SYNTHESIS AND NMR ANALYSIS OF THE STRUCTURE AND COMPOSITION OF TRIBLOCK POLY(ESTER-SILOXANE-ESTER) COPOLYMER BASED ON L-LACTIDE

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Abstract: The synthesis, structure and composition of triblock poly(ester-siloxane-ester) copolymers, PLLA-PDMS-PLLA, based on α,ω–diaminopropyl-poly(dimethyl siloxane) (PDMS) and L-lactide were studied in this work. The samples of the controlled block length were synthesized by ring-opening polymerization of L-lactide in the presence of stannous octoate, Sn(Oct)₂, as a catalyst, and aminopropyl-terminated siloxane prepolymer, as a macroinitiator, in a concentrated toluene solution. Influence of temperature and concentration of the catalyst on the structure, composition and size of the copolymers were investigated by ¹H and ¹³C NMR spectroscopy and dilute solution viscometry.

Keywords: triblock copolymer, poly(ester-siloxane-ester), L-lactide, ¹H NMR spectroscopy.

1. INTRODUCTION

Polylactides, polymers based on lactic acid as a difunctional monomer, have attracted great attention as materials for biomedical applications in the last few decades, due to their excellent biocompatibility and biodegradability. Probably the most attractive feature of polylactides is their degradation, which occurs through hydrolytic or enzymatic cleavage of acyl-oxygen bond to give a natural metabolite, lactic acid. Biocompatibility and safety of the use of polylactide have been well studied and confirmed by numerous in vivo studies. They have shown that the morphology and the rate of biodegradation of polylactide depend on the stereochemical structure of the lactide monomer, molecular weight of polymer and the type of terminal functional groups. Poly(L-lactide) (PLLA) is a semicrystalline polymer with exceptional mechanical properties. The high molecular weight PLLA polymer has the melting point temperature of approximately 180 °C and the glass transition temperature of about 67 °C. Depending on the initiator, the PLLA homopolymer is typically synthesized by ring-opening polymerization (ROP) of L-lactide (a cyclic dimer of lactic acid) through anionic, cationic or pseudo-anionic ring-opening polymerization, referred to as „coordination-insertion“ ROP. The cationic polymerization is seldom used because it is difficult to control and often only low molecular weight polymers are formed. The anionic ROP of L-lactide takes place by the nucleophilic attack of a negatively charged initiator on the carbonyl carbon or on the carbon atom adjacent to the acyl-oxygen, resulting in a linear polyester. The „coordination-insertion“ ROP occurs in the presence of tin compounds, usually carboxylate or alkoxide, wherein the propagation commences through the coordination of the monomer to the active species, which is followed by the insertion of the monomer into the metal-oxygen bond [1,2].

On the other hand, poly(dimethylsiloxane), PDMS, is an extremely flexible molecule with almost complete rotation along the macromolecular chain. Mobility of the PDMS molecule, through rotation and segmental cooperative chain motion, makes the intermolecular distance bigger, and intermolecular interactions significantly lower than for the corresponding carbon polymers, which causes many of the unusual properties of these materials. PDMS polymers have one of the lowest values of the glass transition temperature (\(T_g = -123 \, ^\circ C\)), and a large value of the molar volume (75.5 cm³ mol⁻¹). Flexibility and weak intermolecular forces also lead to low surface tension, low value of solubility parameter and low dielectric constant. PDMSs are tran-
sparent to visible and UV light, ozone resistant, and are very stable to the atomic oxygen. Permeability to various gases, hydrophobicity, ability to build films, surface activity, as well as excellent chemical and physiological inertness are other interesting properties of PDMS polymers [3,4]. However, up to now, a relatively small number of polyester copolymers based on polylactide, as a crystalline block, and PDMS, as the flexible component of materials for various purposes, have been synthesized and characterized [5–10].

The aim of this work was the synthesis of new polyester-polyisoxane thermoplastic triblock copolymers of ABA type and optimization of the experimental conditions for the synthesis. The PLLA-PDMS-PLLA triblock copolymers were prepared under various experimental conditions from L-lactide and a telechelic PDMS prepolymer with terminal aminopropyl-groups by the ring-opening reaction in the presence of a catalyst. The optimization of the reaction included a study of the effect of temperature, the catalyst concentration and the monomers concentration in toluene solution on the molecular weight, structure and yield of PLLA-PDMS-PLLA triblock copolymer. The method of the synthesis was ring-opening polymerization of L-lactide in solution, which has been already successfully applied to obtain PLLA homopolymer [1,2]. The ultimate goal of this work was the preparation of triblock copolymer which would be suitable for incorporation in a segmented polyurethane with high molecular weight by a chain extension reaction in the presence of appropriate diisocyanates. The synthesis of this type of biocompatible and biodegradable copolymers is of the great technological interest, since their potential as polymeric carriers for controlled release of pesticides and other active substances suggests the possible application in agriculture and medicine.

2. EXPERIMENTAL

2.1. Materials

d(2-ethylhexanoate) or stannous octoate (Sn(Oct)₂) catalyst (from Sigma-Aldrich, Germany) was used without further purification as a diluted solution (0.01 mol dm⁻³) in anhydrous toluene.

Toluene (from Lach–Ner, Czech Republic) was dried by refluxing over metallic sodium until hydrogen evolution ceased, and then distilled under atmospheric pressure at 111 °C. Methanol (Zorka–Pharma, Serbia), acetone and chloroform (from Lach–Ner, Czech Republic) were used without further purification. n-Hexane (Lach–Ner, Czech Republic) was purified by distillation under atmospheric pressure, whereby the fraction at 68 °C was collected. All solvents were stored over molecular sieves (4 Å).

2.2. Synthesis of PLLA-PDMS-PLLA triblock copolymers

PLLA-PDMS-PLLA triblock copolymers were synthesized by ring-opening polymerization of L-lactide in a concentrated solution of toluene from α,ω-diaminopropyl-poly(dimethylsiloxane) (PDMS, $M_n=1000$ g mol⁻¹), as the macrorinitiator, and in the presence of (SnOct)₂, as a catalyst. A series of samples with the constant composition was synthesized under different experimental conditions, wherein the temperature, the concentration of the catalyst and the concentration of the reaction mixture varied. The determination of an optimum time of the reaction was conducted by studying the influence of the reaction time on the conversion of monomer at different stoichiometric composition during the synthesis. All syntheses were performed in a two-necked round bottomed flask (Pyrex, 250 mL) equipped with a dry nitrogen inlet, a reflux condenser and a magnetic stirrer. Just before the reaction, traces of moisture were removed from the flask using a Bunsen burner.

The PLLA-PDMS-PLLA triblock copolymers with controlled molecular weight of 1000-1000-1000 g mol⁻¹ were synthesized. L-lactide was added to a nitrogen atmosphere, followed by the addition of the required amount of toluene and the flask was heated over an oil bath at 100 °C. The calculated amount of α,ω-diaminopropyl-PDMS in an appropriate volume of toluene was added to a solution of L-lactide, and the temperature was raised to 130 °C. After 60 minutes, a solution of the catalyst was added to the reaction mixture. The reaction was run for 6 hours and then the reaction mixture was cooled under the nitrogen atmosphere to room temperature. 1 mL of hydrochloric acid (1/1, V/V) was added to the reaction mixture and the synthesized PLLA-PDMS-PLLA copolymers were precipitated
in 300 mL of cooled methanol. The resulting copolymers were dried in a vacuum oven at 40 °C to constant weight and the dried samples were stored in a desiccator. The amount of the catalyst in the syntheses was 500 or 1000 ppm relative to L-lactide, while the reaction temperature was 130 or 145 °C. The samples of the first series were labeled as PLLA-1000 (Table 1 and 2, section Results and discussion).

The effect of reaction time on the synthesis of PLLA-PDMS-PLLA triblock copolymers was studied at 100 °C, during 50 hours, at the catalyst concentration of 500 ppm. L-lactide and PDMS were fed as the solutions in a small volume of dry toluene under nitrogen at 65 °C, in the manner that the concentration of the reaction mixture was 50% (m/V). The temperature was then raised to 100 °C for 60 minutes, when the first sample was taken. After the addition of the catalyst, the reaction was continued for 50 hours, whereby the copolymer samples were taken at regular intervals. The samples of the second series were labeled as PLLA-2000 (Table 3, section Results and discussion).

The reaction mixture was then cooled, the precipitated copolymer was dissolved in chloroform and reprecipitated in n-hexane. Voluminous white precipitate was dried in a vacuum oven at 40 °C to constant weight.

3. RESULTS AND DISCUSSION

Triblock copolymers based on polylactide are often synthesized by ring-opening polymerization of a cyclic monomer in the presence of suitable catalysts and a polymerization co-initiator or macro-initiator. The choice of appropriate experimental conditions is a very important factor to obtain a copolymer of predetermined molecular weight, i.e. predetermined length of blocks. Also, a satisfactory degree of conversion of monomers in polymerization reaction is required [12]. The synthesis of the PLLA-PDMS-PLLA triblock copolymers, in the presence of α,ω-diaminopropyl-PDMS prepolymer as a macroinitiator, at a molar ratio of monomers (PDMS: LLA) of 1:13.9 is shown in Figure 1.

![Figure 1. Synthesis of PLLA-PDMS-PLLA triblock copolymer by ring-opening polymerization of L-lactide.](image)

It can be seen that the central PDMS block is connected with two polyester blocks (PLLA) via amide linkages. The initial concentrations of reactants were selected to obtain ABA type of copolymer with all block lengths of 1000 g mol\(^{-1}\). The starting concentration of the catalyst is selected on the basis of literature data [12,13]. The influence of the reaction conditions on the course of polymerization was determined by measuring the inherent viscosity, \(\eta_{inh}\), of the synthesized samples, as well as by calculating the composition of the obtained triblock copolymers based on the respective \(^1\)H NMR spectra. The poly(ester-siloxane-ester) triblock copolymers were synthesized in the presence of different concentrations of the catalyst (500 and 1000 ppm, based on the weight of L-lactide) and at different temperatures (130 and 145 °C).

The \(\eta_{inh}\) values were relatively low and ranged from 0.13 to 0.22 dL g\(^{-1}\). This was expected with respect to a predetermined molecular weight of the triblock copolymer of 3000 g mol\(^{-1}\). The copolymer sample which was synthesized at the highest temperature had the lowest value of inherent viscosity in the series 1000-1000-1000 g mol\(^{-1}\), indicating a negative effect of increased temperature on the reaction course. Likewise, increasing the concentration of the catalyst to 1000 ppm of Sn(Oct)\(_2\) caused a decrease of the viscosity of the obtained sample.
Unexpectedly, the 2000-1000-2000 g mol$^{-1}$ triblock copolymer had a very low value of inherent viscosity. This suggests that the long-run time of reaction (50 h) likely led to the unwanted depolymerization and other side reactions.

Chemical structure of the synthesized triblock copolymers was confirmed by $^1$H and $^{13}$C NMR spectroscopy. The $^1$H spectra of the PLLA-1000-1 sample, as well as the presumed chemical structure of the copolymers are shown in Figure 2. In the $^1$H NMR spectrum the following characteristic signals were observed: intensive signal at $\delta = 0.04$ of Si–CH$_3$ protons; signals of CH$_2$ protons from the terminal PDMS propylene groups residue at $\delta = 0.50, 1.45$ and $3.20$ ppm; signals of methyl protons, CH$_3$ from the lactide residue which appeared at $\delta = 1.50$ ppm (methyl group from the internal and terminal residues) and overlapped with the signal of internal CH$_2$ protons from the PDMS propylene group. Methyne CH protons from the lactide residue appeared as two signals: signal of internal CH protons at $\delta = 5.20$ ppm and signal of terminal CH protons at $\delta = 4.40$ ppm. Signal of NH urea protons bonded to the L-lactide residue appeared at $\delta = 6.20$ ppm. Hydroxyl OH protons from the copolymer terminal groups appeared at $\delta = 2.40$ ppm.

**Table 1.** The reaction conditions, yields and inherent viscosities of the PDMS prepolymer, PLLA-PDMS-PLLA triblock copolymers of the Series 1 (predetermined block length of 1000-1000-1000 g mol$^{-1}$) and the sample PLLA-2000-50 h

| Sample         | Catalyst concentration, ppm | Temperature, °C | $\eta_{inh}$, dL g$^{-1}$ | Yield, % |
|----------------|------------------------------|-----------------|----------------------------|----------|
| PDMS           | -                            | -               | 0.07                       | -        |
| PLLA-1000-1    | 500                          | 130             | 0.22                       | 40.5     |
| PLLA-1000-2    | 1000                         |                 | 0.19                       | 42.0     |
| PLLA-1000-3    | 500                          | 145             | 0.13                       | 22.0     |
| PLLA-1000-4$^{a}$ | 500              | 130             | 0.12                       | 20.0     |
| PLLA-2000-50 h$^{b}$ | 500              | 100             | 0.09                       | 68.5     |

$^a$The catalyst was added to the reaction mixture at the beginning of the reaction together with the monomers.

$^b$The reaction was conducted for 50 hours at predetermined block length of 2000-1000-2000 g mol$^{-1}$

*Figure 3* shows the $^{13}$C NMR spectrum of the PLLA-1000-1 sample. In the $^{13}$C NMR spectrum, the signal at $\delta = 0.3$ ppm originated from the carbon atoms in the Si-CH$_3$ groups, while at $\delta = 13.7$ and 22.8 ppm appeared the signals of the methylene carbon bonded to silicon and internal methylene carbons from $n$-propylene group, respectively. The strong signals at $\delta = 18.0$ ppm and $\delta = 68.5$ ppm originated from the lactide residue including the methylene carbons and carbon atoms bonded to a carbonyl group and oxygen, respectively. The signal of $n$-propylene group carbons bonded to nitrogen appeared at $\delta = 71.5$ ppm. At $\delta = 169.0$ ppm appeared the signal of carbonyl carbons.

![Figure 2. $^1$H NMR spectrum of PLLA-1000-1.](image-url)
The composition of the copolymers, i.e. the molar and weight ratios of the PLLA and PDMS segments in the synthesized triblock copolymers were calculated based on the intensity ratio of the corresponding signals in the $^1$H NMR spectra. PLLA block length was determined comparing the signal intensities of methine protons from the L-lactide residue, $I(\text{CH})_R$, and methine protons from the terminal groups, $I(\text{CH})_T$, which appeared at $\delta = 5.20$ ppm and $\delta = 4.40$ ppm, respectively, as follows:

$$X_{\text{PLLA}} = \frac{I(\text{CH})_R}{I(\text{CH})_T} \times 2; \quad \text{and}$$

$$M_{\text{PLLA}} = X_{\text{PLLA}} \times 72 \text{ g mol}^{-1} + 73 \text{ g mol}^{-1}$$

where $X_{\text{PLLA}}$ and $M_{\text{PLLA}}$ represent the number average degree of polymerization and number average molecular weight of the PLLA block, respectively, 72 g mol$^{-1}$ is the weight of the repeating unit, and 73 g mol$^{-1}$ is the weight of the terminal group.

The results of the number average degree of polymerization and number-average molecular weight for the PLLA segments, the number-average molecular weight for the PLLA-PDMS-PLLA triblock copolymers, the weight fraction of the PLLA and PDMS segments in the copolymer as well as the weight ratio of the PDMS and PLLA blocks in the copolymer are shown in Table 2. The reference values for comparison were the values predetermined by the composition of the reaction mixtures: $X_{\text{PLLA}} = 13.89$; $M_{\text{PLLA}} = 1000 \text{ g mol}^{-1}$; $M_{\text{PLLA-PDMS-PLLA}} = 3000 \text{ g mol}^{-1}$; PLLA/copolymer = 66.7%; PDMS/copolymer = 33.3% and PDMS/PLLA = 0.5.

As it can be seen, experimental values of the molecular weights of PLLA blocks were ranged from 928 to 1144 g mol$^{-1}$, while the corresponding values of triblock copolymers were in the range from 2856 to 3288 g mol$^{-1}$, and both showed relatively good agreement with theoretical values predetermined by the composition of the initial reaction mixtures. The largest positive deviation from the theoretical value was observed for the sample synthesized at the highest temperature ($145 ^\circ \text{C}$) in the presence of the catalyst. This result could be due to the thermal instability of the terminal aminopropyl groups under the given experimental conditions. Earlier studies have shown that less reactive hydroxyalkyl end-groups were the subject of the cyclization reactions upon heating which led to a decrease in the concentration of reactive functional groups at the ends of the siloxane chains [14,15]. This suggests that increasing the length of lactide blocks in the copolymer chains may be a consequence of disruption of stoichiometric ratio in the initial reaction mixture, due to a decrease in the concentration of the PDMS reactive groups, i.e. an increase in the concentration of L-lactide relative to reactive, telechelic PDMS prepolymer. The largest negative deviation from the theoretical values showed the PLLA-1000-4 sample. The PLLA-1000-4 sample was synthesized at a lower temperature ($130 ^\circ \text{C}$, Table 1), whereby the catalyst was added to the reaction mixture at the beginning of the reaction, along with L-lactide and siloxane prepolymer. This indicates the importance of the presence of a reactive PDMS macroinitiator to
start a ring-opening reaction of L-lactide and form the prepolymer with terminal hydroxyl groups.

As shown in the previous studies, the amino-groups are reactive enough to initiate ring-opening of L-lactide. However, it is necessary to add a catalyst (i.e. stannous octoate) to the reaction mixture to continue polymerization reaction [1]. When the catalyst is added at the beginning of the reaction, in the presence of trace of moisture, the polymerization of L-lactide occurs giving short PLLA homopolymer chains, and this reaction becomes competitive with the macroinitiation. Under such conditions, a substantial portion of the lactide monomer reacts and forms short PLLA chains. During precipitation of triblock copolymer, these short chains remain in solution and do not contribute to its molar mass. If the prepolymer with amino end-groups are used, it is necessary that the reaction is carried out without the presence of a catalyst for a certain time in order to enable efficient macroinitiation and the formation of other kind of macroinitiator, i.e. prepolymer with one L-lactide residue and hydroxyl end-groups on each end of the PDMS chain.

Table 2 also shows the values of the weight fraction of PLLA and PDMS in the triblock copolymer and the weight ratio of PDMS and PLLA blocks that generally showed good agreement with theoretical values. Similarly to the previous consideration, the maximum deviation from the theoretical value was observed for the samples synthesized at the highest temperature when the catalyst was added at the beginning of the reaction.

Table 2. $^1$H NMR analysis of the PLLA-PDMS-PLLA triblock copolymers (1000-1000-1000 g mol$^{-1}$) synthesized under various experimental conditions

| Sample      | $I_{(CH)}_R$ | $I_{(CH)}_T$ | $X_{PLLA}$ | $M_{PLLA}$ | $M_{PLLA-PDMS-PLLA}$ | PLLA/copolymer | PDMS/copolymer | PDMS/PLLA |
|-------------|--------------|---------------|-------------|------------|----------------------|----------------|----------------|-----------|
| PLLA-1000-1 | 27.61        | 13.81         | 1067        | 3134       |                      | 68.09          | 31.91          | 0.469     |
| PLLA-1000-2 | 29.73        | 14.87         | 1144        | 3288       |                      | 69.59          | 30.41          | 0.437     |
| PLLA-1000-3 | 27.71        | 13.86         | 1071        | 3142       |                      | 68.17          | 31.83          | 0.467     |
| PLLA-1000-4 | 23.76        | 11.88         | 928         | 2856       |                      | 64.99          | 35.01          | 0.539     |

$^a$ The ratio of the signal intensities of methine protons from the L-lactide residue, $I_{(CH)}_R$, and methine protons from the terminal groups, $I_{(CH)}_T$.

$^b$ The degree of polymerization of L-lactide (the L-lactide residue consists of two repeating units).

$^c$ Molecular weight of the PLLA segment.

$^d$ Molecular weight of the PLLA-PDMS-PLLA triblock copolymer.

$^e$ The weight fraction of the PLLA segment in the copolymer.

$^f$ The weight fraction of the PDMS segment in the copolymer.

$^g$ The weight ratio of the PDMS and PLLA segments in the copolymer.

Figure 4. $^1$H NMR spectrum of PLLA-2000-1 h.
The determination of the optimal reaction time for the preparation of the PLLA-PDMS-PLLA triblock copolymer was carried out in mild reaction conditions, as increasing both the temperature and amount of the catalyst was found to affect negatively the yield of the synthesized copolymer. The reaction was conducted at 100 °C for 50 hours, whereby the catalyst concentration was 500 ppm. Also, in this reaction, the molar fraction of L-lactide in the reaction mixture was increased and the composition of the reaction mixture was adjusted to obtain PLLA block with molecular weight of 2000 g mol⁻¹, which should make it easier to track conversions. The reaction was run for 60 minutes in the absence of a catalyst. After the first sample was taken, the catalyst in the lower examined concentration of 500 ppm was added to the reaction mixture.

Table 3. NMR analysis: the dependence of the conversion on the reaction time for the synthesis of the PLLA-2000 triblock copolymer (PLLA-PDMS-PLLA=2000-1000-2000 g mol⁻¹)

| Sample           | I(CH)₇L₈A / I(CH)₁₉G |
|------------------|-----------------------|
| PLLA-2000-1 h    | 37.23                 |
| PLLA-2000-7 h    | 27.55                 |
| PLLA-2000-19 h   | 9.76                  |
| PLLA-2000-29 h   | 13.29                 |
| PLLA-2000-43.5 h | 16.39                 |

a) The ratio of the signal intensities of the methine protons from unreacted L-lactide (LLA) and the terminal groups (TG) of triblock copolymer.

In Figure 4, the ¹H NMR spectrum of the sample of PLLA-2000-1h is shown. This sample was taken from the reaction mixture before the addition of the catalyst. As it can be seen in the ¹H NMR spectrum, the signal at δ = 4.4 ppm from the methine protons of the end-groups was observed, which clearly proved a chemical bonding between the PDMS prepolymer and L-lactide. This also confirmed that the presence of the amino groups of prepolymer was sufficient to cause the initiation of the L-lactide ring-opening, without the addition of stannous octoate catalyst. The ratio of intensities of the methine proton signal and the signal of the methylene proton from the aminopropyl group was 0.47, only slightly lower than the theoretical value of 0.5 (1:2 ratio). Based on these results, it can be concluded that 60 minutes was the optimal reaction time for macroinitiation of the L-lactide ring-opening by amino groups of the PDMS prepolymer.

![Figure 5. ¹H NMR spectrum of PLLA-2000-50 h.](image)

The complete quantitative assessment of the degree of conversion based only on proton NMR spectra was somewhat ambiguous, due to the overlap of certain signals that are necessary to quantify the reaction. In the first place, the strong signal of the methine protons from the unreacted L-lactide obser-
ved at around $\delta = 5.0$ ppm, was partially overlapped with the signal of the internal methine protons of the PLLA blocks at $\delta = 5.2$ ppm. Nevertheless, analysis of the NMR spectra allowed for a rough assessment of the degree of conversion of L-lactide and the obtained results are shown in Table 3.

As it can be seen, the proportion of the methine protons of unreacted L-lactide was decreased with increasing the reaction time to 19 h, after which their proportion increased again. Also, in the spectra of samples at the reaction times of 19, 29 and 43.5, a very broad signal at about $\delta = 3.0$ ppm (19 hours) appeared. With the further increase of the reaction time, this signal was intensified, expanded and moved to higher values of $\delta$ ($\delta = 3.8$ ppm after 43.5 h). The origin of this signal is not clear, but may be linked to the decreasing of the degree of conversion and the appearance of depolymerization at the extremely long duration of the reaction. It can be assumed that the long-term duration of the reactions led to increased probability of exposure to traces of moisture and/or similar effects. The results of NMR calculations for the PLLA-2000-50 h sample, which was obtained by precipitation after 50 hours of the reaction, contributed to this conclusion. $^1$H NMR spectrum of this sample is shown in Figure 5. Although the yield of this sample of 70% was significantly higher than the yields of the other samples in the first series, degree of polymerization, i.e. average length of the PLLA blocks, was significantly lower, whereby number-average molecular weight was about 500 $g \text{ mol}^{-1}$. This suggests that a greater number of synthesized molecules had a lower degree of polymerization, which is also in very good correlation with the results of inherent viscosity measurements, where this sample had the lowest measured value.

The results also showed that the fraction of the PDMS block in the copolymer synthesized under these experimental conditions, during 50 h, was very low, almost ten times lower than the value which was expected on the basis of the reaction mixture composition. In addition to depolymerization and other side reactions, it is highly possible that there was a loss of functionality of the siloxane prepolymer.

4. CONCLUSION

The PLLA-PDMS-PLLA triblock copolymers were synthesized successfully by the ring-opening polymerization of L-lactide, with aminopropyl-terminated PDMS prepolymer as macroinitiator and stannous octoate as a catalyst. The optimal temperature for this reaction was 130 °C, while the copolymer with the predetermined composition was obtained in the presence of 500 ppm catalyst related to L-lactide. The yield of the synthesized copolymers was generally low, about 40% for the samples whose composition showed the best match with the one predetermined by the molar ratios of the comonomers. The structure and composition of the synthesized copolymers were confirmed by $^1$H NMR and $^{13}$C NMR spectroscopy. At the highest reaction temperature (145 °C), the largest positive deviation from the predetermined composition was observed. This result was most likely a result of the thermal instability of the PDMS terminal groups under the given experimental conditions. The largest negative deviation from the theoretical values was observed when the catalyst was added to the reaction mixture at the beginning of the reaction. In this case, a competition between the polymerization of L-lactide and the macroinitiation reaction has occurred, wherein the number of short chains of the formed PLLA homopolymer was increased. Also, prolonged reaction times increased the probability of depolymerization reaction and other side reactions, which was supported by the low content of the PDMS block, as well as by a relatively low value of inherent viscosity of the sample obtained at the reaction time of 50 h. Further studies of the structure - reaction conditions relationship, as well as the effects that lead to side reactions during the synthesis, especially the depolymerization reaction, are necessary.

5. ACKNOWLEDGEMENT

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