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СОПОЛИМЕРИЗАЦИЯ D,L-ЛАКТИДА И ϵ -КАПРОЛАКТОНА
В ПРИСУТСТВИИ ОКТАНОАТА ОЛОВА(II) В КАЧЕСТВЕ КАТАЛИЗАТОРОВ:
ИЗУЧЕНИЕ МИКРОСТРУКТУРЫ СОПОЛИМЕРАС. В. КОСТЮК^{1), 2)}¹⁾Белорусский государственный университет, пр. Независимости, 4, 220030, г. Минск, Беларусь²⁾Научно-исследовательский институт физико-химических проблем БГУ,
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Исследована сополимеризация с раскрытием цикла D,L-лактида и ϵ -капролактона в массе при 130 °C и различных соотношениях D,L-лактида и ϵ -капролактона, катализируемая $\text{Sn}(\text{Oct})_2$. Было показано, что независимо от исходного соотношения сомономеров синтезированные сополимеры на начальных стадиях реакции обогащены D,L-лактидом, что указывает на образование градиентоподобного сополимера. Однако интенсивное протекание реакции переэтерификации как во время полимеризации, так и в условиях отсутствия мономера приводит к перераспределению мономерных последовательностей и формированию статистического сополимера. Синтезированные сополимеры характеризуются высокой полидисперсностью ($\bar{M}_w > 2,0$), которая возрастает при выдерживании реакционной смеси в условиях недостатка мономера, что доказывает протекание реакции переэтерификации. Образование случайных сополимеров подтверждается наличием только одного значения T_g , которое постепенно увеличивается с ростом содержания D,L-лактида в сополимере при температуре от –48,6 до +33,3 °C для соотношений D,L-лактида и ϵ -капролактона в сополимере 20 : 80 и 90 : 10 моль/моль соответственно.

Ключевые слова: полимеризация с раскрытием цикла; D,L-лактид; ϵ -капролактон; октаноат олова(II); биodeградируемые сополимеры.

COPOLYMERIZATION OF D,L-LACTIDE
AND ϵ -CAPROLACTONE USING TIN(II) OCTANOATE AS CATALYSTS:
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$\text{Sn}(\text{Oct})_2$ -catalyzed ring-opening copolymerization of D,L-lactide and ϵ -caprolactone in bulk at 130 °C at different D,L-lactide and ϵ -caprolactone has been studied. It was shown that independent on the initial comonomers ratio, the syn-

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thesized copolymers are enriched by D,L-lactide at the early stage of reaction indicating the formation of gradient-like copolymer. However, the intensive transesterification reaction both during the polymerization and at the monomer-starved conditions leads to the redistribution of the monomer sequences and formation of the random copolymer. The synthesized copolymers are characterized by high polydispersity ($\bar{M}_w/\bar{M}_n > 2.0$), which raises when the reaction mixture was kept under monomer-starved conditions that confirms the occurrence of transesterification. The formation of random copolymer is confirmed by single T_g value, which gradually increased with the increase of the amount of D,L-lactide in the copolymer from -48.6 to $+33.3$ °C for D,L-lactide and ϵ -caprolactone ratio in copolymer of 20 : 80 and 90 : 10 mol/mol respectively.

Keywords: ring-opening copolymerization; D,L-lactide; ϵ -caprolactone; tin(II) octanoate; biodegradable copolymers.

Introduction

Among the biodegradable polymers, polylactide (PLA) and polycaprolactone (PCL) attract significant attention due to they use for packaging applications as well as in biomedical and pharmaceutical field [1–3]. It is well-known that PLA exhibits relatively high degradation rate (from months *in vitro* to several weeks *in vivo*) and possesses good mechanical properties but suffers from its brittleness and stiffness [2; 4; 5]. In contrast to PLA, PCL is semicrystalline elastic material at room temperature due to its low glass transition temperature (T_g) (T_g (PCL) ~ -60 °C), which is characterized by much lower degradation rate (about 1 year *in vivo*) as compared to PLA [3; 6]. On the other hand, PCL is quite promising polymer for biomedical field due to its remarkable drug permeability [3]. Therefore, the copolymerization of lactide (both racemic D,L-lactide or stereoisomeric L-lactide) with ϵ -caprolactone allows to adjust the properties of the copolymer by tuning the comonomer ratio, monomer sequencing and the molecular weight and polydispersity providing by biodegradable copolymers with desired (tuned) properties. For example, a number of copolymers of D,L-lactide with ϵ -caprolactone was synthesized using $[\text{OC}(\text{Me})_2\text{CH}_2\text{N}(\text{Me})\text{CH}(\text{Me})\text{CH}(\text{Ph})\text{O}]\text{Ti}(\text{O}^i\text{Pr})_2$ as catalyst, which provided much better foaming in supercritical CO_2 as compared to neat polylactide [7]. Moreover, the porosity and pore size of the obtained scaffolds could be easily controlled by the copolymer composition [7; 8].

However, despite the fact that rate of propagation of homopolymerization of ϵ -caprolactone being typically much faster than that of lactide, the copolymerization of these monomers often leads to the preferential consumption of lactide as compared to ϵ -caprolactone as well to significant slowdown of the polymerization process [9–11]. Therefore, the copolymerization of lactide and ϵ -caprolactone may leads to formation of block or gradient copolymers [11]. In addition, the copolymerization process is often accompanied by occurrence of transesterification reactions, especially for the copolymerizations performed at high temperatures and in bulk [9–11]. During the last decade, the number of catalytic system based on Al complexes bearing bulky phenoximine [12], salalen type [13] or amidinate [14] ligands as well as complexes of Zn [15], La [16] and many others [11] were shown to induce the statistical copolymerization of lactide and ϵ -caprolactone. However, there are no or little information about the structure of copolymer obtained in the course of $\text{Sn}(\text{Oct})_2$ -catalyzed ring-opening copolymerization of lactide and ϵ -caprolactone in bulk. On the other hand, this catalyst and conditions (polymerization in bulk, temperature > 130 °C) is currently used for the production of polylactide at the industrial scale [2].

This article is devoted to the investigation of bulk $\text{Sn}(\text{Oct})_2$ -catalyzed ring-opening copolymerization (ROP) of D,L-lactide and ϵ -caprolactone at different comonomer ratios. ^1H NMR spectroscopy study of the copolymer composition at different conversions indicates much faster consumption of the D,L-lactide at the beginning of the reaction that should leads to formation of gradient copolymer. However, according to ^1H NMR spectroscopy and DSC measurements the synthesized copolymers possess predominantly random distribution of (co)monomers along the polymer chain at complete monomers conversion due to the transesterification reaction.

Experimental part

Materials. All manipulations were carried out using Schlenk vacuum line under dried argon atmosphere. ϵ -Caprolactone ($\geq 99\%$) (*Fluka*, Germany) was dried over CaH_2 , distilled over CaH_2 under reduced pressure and stored under argon. D,L-lactide ($\geq 98\%$) (*Aldrich*, Germany) was recrystallized twice from toluene and then dried in vacuum 5 h at 50 °C. Tin(II) octanoate ($\text{Sn}(\text{Oct})_2$, 92.5–100 %) (*Sigma-Aldrich*) and benzyl alcohol (99.8 %) (*Sigma-Aldrich*) were dried over CaH_2 and then distilled under reduced pressure.

Characterization. Size exclusion chromatography (SEC) was performed on an Ultimate 3000 apparatus (*Thermo Scientific Dionex*, Germany) with Agilent PL gel 5 μm MIXED-C (300 \times 7.5 mm) and one preco-

lumn (PL gel 5 μm guard 50 \times 7.5 mm) thermostated at 30 $^{\circ}\text{C}$. The detection was achieved by differential refractometer (RI) as well as diode array detector (UV). Tetrahydrofuran (THF) was eluted at a flow rate of 1.0 mL/min. The calculation of molecular weight and polydispersity was carried out using polystyrene standards (EasiCal, M_n from 580 $\text{g} \cdot \text{mol}^{-1}$; $M_w/M_n \leq 1.05$) using *Chromeleon software* (Germany). ^1H NMR (500 MHz) spectra were recorded in CDCl_3 at 25 $^{\circ}\text{C}$ on a Bruker AC-500 spectrometer (Germany) calibrated relative to the residual solvent resonance.

Differential scanning calorimetry (DSC) was performed using simultaneous thermal analyzer (NETZSCH STA 449 F3 Jupiter[®], NETZSCH, Germany), equipped with steel furnace, liquid nitrogen cooling system, and TGA-DSC-Cp Type P sample holder. The measurements was performed in opened Al crucible and helium flow. Data were recorded during the second run (from 120 to 200 $^{\circ}\text{C}$) at a heating rate of 10 $^{\circ}\text{C} \cdot \text{min}^{-1}$. The cooling rate between the first and a second run was also equal to 10 $^{\circ}\text{C} \cdot \text{min}^{-1}$. The glass transition temperature (T_g) was given by the inflection point of the transition and melting point (T_m) was given as a maximum of the corresponding peak. T_g and T_m was performed using *NETZSCH Proteus[®] 8.0 software*.

Copolymerization. Copolymerizations were performed in Schlenk reactors equipped with a magnetic stirrer bar in bulk at 130 $^{\circ}\text{C}$. The reactor was charged by required amounts of ϵ -caprolactone, D,L-lactide and benzyl alcohol and immersed into oil bath preheated to 130 $^{\circ}\text{C}$. The polymerization was initiated by the addition of catalyst ($\text{Sn}(\text{Oct})_2$). The samples were withdrawn from the reactor after predetermined time intervals and subjected to ^1H NMR analysis for the determination of the monomer conversion as well as the composition of the copolymer. In a typical copolymerization experiments (20 mol % of ϵ -caprolactone), the reactor was charged by 5 g (0.035 mol) of D,L-lactide, 0.96 mL (0.009 mol) of ϵ -caprolactone and 0.025 mL (0.24 mmol/L) of benzyl alcohol. The polymerization was initiated by the addition of 0.04 mL (0.12 mmol/L) of $\text{Sn}(\text{Oct})_2$.

Results and discussion

The conversion of each monomer (D,L-lactide (LA) and ϵ -caprolactone (CL)) as well as copolymer structure and composition was determined by ^1H NMR spectroscopy. The ^1H NMR spectrum of copolymer containing 60 mol % of LA and 40 mol % of CL is presented in fig. 1. The series of signals between 1.2 and 2 ppm belongs to main chain protons of methylene group of CL (e) units and methyl group of LA units (d) (fig. 1, table 1). In addition to these resonances, the signals correspond to CL–LA heterodyad appeared at 2.38 ppm (c^2), 4.13 ppm (b^2) and 5.08 ppm (a^2), while the signals of CL–CL and LA–LA homodyads were detected at 2.30 ppm (c^1), 4.05 ppm (b^1) and 5.21 ppm (a^1), respectively (see fig. 1, table 1). Finally, the signals at 2.65 ppm (c^0) and 4.21 ppm (b^0) were assigned to methylene protons of CL, while the resonance at 5.04 (a^0) was attributed to methine proton of LA monomer (see fig. 1, table 1).

Based on ^1H NMR spectrum, the conversion of LA and CL (ω_{LA} and ω_{CL} (in %) respectively), the average sequence lengths of LA and CL units in a polymer chain (L_{LA} and L_{CL} respectively), and randomness character (RC) were calculated employing the following equations:

$$\omega_{\text{LA}} = \frac{A_{5.17}}{A_{5.17} + A_{5.04}} \cdot 100,$$

$$\omega_{\text{CL}} = \frac{A_{4.10}}{A_{4.10} + A_{4.21}} \cdot 100,$$

$$L_{\text{LA}} = \frac{2F_{\text{LA}}}{F_{\text{CL-LA}}},$$

$$L_{\text{CL}} = \frac{2F_{\text{CL}}}{F_{\text{CL-LA}}},$$

$$\text{RC} = \frac{F_{\text{CL-LA}}}{2 \cdot F_{\text{LA}} \cdot F_{\text{CL}}},$$

where A_i is the integral of the signal at i shift.

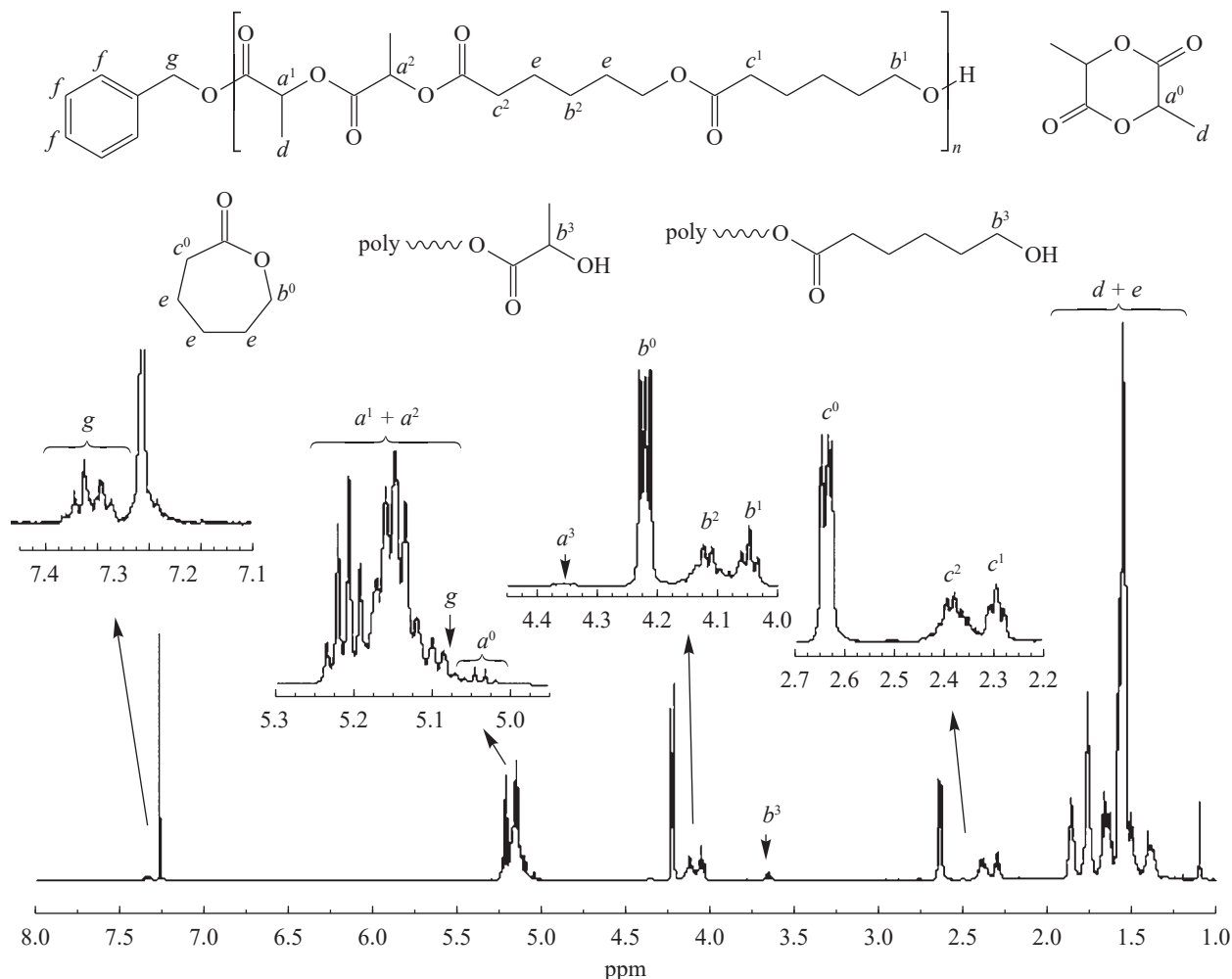


Fig. 1. ^1H NMR spectrum of PLA-co-PCL at low monomer conversions obtaining for initial LA/CL = 60/40 mol % ratio. The superscript in the designation of signals indicates their belonging to the monomers (0), LA-LA or CL-CL dyad (1), CL-LA dyad (2) and to the end groups (3)

Table 1

The assignments of the signals in ^1H NMR spectrum of copolymer to corresponding structural units

Signal, ppm	Description
5.17	PLA methine proton
5.21	LA-LA dyad methine proton
5.08	LA-CL dyad methine proton
5.04	LA monomer methine proton
4.21	CL monomer methylene protons next to OCO
4.10	PCL methylene protons next to OCO
4.13	CL-LA dyad methylene protons
4.05	CL-CL dyad methylene protons
2.65	CL monomer methylene protons next to COO
2.38	CL-LA dyad methylene protons
2.30	CL-CL dyad methylene protons

F_{LA} and F_{CL} are comonomer molar fractions, and F_{CL-LA} is the LA–CL (or CL–LA) average dyad relative molar fraction which were calculated using the following equations:

$$F_{LA} = \frac{A_{5.17}}{A_{5.17} + 0.5(A_{4.10} + A_{2.38} + A_{2.30})},$$

$$F_{CL} = \frac{0.5(A_{4.10} + A_{2.38} + A_{2.30})}{A_{5.17} + 0.5(A_{4.10} + A_{2.38} + A_{2.30})},$$

$$F_{CL-LA} = \frac{A_{4.13} + A_{2.38}}{A_{5.17} + 0.5(A_{4.10} + A_{2.38} + A_{2.30})}.$$

In addition to 1H NMR spectroscopy, all copolymers at close to complete conversion of both monomers (LA and CL) were characterized by DSC. As it can be seen from fig. 2 and table 2, all synthesized copolymers are characterized by one glass transition temperature (T_g), which is decreased with increasing content of CL in a copolymer chain. This observation indicates on the formation of random copolymer under investigated conditions. It should be noted that T_g of polylactide is slightly lower than reported in the literature (44.3 vs 60 °C [2; 10]) due to the relatively low molecular weight ($M_n = 13\,800\text{ g} \cdot \text{mol}^{-1}$) of polymer prepared in this work (see table 2). Another interesting observation from fig. 2 is the presence of peak corresponds to melting point (T_m) of polycaprolactone on DSC curve of copolymer enriched by CL (PLA 10). However, the value of T_m for PLA 10 is lower than for neat PCL (PLA 0) with similar molecular weight (44.5 vs 56.8 °C respectively) (see fig. 2, table 2) indicating the presence of quite long polycaprolactone sequences separated by lactide units.

Table 2

Copolymerization of D,L-lactide and ϵ -caprolactone*

LA/CL, mol %	Time, h	Conversion of LA; CL**, %	LA/CL***, mol %	M_n (SEC), $\text{g} \cdot \text{mol}^{-1}$	M_w/M_n (SEC)	T_g , °C	T_m , °C	L_{LA}^{****}	L_{CL}^{****}	RC****
100/0	1	95; 0	100/0	13 800	—	44.3	—	—	—	—
	6	100; 0	100/0	12 100	2.33	—	—	—	—	—
90/10	6	98; 66	94/6	12 800	2.19	—	—	16.8	1.2	0.922
	24	98; 99	90/10	11 300	2.68	33.3	—	10.5	1.2	0.962
80/20	6	95; 27	89/11	17 100	2.23	—	—	10.5	1.4	0.825
	24	99; 98	80/20	14 700	2.54	20.5	—	5.3	1.3	0.960
60/40	6	99; 85	67/33	13 100	2.77	—	—	3.4	1.7	0.885
	24	100; 100	61/39	13 400	2.80	–2.3	—	2.7	1.8	0.931
40/60	6	98; 69	43/57	14 700	2.31	—	—	1.9	2.6	0.908
	24	100; 100	39/61	17 900	2.99	–27.8	—	1.5	2.4	1.072
20/80	4	96; 99	17/83	25 800	2.53	—	—	1.0	4.8	1.216
	8	99; 100	19/81	24 500	2.54	–48.6	—	0.9	4.1	1.304
10/90	1.5	100; 73	11/89	26 200	2.36	—	—	1.3	10.3	0.892
	4	100; 99	10/90	25 700	2.46	—	44.5	1.1	10.8	0.972
0/100	1	0; 98	0/100	11 700	1.97	—	—	—	—	—
	6	0; 100	0/100	20 700	2.76	—	56.8	—	—	—

*Copolymerization conditions: $T = 130\text{ °C}$, $[\text{Sn}(\text{Oct})_2]/[\text{BnOH}] = 1 : 2$.

**Conversion of D,L-lactide and ϵ -caprolactone respectively.

***D,L-lactide and ϵ -caprolactone monomer units content in copolymer determined by 1H NMR.

****Microstructure parameters obtained by 1H NMR.

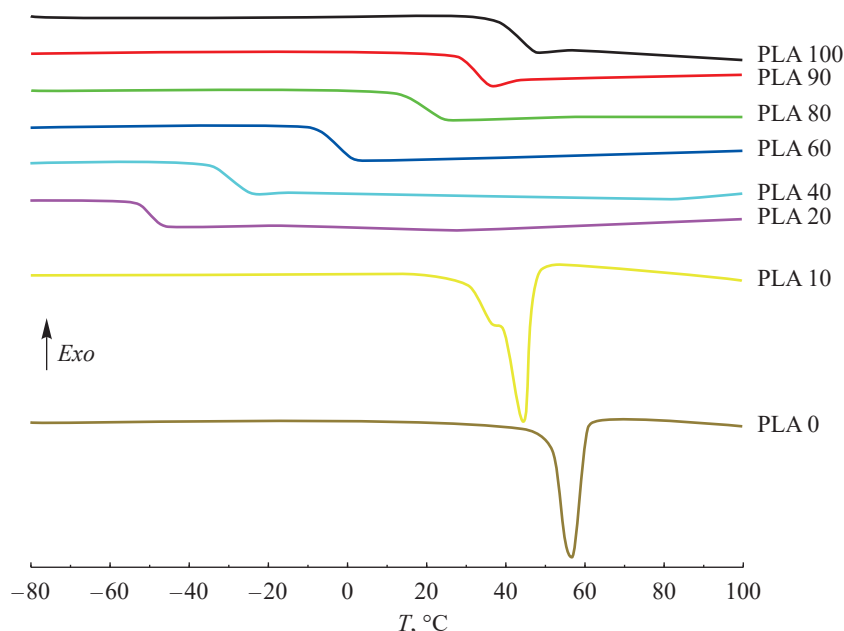


Fig. 2. DSC curves of polylactide (PLA 100), polycaprolactone (PLA 0) and copolymers of D,L-lactide with ϵ -caprolactone with different content of lactide in the copolymer (PLA 10, PLA 20, PLA 40, PLA 60, PLA 80, PLA 90)

As we already mentioned above, all copolymers possess predominantly random distribution of (co)monomers along the polymer chain at complete monomers conversion. However, as it can be seen from table 2, D,L-lactide is consumed much faster than ϵ -caprolactone that leads to enrichment of the copolymer by LA at the beginning of the reaction. In addition, copolymers display higher length of LA sequences at the beginning of the polymerization (4–6 h) as compared to end of the reaction (24 h). These data indicate that copolymers should have gradient composition. On the other hand, the randomness character (RC) is close to unity for most of the copolymers obtained in this work, although RC is slightly lower at the beginning of the reaction than at the end of the process (see table 2). According to the literature, when $RC \rightarrow 0$, the block copolymer is formed, the random and alternating copolymers are generated when $RC \rightarrow 0$ and $RC \rightarrow 2$ respectively [17]. Besides, T_g values were also calculated using the Fox equation:

$$\frac{1}{T_g} = \sum \frac{w_i}{T_{gi}}$$

where T_g is the glass transition temperature of copolymer, w_i the weight (%) content of monomer i in copolymer, and T_{gi} the glass transition temperature of homopolymer composed of monomer i . Figure 3 shows that the experimental values correlate well with the theoretically predicted ones. These data support the random distribution of the comonomers along the polymer chain.

The relevant explanation of the observed discrepancy lies in the transesterification reaction, which plays key role in the redistribution of the monomer sequences, thereby influence the copolymer microstructure [10]. The high values of the polydispersity of the synthesized copolymers even at incomplete monomer conversion (see table 2) indicate that transesterification proceeds in the course of $\text{Sn}(\text{Oct})_2$ -catalyzed the ring-opening copolymerization of LA and CL in bulk. Moreover, the polydispersity also increases in conjunction with approaching of RC value to 1 under monomer-starved conditions (see table 2). Based on these results, we can conclude that transesterification proceeds efficiently even in the absence of monomer. Therefore, the keeping the reaction system for the prolonged period of time under monomer-starved conditions could be an efficient approach to «randomize» the initially formed gradient-like copolymer.

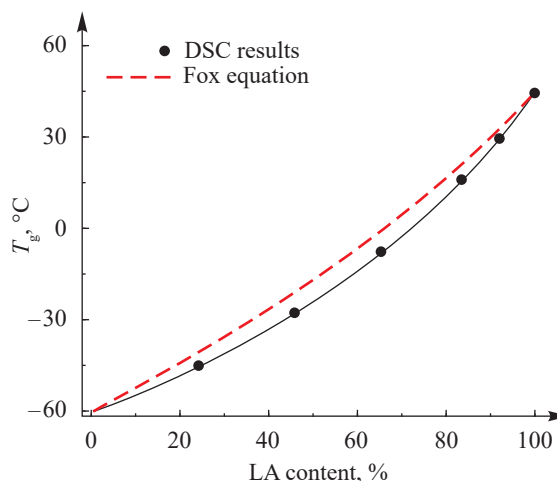


Fig. 3. Variation of glass transition temperature (T_g) of copolymers versus LA content

Conclusions

The $\text{Sn}(\text{Oct})_2$ -catalyzed ring-opening copolymerization of D,L-lactide and ϵ -caprolactone in bulk is accompanied by much faster consumption of LA than CL that theoretically should lead to formation of gradient-like copolymer. This assumption is consistent with the enrichment of the copolymer by LA units at low monomer conversions. However, the intensive transesterification reaction both during the polymerization and at the monomer-starved conditions leads to the redistribution of the monomer sequences and formation of the random copolymer. The random structure of copolymers synthesized at different LA/CL ratios (LA/CL from 10/90 to 90/10 mol/mol) was confirmed by the presence of single T_g values on DSC curves. The occurrence of transesterification reaction is consistent with the high polydispersity of obtained copolymers as well as with the increase of the polydispersity under monomer-starved conditions. Keeping the reaction system for the prolonged period of time under monomer-starved conditions could be an efficient approach to «randomize» the initially formed gradient-like copolymer.

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