poly(ε-caprolactone) (PCL) was obtained by anionic ring-opening polymerization of CL initiated with anhydrous KOH activated 12-crown-4 cation complexing agent. Reaction was carried out in tetrahydrofuran solution and argon atmosphere at room temperature. Then, β-butyrolactone (BL) and 18-crown-6 were added to the system, resulting in PCL-*block*-PBL copolymer, which contains after methylation hydroxyl starting group and methyl ester end group. The main product was contaminated with PCL and PBL homopolymers formed in a side reactions. ^{13}C NMR technique was used for determination of chemical structure of polymers obtained. The course of the studied processes was proposed. MALDI-TOF technique was used to reveal the macromolecules' architecture where several series were found. The identified series shown that mainly copolymeric macromolecules were formed with scare contribution of homopolymeric polybutyrolactone with *trans*-crotonate starting groups and polycaprolactone, which is congruent with the proposed reaction mechanism. Moreover, critical approach concerning previously reported PCL-*block*-PBL copolymer synthesis by use of NaH as initiator was also presented.

Keywords Polymer synthesis · Anionic ring opening polymerization · Copolymers · ε-caprolactone · β-butyrolactone

Introduction

Biodegradable polymers, such as poly(glycolide), poly(lactide), poly(β-butyrolactone) and poly(ε-caprolactone) [1–3] have several medical application, for example as bioabsorbable materials. It is necessary for the polyesters to present different mechanical and physical properties to adjust the adequate time of their degradation. Copolymerization is attractive for modulating the basic properties of each homopolymer [4–6]. Particularly interesting are block copolymers, which have a larger number of applications. Blocks with different physical properties, for example a soft, amorphous segment together with a hard semicrystalline one, can be used to modulate the thermal and mechanical material behavior [4, 7–9]. The soft phase provides elasticity and influences on the degradation behavior, whereas the rigid phase gives mechanical strength and acts as a physical crosslinker [6]. The successive ring opening polymerization of β-butyrolactone (BL) and *L*-lactide (LLA) [7] or ε-caprolactone (CL) [8, 10] results in block copolymers consisting of PBL as a softer segment and PLLA or PCL as a harder ones. However, many effective catalysts based on tin-compounds were applied for the synthesis. These compounds are toxic and polymers obtained become non useful for pharmaceutical and biomedical applications [2, 6]. In the literature one may found examples of application of anionic polymerization to obtain the copolymers comprising of CL and BL blocks [11–13]. Till now, only one paper presents the possibility of the anionic copolymerization of BL and CL by use of low toxic sodium hydride as initiator [14]. The mentioned process was conducted in bulk containing both monomers at 70 °C. Yields of copolymers are greatly influenced by the molar ratio of monomers BL/CL. The molar composition of PBL-*block*-PCL copolyesters, determined by NMR spectra showed, that incorporation of CL is favored over the incorporation of BL. These copolymers are stable up to temperatures near 200 °C. The crystallization process was studied by DSC and WAXS showing,

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✉ Zbigniew Grobelny
zbigniew.grobelny@us.edu.pl

[1] Institute of Chemistry, Faculty of Science and Technology, University of Silesia, 40-007 Katowice, Poland

[2] Institute of Materials Engineering, Faculty of Science and Technology, University of Silesia, 40-007 Katowice, Poland

that the amorphous PBL segments chain do not affect the crystallinity of the PCL blocks. However, the course of copolymerization proposed by authors [14] seems to be questionable.

The aim of the present work was reinvestigation of PCL-*block*-PBL copolymerization initiated with NaH. Moreover, new concept of block copolymers synthesis was proposed by using of anhydrous KOH as initiator in tetrahydrofuran solution at room temperature. The course of the process was proposed and discussed.

Experimental

Materials

β-Butyrolactone (Aldrich, Poland) was heated over CaH_2 for 5 h at 50 °C and then distilled under a dry argon atmosphere. The fraction boiling at 47 °C/ 5 Torr with purity 99.6% was collected. ε-Caprolactone (Aldrich, Poland) was distilled in vacuum at 39°-41 °C/0.7 Torr. Anhydrous tetrahydrofuran (THF) (Acros Organics, Poland) was kept over CaH_2 at room temperature and distilled at 66 °C before use. 12-Crown-4 (12C4), 18-crown-6 (18C6) (Merck, Poland), NaH (Aldrich, Poland) and CH_3I (Aldrich, Poland) were used for synthesis without purification. Potassium hydride (KH) was purified as it was described previously [15].

Polymerization

All syntheses were carried out at room temperature in a 50 cm^3 reactor equipped with a magnetic stirrer and a Teflon valve enabling substrates delivery and sampling under argon atmosphere. Homopolymerization of BL and CL and their copolymerization mediated with NaH were carried out in bulk at 70 °C according to literature data [14]. Polymerization of CL initiated with anhydrous KOH activated 12C4 in THF solution at room temperature was performed according to the method described previously [14]. Potassium hydroxide was obtained in the reaction of pure potassium hydride with distilled water in THF. KH (0.08 g, 2.0 mmol), THF (15.8 cm^3) and 12C4 (0.88 g, 4.0 mmol) were introduced into the reactor, and then water (0.036 g, 2.0 mmol) was added by use of a microsyringe. The reaction mixture was then stirred for 30 min until all hydrogen (44.7 cm^3) was evolved. This resulted in a fine dispersion of pure anhydrous potassium hydroxide in the ether medium. The reactors for synthesis of KOH and polymerization of BL initiated with NaH were performed in glass apparatus à 50cm^3 equipped with a magnetic stirrer and two Teflon valves. One of them enabled substrates delivery, the second was joined by elastic canula with calibrated tube filled with water and placed vertically in the vessel containing water. The envolved H_2 was collected in the tube and then it was analyzed by chromatographic method. The obtained system was used as the initiator, when CL (4.2 cm^3, 4.6 g, 40 mmol) was introduced into the reactor. The reaction mixture was then stirred for several hours (~ 120 h). After this time relatively high conversion (90%) of the monomer was observed by SEC technique. Then, unreacted KOH was removed by centrifugation and polymer solution was introduced under argon into the second reactor containing 18C6 (0.53 g, 2.0 mmol) and BL at CL/BL equal to 1/0.5 or 1/1 molar ratio. The system was then mixed by 50 h. After total BL conversion the reaction mixture was treated with HCl/H_2O or CH_3I quenching agents and mixed by 30 min. Then, the mixture was placed in a 250 cm^3 separator containing H_2O (10 cm^3) and $CHCl_3$ (100 cm^3). After shaking during 5 min two layers were formed, i.e. interior polymer layer and superior layer containing water and the potassium salt. The layers were separated and the superior layer was removed. After two washings with distilled water, copolymer was obtained by evaporating of chloroform and water in vacuum. The concentration of the monomers during the polymerization was monitored by SEC method. The yields of the reactions were 98–99%. All investigated processes were homogeneous.

Measurements

100 MHz ^{13}C NMR spectra were recorded in $CDCl_3$ at 25 °C on a BruckerAvance 400 pulsed spectrometer equipped with 5 mm broad band probe and applying Waltz16 decoupling sequence. Chemical shifts were referenced to tetramethylsilane serving as an internal standard. In order to obtain a good spectrum of the copolymer main chain exhibiting its microstructural details, about 3000 scans were satisfactory, but in order to observe the signals of the polymer chain ends more then 10 000 scans were necessary. Molar masses and dispersities of copolymers were obtained 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. Polystyrenes were used as calibration standards. Matrix-assisted laser desorption/ionization-time of flight (MALDI-TOF) spectra was recorded on a Shimadzu AXIMA Performance instrument. Dithranol (1,8-dihydroxy-9,10-dihydroanthracen-9-one) was used as a matrix. All data were obtained in a positive-ion linear mode, applying the accumulation of 200 scans per spectrum. The calibration of the linear-mode analysis was done using protein standards in mass range up to 8000 Da. The samples were dissolved in dichloromethane at a concentration of 2 mg/mL. The sample solutions were mixed with a matrix solution in the same solvent. Data were acquired in continuum mode until acceptable averaged data were obtained and were analyzed using a Shimadzu Biotech Launchpad program.

Results and discussion

In 2010 Monsalve et al. [14] reported the possibility of preparation of PBL-*block*-PCL copolymers by anionic ring-opening polymerization using NaH as initiator. BL and CL were polymerized in bulk at 70 °C in glass reactor equipped with magnetic stirrer. After removing of BL oligomers and unreacted NaH from the prepared copolymer, it was then precipitated in methanol and dried in vacuum. Basing on analysis of NMR spectrum of the product, the authors proposed, that in the first step of the process NaH exclusively deprotonates BL (Scheme 1).

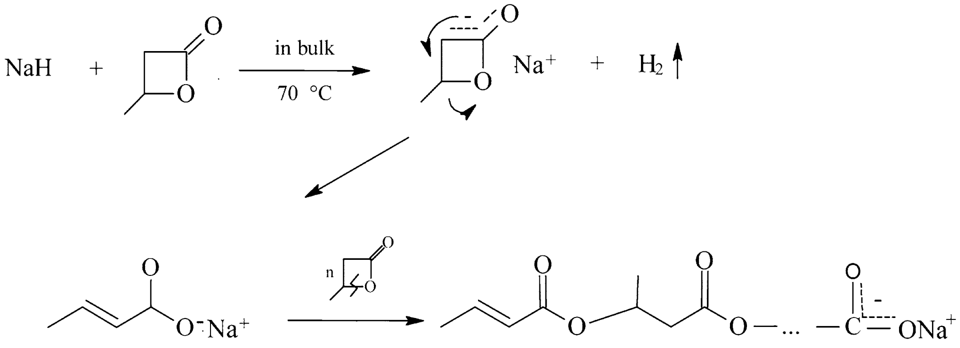
In this reaction hydrogen evolves and sodium *trans*-crotonate forms, which initiates anionic BL ring opening polymerization via carboxylate anions as propagating species. It leads to blocks of PBL of a relatively low molar mass. Then, the latter initiates the polymerization of CL being in the reaction mixture through alkoxide anions as propagating species leading to blocks of PCL with relatively higher molar mass. This suggestion was visualized by us on Scheme 2.

However, according to the literature data the above course of the process seems to be questionable. It was previously well established by Penczek et al. [16], that carboxylate anions do not initiate CL polymerization. It is in accordance with the general inability of these anions to react with esters. The only exception are esters with good leaving group. The strained ring, like in BL can be considered as an equivalent of a good leaving group. Thus, carboxylate anions initiate easily BL polymerization forming exclusively carboxylate growing species [16]. Moreover, sodium hydride appeared also to be active initiator of CL polymerization in bulk at 70 °C [17]. The authors proposed, that initiation proceeds by acyl-oxygen bond cleavage, resulting in the formation of macromolecules with aldehyde starting groups and alkoxide end groups as the growing species (Scheme 3).

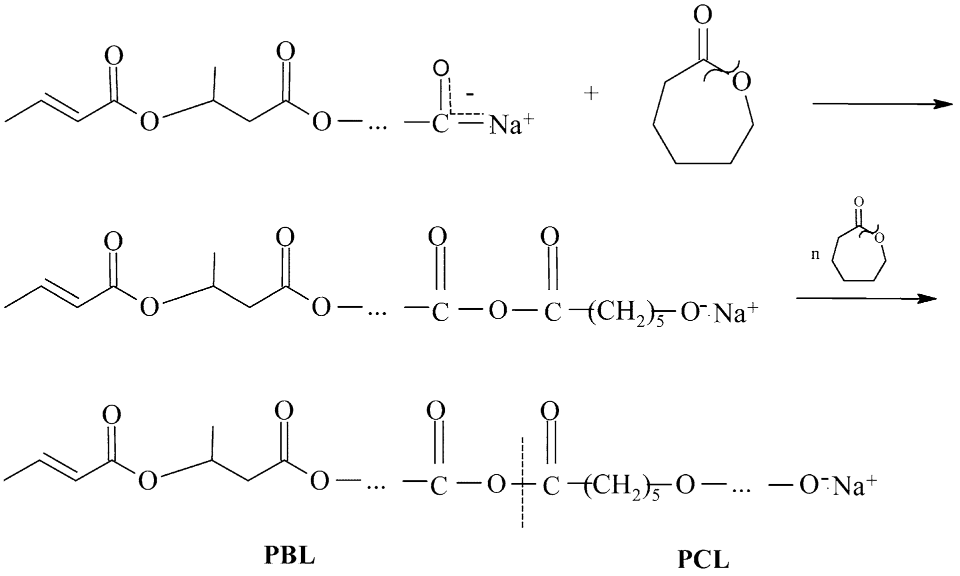
Therefore, we concluded, that it is unlikely that PBL-*block*-PCL copolymers could be synthesized in the system containing mixture of both monomers and sodium hydride as initiator. Homopolymerization of BL and CL should be rather expected in this case.

In order to confirm this hypothesis experimentally we repeated in the first step homopolymerization of BL and

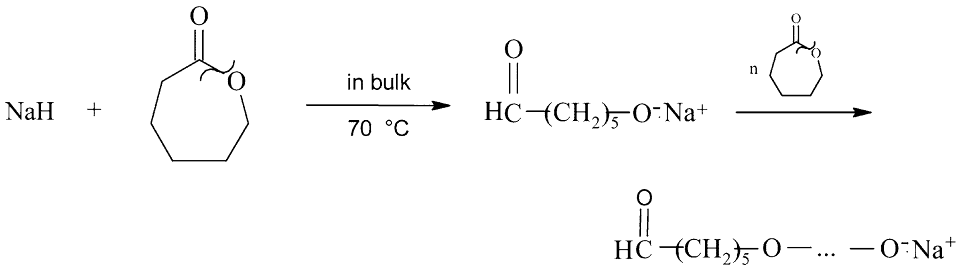
Scheme 1 Anionic polymerization of β-butyrolactone initiated with NaH [11]



Scheme 2 Course of ε-caprolactone polymerization through alkoxide anions as propagating species leading to PBL-*block*-PCL copolymer according to suggestion proposed in [11]



Scheme 3 Anionic polymerization of ε-caprolactone initiated with NaH [17]



CL in the presence of NaH in bulk at 70 °C. The polymers obtained were dissolved in anhydrous tetrahydrofuran and treated with CH_3I as quenching agent. The most interesting are carbon signals of terminal groups, i.e. starting and end ones shown in ^{13}C NMR spectra of both hompolymers (Fig. 1).

These results confirm previous data concerning homopolymerization of BL and CL initiated with NaH [14, 17]. Then, we repeated polymerization of BL and CL mixture in the same conditions. ^{13}C NMR spectrum of the products isolated after 96 h (Fig. 2) reveals main signals derived from carbons of PBL and PCL [18] as well as the same signals of terminal groups (additional signals at 23.0, 28.9, 29.4, 34.6, 69.3 and 176.2 derive from unreacted CL [18].

It early indicated, that homopolymers were formed in this system and not expected copolymer, which should possesses exclusively *trans*-crotonate starting groups and methoxy end groups. Therefore, we decided to prepare CL/BL block copolymer using different method.

First step of the synthesis was PCL preparation by ring-opening polymerization of CL initiated with anhydrous KOH activated by weak ligand 12-crown-4 (12C4). It allowed to obtain linear polyester with relatively high yield. Stronger ligands, i.e. 15C5 or 18C6 are inconvenient, because of high tendency of CL to the formation of cyclic macromolecules in these systems [19]. ^{13}C NMR analysis of polymer obtained after methylation reveals several strong signals characteristic for carbons derived from mers of CL. They are following signals which correspond well with literature data [17]: δ (in ppm) = 24.7, 25.7, 28.5, 34.3, 64.3 ($OCO(\underline{C}H_2)_5$), 173.7 ($\underline{C}OO$). Moreover, Fig. 3 shows weak carbon signals of terminal groups, which were identified as $HOOC\underline{C}H_2$- (at

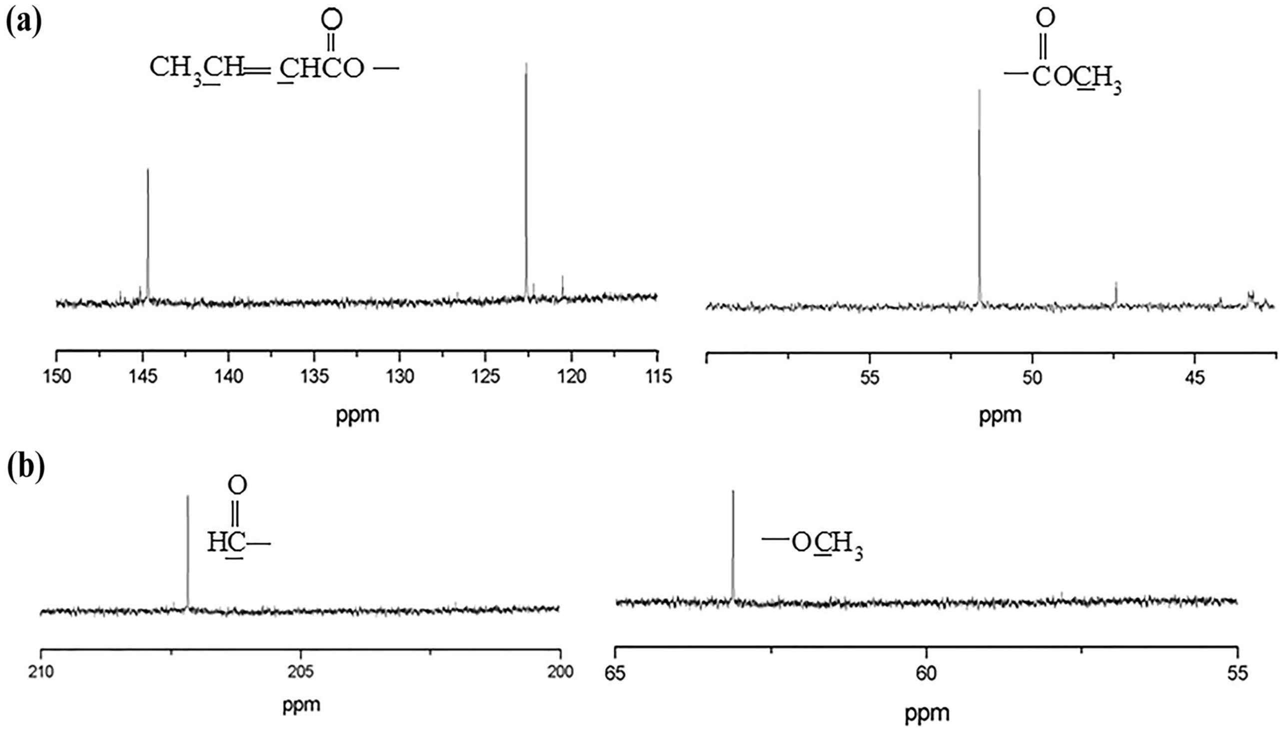


Fig. 1 Selected regions of the ^{13}C NMR spectra of PBL (a) and PCL (b) obtained in the presence of NaH exhibiting carbon signals of starting and end groups (after quenching with CH_3I)

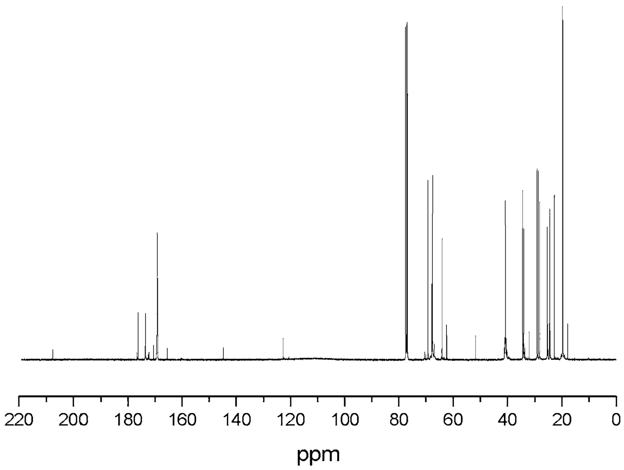


Fig. 2 ^{13}C NMR spectrum of the products formed by polymerization of the mixture of BL and CL in bulk at 70 °C; $[NaH]_o = 1.2$ mmol, $[BL]_o = [CL]_o = 12.3$ mmol

33.8 ppm), -COO$\underline{C}H_3$ (at 51.5 ppm), HO$\underline{C}H_2$- (at 62.4 ppm) and –O$\underline{C}H_3$ (at 62.9 ppm).

Basing on these data the course of the process was proposed on Scheme 4.

After initiation of CL polymerization by acyl-oxygen bond cleavage propagation takes place on alkoxide centers resulting in macromolecules **1**, which undergo transformation willingly during polymerization to **2** by cation exchange reaction. Equlibrium between **1** and **2** is postulated to be strongly shifted to the right similarly to that, observed previously in early stage of BL polymerization with KOH [19, 20]. In the second step BL was added to produce copolymer chains. The amount of BL was calculated to supply either 1/0.5 or 1/1 feed ratio of CL to BL. After BL addition, **2** behaves as macroinitiators, when strong ligand 18C6 is added to the system [21]. It is necessary to apply 18C6 rather than 12C4 to enhance the

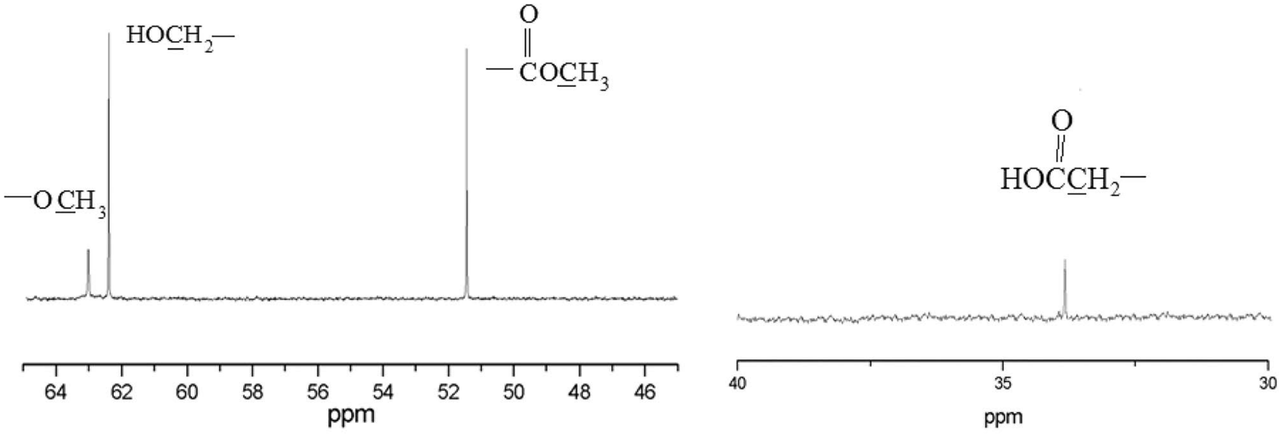
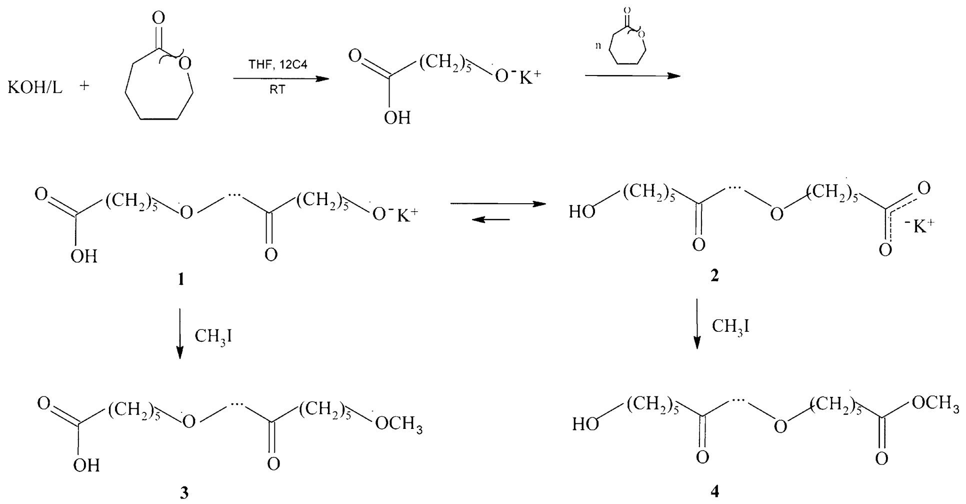
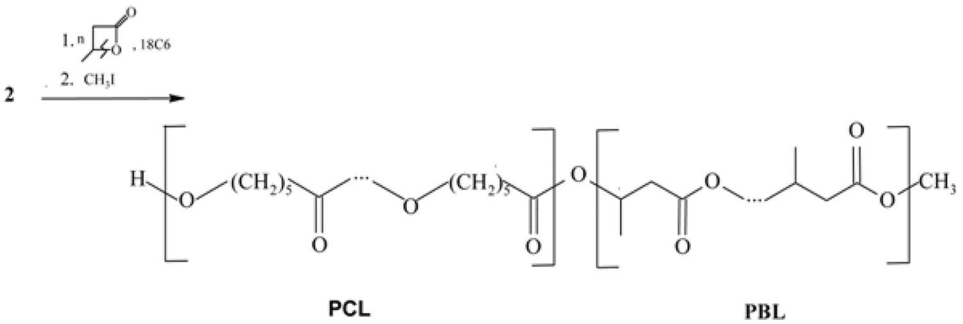


Fig. 3 ^{13}C NMR signals of terminal groups in PCL obtained with anhydrous KOH activated 12C4 after quenching with CH_3I

Scheme 4 Synthesis of PCL mediated with KOH activated by 12C4



Scheme 5 Synthesis of PCL-*block*-PBL copolymer (the main reaction)



reactivity of carboxylate centers in order to polymerize BL. Scheme 5 shows polymerization of BL mediated with macroinitiator **2** by ring-opening in alkyl-oxygen position.

However, macroinitiator **1** can also react with BL but in different way, i.e. by monomer deprotonation (Scheme 6), similarly to proposed earlier by Kricheldorf et al. [21] for BL polymerization initiated with *t*-BuOK.

Similar reaction occurs with carboxylate anions, which was known as side chain transfer reaction to monomer [22]. Both reactions lead to the formation of some PBL macromolecules with unsaturated *trans*-crotonate starting groups. ^{13}C NMR analysis of the final products confirmed the proposed course of the process. The spectrum reveals signals characteristic for carbons derived from mers of both monomers [14, 17]. These are following strong signals: (1) poly(ε-caprolactone) blocks: δ (in ppm) = 24.7, 25.7, 28.5, 34.3, 64.3 ($OCO(CH_2)_5$), 173.7 (COO); (2) poly(β-butyrolactone) blocks: δ (in ppm) = 19,8 (CH_3), 40.9 (CH_2), 67.7 (CH), 169.3 (COO). Moreover, signals of terminal groups in copolymer are shown, i.e., $HO\underline{C}H_2$- (at 62.4 ppm) and $–COO\underline{C}H_3$ (at 51.5 ppm) as well as weak signals of terminal groups in homopolymers, i.e. $CH_3\underline{C}H=\underline{C}HCOO–$ (at 122.6 and 144.7 ppm) and $–\underline{C}H_2COOH$ (at 33.6 ppm) (Fig. 4).

Table 1 shows results of polymers analysis obtained by SEC method with exemplary SEC chromatogram of PCL/PBL (1/1) copolymer shown on Fig. 5. In order to properly evaluate the obtained data we assume that in the course of the synthesis linear block copolymers were synthesized.

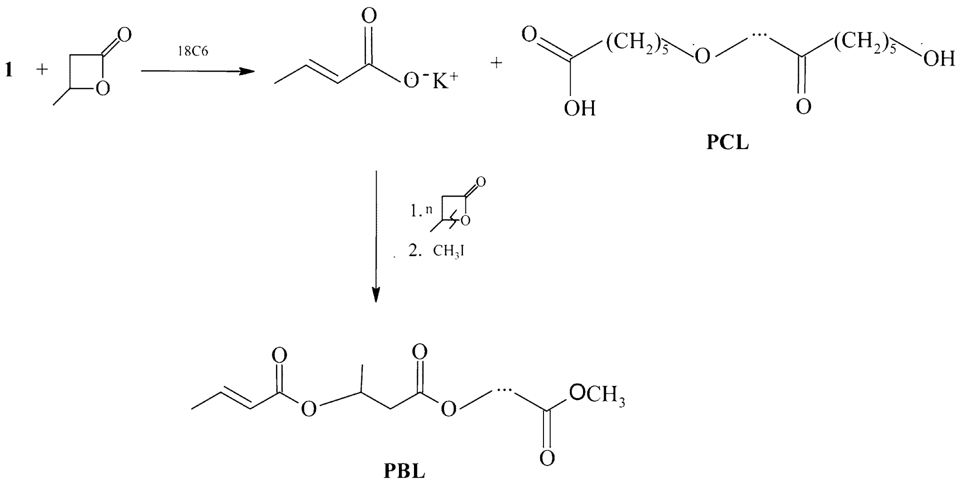
PS standards—Mark-Houwink constants—$K = 1.76 \bullet 10^{-2}$ mL/g, a = 0.679.

Dispersity of the synthesized block copolymers is rather high, that may indicate the occurrence of transesterification reaction due to the polymerization in polar solvent. It is also presumably caused by cation exchange reaction, which transforms reactive alkoxide centers of growing chains to carboxylate anions, which are inert in anionic polymerization of CL. Moreover, chain transfer reaction with BL comonomer could result in higher dispersity of CL/BL copolymers. These reactions are also responsible for lowering of molar mass of the polymers obtained.

Analysis of the products by MALDI-TOF technique confirm chemical structure of macromolecules. Figure 6 shows spectrum of the products obtained at equimolar ratio of co-monomers.

Some series of MALDI-TOF signals were identified. There are several series identified that correspond to adducts of either H$^+$, Na$^+$ or K$^+$ to the respective macromolecules.

Scheme 6 Formation of homopolymers in the side reactions



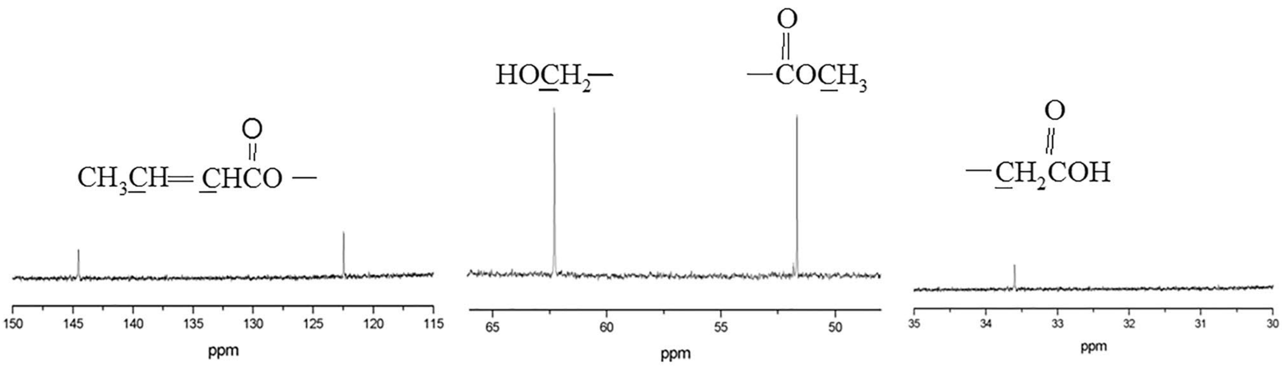


Fig. 4 ^{13}C NMR signals of terminal groups in PCL-*block*-PBL (1:1) copolymer and side products

Table 1 Characterization of the products formed in CL polymerization initiated with KOH and CL/BL block copolymers

Polymer	Yield %	M_{calc} a/	M_n (SEC)	M_w/M_n (SEC)
PCL	90	2283	1350	1.99
PCL/PBL(1/0.5) b/	92	3133	2200	2.09
PCL/PBL(1/1) b/	87	3983	3000	2.25

a/ $M_{calc} = ([CL]_o + [BL]_o)/[KOH]_o$.

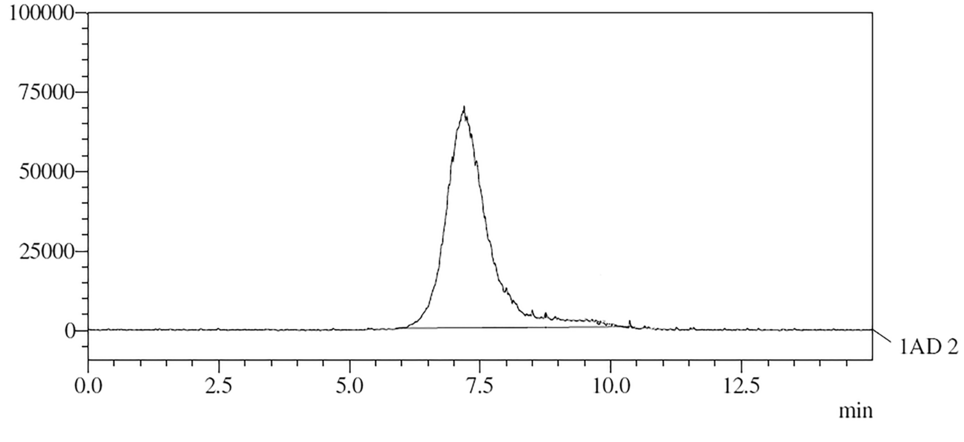
b/ CL/BL ratio.

There are copolymeric macromolecules with proton adduct $[BL_n/CL_m + H]^+$ (signals marked with full circle), with potassium adduct $[BL_n/CL_m + K]^+$ (signals marked with square) and sodium adduct $[BL_n/CL_m + Na]^+$ (signals marked with triangle). In addition to these there are also signals of homopolymeric macromolecules of polybutyrolactone with *trans*-crotonate starting groups and COOH end group which form adducts with sodium ion $[BL_n + Na]^+$ (signals marked with star). Finally some homopolymers of CL for macromolecules with COOH starting groups and CH_2OH end groups in a protonated form $[CL_m + H]^+$ (signals marked with empty dot) are also visible.

For series from *m/z* 705.6 to 1138.7 signals of PCL-*block*-PBL copolymer were identified for macromolecules containing 3 mers of CL and 4 ÷ 9 mers of BL. For example, signal at *m/z* 705.6, 792.0, 965.7, 1052.8 and 1138.7 represent macromolecules containing 4, 5, 7, 8 and 9 mers of BL, respectively ($M_{calc} = 705.8$, 791.8, 964.1, 1050.2 and 1136.2, respectively). These macromolecules with OH starting group and COOH end group form protonated adducts. The same structural scheme is prescribed to the signals of the macromolecules containing 11 mers of CL and 8 or 10 mers of BL at *m/z* 1962.5 and 2135.3 ($M_{calc} = 1963.2$ and 2135.4, respectively) and 13 mers of CL and 4 mers of BL at *m/z* 1848.0 ($M_{calc} = 1847.2$) as well as 14 mers of CL and 5 mers of BL at *m/z* 2047.9 ($M_{calc} = 2047.4$).

The second series from *m/z* 1225.1 to 1571.8 reveals signals of copolymer containing 8 mers of CL and 3 ÷ 7 mers of BL. For example, peaks at *m/z* 1225.1, 1399.1, 1485.6 and 1571.8 represent macromolecules with 3, 5, 6 and 7 mers of BL, respectively ($M_{calc} = 1228.5$, 1400.7, 1486.7 and 1572.8, respectively). The macromolecules with the architecture

Fig. 5 SEC chromatogram of PCL/PBL (1/1) copolymer obtained with anhydrous KOH



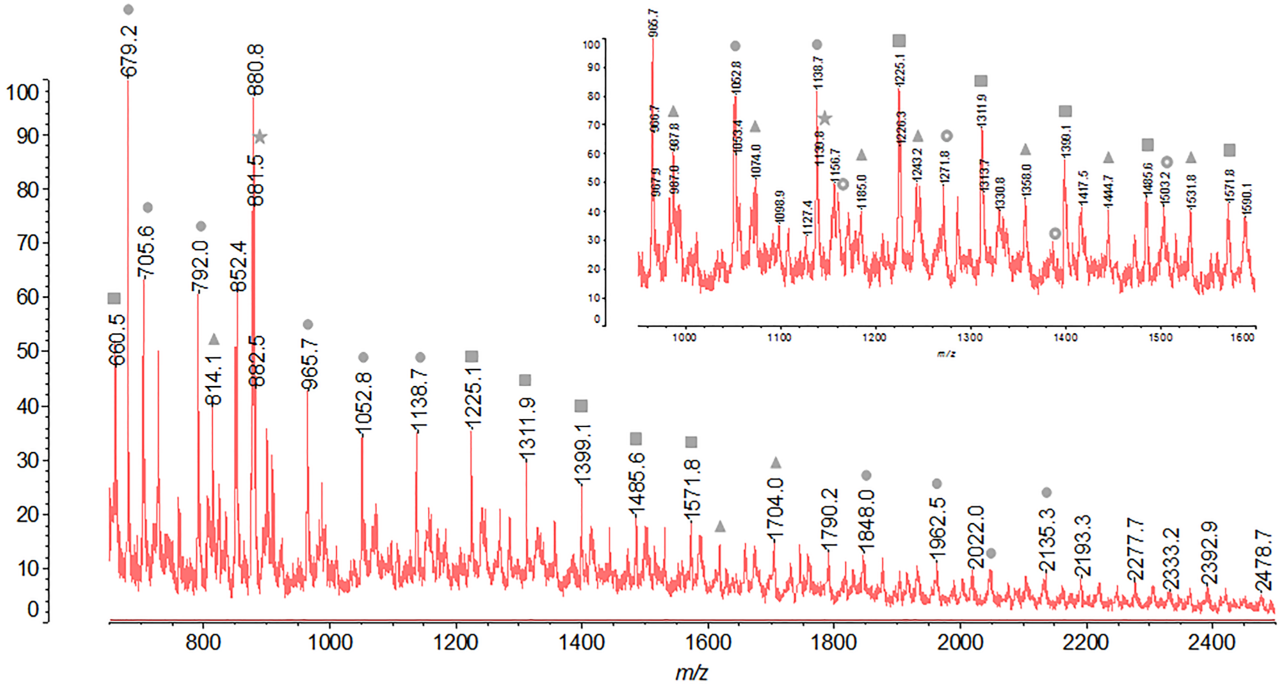


Fig. 6 MALDI-TOF spectrum of polymers formed in CL/BL (1/1) copolymerization after protonation with HCl (insert: part of the spectrum in a m/z range of 980–1600)

built with OH starting group and COOH end group form adducts with potassium ion.

The next series spanning from *m/z* 814.1 to 1531.8 reveals signals of copolymeric macromolecules built with either 3 or 4 mers of CL and 5 ÷ 12 mers of BL ionized by formation of sodium adducts. For example, peaks at *m/z* 814.1, 987.0 and 1074.0 represent macromolecules of 3 CL mers with 5, 7 and 8 mers of BL, respectively (M_{calc} = 813.8, 986.0 and 1072.1, respectively), while peaks at *m/z* 1185.0, 1358.0, 1444.7 and 1531.8 represent macromolecules composed of 4 CL mers with 8, 10, 11 and 12 mers of BL, respectively (M_{calc} = 1186.2, 1358.4, 1444.7 and 1530.6, respectively).

The same structural pattern is prescribed to the signals of the macromolecules containing 1 mer of CL and 17 or 18 mers of BL at *m/z* 1618.3 and 1704.0 (M_{calc} = 1618.7 and 1704.7, respectively) as well as for signal of 6 mers of CL and 6 mers of BL at *m/z* 1243.2 (M_{calc} = 1242.4).

The series of signals from m/z 881.5 to 1139.8 belongs to BL homopolymers ionized by sodium adduct formation. For example, signals at m/z 881.5 and 1139.8 represents macromolecules with 9 and 12 mers of BL, respectively (M_{calc} = 884.2 and 1142.5, respectively). These macromolecules possess *trans*-crotonate starting groups and COOH end group and form adducts with sodium ion. Finally the low intensity series with signals in range of *m/z* 1160.7 to 1503.2 represent CL homopolymers containing 10 ÷ 13 mers of CL. The macromolecules with COOH starting groups and CH_2OH end groups form adducts with proton being responsible for the signals at *m/z* 1160.7, 1271.8, 1386.9 and 1503.2 (M_{calc} = 1160.4, 1274.5, 1388.7 and 1502.8, respectively).

Formation of homopolymers in the process is undesired. It is impossible to eliminate chain transfer reaction with monomer but it could be possible to minimalize it. Kricheldorf et al. [21] observed, that unsaturation of PBL decreases in less polar solvents and lower temperatures. It seems also to be reasonable, that decreasing of basicity of carboxylate active centres should be expected by use of Na^+ counterion in bulk or non-polar solvent. Optimalization of synthesis presented in this work needs further investigations.

Conclusions

In the present work we proposed new method of PCL-*block*-PBL lactones copolymers synthesis in THF solution at room temperature. The main features of this process are:

- In the first step CL polymerizes with anhydrous KOH in the presence of 12-crown-4, giving homopolymer with potassium carboxylate centers after cation exchange; the latter initiates polymerization of added BL after activation by 18-crown-6.

- PCL-*block*-PBL copolymers after methylation possess hydroxyl starting groups and ester end groups and have relatively high dispersity ($M_w/M_n \approx 2.1–2.25$).
- Derived samples contain small amounts of CL and BL homopolymers which can be formed in side chain transfer reaction with BL comonomer.
- The proposed procedure for minimalisation of side reactions involves use of Na^+ counterion and/or less polar solvent and weak cation complexing ligands, which is the subject of the further studies.
- Preparation of BL/CL block copolymers in the presence of NaH described previously is improbable to realize, due to inability of carboxylate anions to initiate polymerization of ε-caprolactone. In this system homopolymers of BL and CL should be formed rather, than copolymers.

Acknowledgements No external sources of financing was used.

Author contributions Conceptualization was performed by [Zbigniew Grobelny]; Investigations were performed by [Zbigniew Grobelny] and [Justyna Jurek-Suliga]; Methodology was performed by [Zbigniew Grobelny] and [Sylwia Golba]; Writing Original Draft was performed by [Zbigniew Grobelny] and [Justyna Jurek-Suliga]; Formal analysis, Visualization, Resources, Validation were performed by [Sylwia Golba] and [Justyna Jurek-Suliga].

Funding This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

Data Availability Data will bemade available on request.

Compliance with ethical standards

Conflicts of interest No potential conflict of interest relevant to this article was reported.

References

1. Pisani S, Dorati R, Conti B, Modena T, Bruni G, Genta I (2018) Design of copolymer PLA-PCL electrospun matrix for biomedical applications. React Funct Polym 124:77–89. https://doi.org/10.1016/j.reactfunctpolym.2018.01.011
2. Dobrzyński P (2002) Synthesis of biodegradable copolymers with low-toxicity zirconium compounds. III. Synthesis and chain-microstructure analysis of terpolymer obtained from L-lactide, glycolide, and ϵ-caprolactone initiated by zirconium(IV) acetylacetonate. J Polym Sci Pol Chem 40:3129–3143. https://doi.org/10.1002/pola.10401
3. Sisson AL, Ekinci D, Lendlein A (2013) The contemporary role of ε-caprolactone chemistry to create advanced polymer architectures. Polymer 54:4333–4350. https://doi.org/10.1016/j.polymer.2013.04.045
4. Stridsberg K, Albertsson A-C (2000) Controlled ring-opening polymerization of L-lactide and 1,5-dioxepan-2-one forming a triblock copolymer. J Polym Sci Pol Chem 38:1774–1784. https://doi.org/10.1002/(SICI)1099-0518(20000515)38:10%3c1774::AID-POLA620%3e3.0.CO;2-F
5. Isnard F, Carratù M, Lamberti M, Venditto V, Mazzeo M (2018) Copolymerization of cyclic esters, epoxides and anhydrides: evidence of the dual role of the monomers in the reaction mixture. Catal Sci Technol 8:5034–5043. https://doi.org/10.1039/C8CY01174E
6. Kricheldorf HR, Rost S (2005) A-B-A-Triblock and multiblock copolyesters prepared from ε-caprolactone, glycolide and l-lactide by means of bismuth subsalicylate. Polymer 46:3248–3256. https://doi.org/10.1016/j.polymer.2005.02.004
7. García-Valle FM, Cuenca T, Mosquera MEG, Milione S, Cano J (2020) Ring-Opening Polymerization (ROP) of cyclic esters by a versatile aluminum Diphenoxyimine Complex: From polylactide to random copolymers. Eur Polym J 125:109527. https://doi.org/10.1016/j.eurpolymj.2020.109527
8. Chen C, Peng S, Wu H, Zhuang Y, Chen X, Dong L, Feng Z (2002) Synthesis and characterization of poly(β-hydroxybutyrate) and poly(ϵ-caprolactone) copolyester by transesterification. J Polym Sci Pol Phys 40:1893–1903. https://doi.org/10.1002/polb.10242
9. Phetsuk S, Molloy R, Nalampang K, Meepowpan P, Topham PD, Tighe BJ, Punyodom W (2020) Physical and thermal properties of l-lactide/ε-caprolactone copolymers: the role of microstructural design. Polym Int 69(3):248–256. https://doi.org/10.1002/pi.5940
10. Guillaume SM (2013) Recent advances in ring-opening polymerization strategies toward α, ω-hydroxy telechelic polyesters and resulting copolymers. Eur Polym J 49(4):768–779. https://doi.org/10.1016/j.eurpolymj.2012.10.011
11. Li S, Pignol M, Gasc F, Vert F (2004) Synthesis, Characterization, and Enzymatic Degradation of Copolymers Prepared from e-Caprolactone and b-Butyrolactone. Macromolecules 37:9798–9803. https://doi.org/10.1021/ma0489422
12. Song Q, Pascouau Ch, Zhao J, Zhang G, Peruch F, Carlotti S (2020) Ring-opening polymerization of γ-lactones and copolymerization with other cyclic monomers. Prog Polym Sci 110:101309. https://doi.org/10.1016/j.progpolymsci.2020.101309
13. Gruszka W, Walker LC, Shaver MP, Garden JA (2020) In Situ Versus Isolated Zinc Catalysts in the Selective Synthesis of Homo and Multi-block Polyesters. Macromolecules 53(11):4294–4302. https://doi.org/10.1021/acs.macromol.0c00277
14. Monsalve M, Contreras JM, Laredo E, López-Carrasquero F (2010) Ring-opening copolymerization of (R, S)-β-butyrolactone and ε-caprolactone using sodium hydride as initiator. EXPRESS Polym Lett 4:431–441. https://doi.org/10.3144/expresspolymlett.2010.54
15. Grobelny Z, Matlengiewicz M, Skrzeczyna K, Swinarew A, Golba S, Jurek-Suliga J, Michalak M, Swinarew B (2015) Ring-Opening Polymerization of Lactones Initiated with Metal Hydroxide-Activated Macrocyclic Ligands: Determination of Mechanism and Structure of Polymers. Int J Polym Anal Ch 20:457–468. https://doi.org/10.1080/1023666X.2015.1036219
16. Hofman A, Słomkowski S, Penczek S (1984) Structure of active centers and mechanism of the anionic polymerization of

lactones. Macromol Chem 185:91–101. https://doi.org/10.1002/macp.1984.021850110

17. Gorrasi G, Pappalardo D, Pellecchia C (2012) Polymerization of ε-caprolactone by sodium hydride: From the synthesis of the polymer samples to their thermal, mechanical and barrier properties. Reac Funct Polym 72:752–756. https://doi.org/10.1016/j.reactfunctpolym.2012.07.007
18. Kricheldorf HR, Berl M, Scharnagl N (1988) Polymerization mechanism of metal alkoxide initiated polymerizations of lactide and various lactones. Macromol 21:286–293. https://doi.org/10.1021/ma00180a002
19. Grobelny Z, Stolarzewicz A, Morejko B, Pisarski W, Maercker A, Skibiński A, Krompiec S, Rzepa J (2006) Anionic polymerization of beta.-lactones initiated with alkali-metal alkoxides: reinvestigation of the polymerization mechanism. Macromolecules 39:6832–6837. https://doi.org/10.1021/ma00033a027
20. Grobelny Z, Golba S, Jurek-Suliga J (2019) Ring-opening polymerization of β-butyrolactone in the presence of alkali metal salts: investigation of initiation course and determination of polymers structure by MALDI-TOF mass spectrometry. Polym Bull 76:4951–4966. https://doi.org/10.1007/s00289-018-2640-3
21. Kricheldorf HR, Scharnagl N (1989) Polyactones. 17. Anionic Polymerization of β-D. L-Butyrolactone J Macromol Sci A A26:951–968. https://doi.org/10.1080/00222338908052023
22. Duda A (1992) Anionic polymerization of 4-methyl-2-oxetanone (β-butyrolactone). J Polym Sci Polym Chem 30:21–29. https://doi.org/10.1002/pola.1992.080300103