Synthesis and characterization of high-molar-mass star-shaped poly(L-lactide)s

Adam Michalski[1], Grzegorz Łapienis[1], [*]

Abstract: The synthesis of high-molar-mass linear and 6-arm star-shaped poly(L-lactide)s (PLLA's) is presented. Dipentaerythritol and benzyl alcohol were used as initiators and $Sn(Oct)_2$ was applied as a catalyst in the ring-opening polymerization (ROP) of L-lactide (L-LA) carried out at 130 °C. The prepared PLLA's were characterized by SEC (size exclusion chromatography), ^{1}H NMR (proton nuclear magnetic resonance spectroscopy), DSC (differential scanning calorimetry), and TGA (thermogravimetric analysis). The structure of the obtained star-shaped polymers was confirmed by comparison of the radii of gyration (R_g) determined by SEC for the linear and star macromolecules. The thermal properties of PLLA's were shown for the wide range of molar masses. Additionally, it was confirmed that Irganox stabilizer has an influence on the thermal stability of PLLA's.

Keywords: poly(L-lactide), stabilization, DSC, NMR, thermal properties.

Synteza i charakterystyka gwiaździstych poli(L-laktydów) o dużych masach molowych

Streszczenie: Przedstawiono syntezę liniowych i 6-ramiennych gwiaździstych poli(L-laktydów) (PLLA) o dużych masach molowych. Polimeryzację z otwarciem pierścienia (ROP) L-laktydu (L-LA) inicjowaną dipentaerytrytem oraz alkoholem benzylowym prowadzono w temperaturze 130 °C wobec $Sn(Oct)_2$ jako katalizatora. Otrzymane PLLA scharakteryzowano za pomocą SEC (chromatografia żelowa), ^{1}H NMR (spektroskopia magnetycznego rezonansu jądrowego), DSC (różnicowa kalorymetria skaningowa) i TGA (analiza termograwimetryczna). Strukturę otrzymanych polimerów gwiaździstych potwierdzono przez porównanie wyznaczonych w SEC promieni bezwładności (R_g) dla gwiaździstych i liniowych makrocząsteczek. Właściwości termiczne PLLA przedstawiono dla szerokiego zakresu mas molowych. Dodatkowo potwierdzono, że stabilizator Irganox ma wpływ na stabilność termiczną PLLA.

Słowa kluczowe: poli(L-laktyd), stabilizacja, DSC, NMR, właściwości termiczne.

Poly(L-lactide) (PLLA) is a renewable, biodegradable, and compostable thermoplastic polymer with mechanical properties similar to polystyrene. It is one of the most promising candidates capable to replace petrochemical polymers [1, 2]. However, PLLA has limited toughness, as evidenced by low tensile elongation at break, impact strength, and fracture toughness, limiting more widespread applications of the material [2, 3]. As a compostable polymer PLLA has distinct advantages over other plastics in terms of waste management. A wide use of PLLA will reduce the impact of plastics on the environment [4, 5]. Lactic acid, the degradation product of PLLA, is absolutely non-toxic and non-immunogenic, as it occurs in the metabolism of all animals and microorganisms [5, 6].

Linear PLLA has a melting point of 170–183 °C and a glass-transition temperature of 55–65 °C [2, 7–10] and a degree of crystallization around 70 % [11]. PLLA has a narrow window of processing (~ 12 °C) [12], whereas a 90/10 L- to D-copolymer has a much wider range of processing (~ 40 °C) due to its lower melting temperature [2]. Not stabilized polylactides are highly sensitive to heat, especially at temperatures higher than 190 °C [13].

Recently, it is observed an increased interest in star-shaped PLLA materials as they exhibit highly desirable rheological, mechanical and biomedical properties that are inaccessible in the case of linear polymers. These branched polyesters have the higher concentration of functional end-groups that additionally influenced their properties, *e.g.*, improved solubility [14, 15]. Long-chain branches predominantly affect the viscoelasticity of fluidity range, decrease the viscosity, and increase the elasticity. By introducing the branched structure into PLLA, physical properties such as crystallinity, glass-transition point (T_g) and melting point (T_m) will be influenced [16–21].

[1] Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, Department of Polymer Chemistry, Sienkiewicza 112, 90-363 Lodz, Poland.

[*] Author for correspondence; e-mail: lapienis@cbmm.lodz.pl

Star polymers can be processed at lower temperatures than their linear counterparts, which could be advantageous, especially in the processing of thermo-labile polymers like PLLA's [22]. Usually, star PLLA's with short arms were synthesized and investigated. There are only a few reports on the synthesis star polymers with long arms but their properties were not studied in detailed [16, 23–26]. The highest reported molar mass for star PLLA with the defined number of arms (*n* = 4) did not exceed 460 000 g/mol [24].

The most commonly method used for the preparation of star PLLA is the ring-opening polymerization (ROP) of ʟ-lactide (ʟ-LA) carried out in bulk at a higher temperature (*e.g.*, 130 °C [24, 27]) above the melting point of the monomer (~ 99 °C), in the presence of initiators containing hydroxyl end-groups. Usually, stannous octoate [Sn(Oct)$_2$] yielded high-molar-mass polymers was used as a catalyst [24, 27–31].

In this work, the synthesis of high-molar-mass linear and star-shaped PLLA's with 6 arms and with high thermal stability is described. The investigation of some their thermal characteristics is reported. The elaborated method of the preparation of stabilized linear and star PLLA's, using an Irganox 1010 as the thermal stabilizer and an Irganox 1024 as catalyst deactivator, is also described. It is well known that to all commercial PLLA's certain stabilizers in a small amount, usually not exceed 0.80 wt % are added [32–35]. Another work on the comparison of the crystallization properties of the high-molar-mass star and linear PLLA's will be published elsewhere [36].

EXPERIMENTAL PART

Materials

Tin(II) octoate (2-ethyl hexanoate) [Sn(Oct)$_2$] (Aldrich, 92.5–100 %) was purified by two consecutive high-vacuum distillations at 140 °C/3 · 10^{-3} hPa. The purified Sn(Oct)$_2$, stored on the vacuum line, finally was directly distributed into thin-walled vials or ampoules equipped with break-seals and then sealed off and stored at -12 °C. Benzyl alcohol (Aldrich, ≥ 99 %) was purified by distillation under normal pressure and finally directly distributed into thin-walled vials. Dipentaerythritol (ACROS Organics, 90 %) was dried under high vacuum (10^{-3} hPa, 85 °C) before use. ʟ-Lactide (ʟ-LA) (Purac,

99 %) was consecutively crystallized from dry 2-propanol and toluene and purified just before use by sublimation in a vacuum (10^{-3} hPa, 85 °C). Methanol (Chempur, pure), methylene chloride (Stanlab, p.a.), Irganox 1010 {pentaerythritol tetrakis[3-(3,5-di-tert-butyl-4-hydroxyphenyl)-propionate]} and Irganox 1024 {2',3-bis[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionyl]propionohydrazide} (BASF) were used as received.
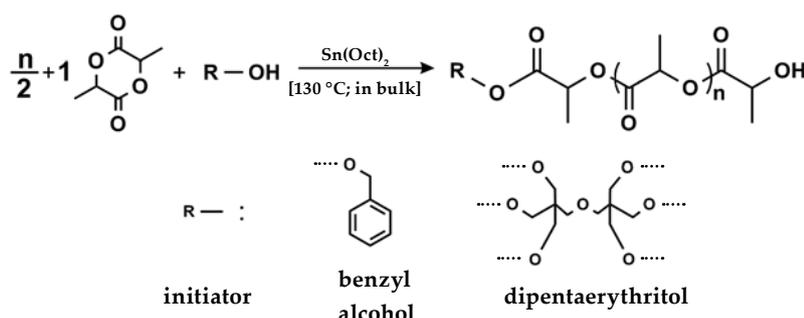
Synthesis of linear and star poly(ʟ-lactide)s

The linear poly(ʟ-lactide)s containing at one chain end benzyl group and star-shaped poly(ʟ-lactide)s containing as a core dipentaerythritol were synthesized in glass ampoules in bulk at 130 °C (~ 24 h) in the presence of Sn(Oct)$_2$ as a catalyst according to the method previously described [30, 31]. The resulting polymer was dissolved in methylene chloride and precipitated into methanol, separated by filtration and washed several times with methanol. This procedure was repeated twice. After precipitation polymers did not contain a residual amount of unreacted ʟ-LA (according to ^{1}H NMR).

Stabilization of poly(ʟ-lactide)s

Polymers after purification were additionally stabilized by adding the thermal stabilizer (Irganox 1010, 0.2 wt %) and the catalyst deactivator (Irganox 1024, 0.2 wt %). Both stabilizers in the appropriate amounts were added to the solution of purified polymers in methylene chloride. After 0.5 h stirring the mixture was concentrated and finally dried in vacuum for several hours at 85 °C. The complete removal of methylene chloride from polymer was confirmed by TGA (thermogravimetric analysis) method. No weight loss below 100 °C in TGA traces was observed.

Methods of testing

The molar masses (M_n and M_w) and radii of gyration (R_g) of polymers were determined by size exclusion chromatography (SEC) using an instrument composed of an Agilent 1100 isocratic pump, an auto-sampler, a degasser, a thermostatic box for columns, a MALS DAWN HELEOS photometer (Wyatt Technology Corporation, Santa Barbara, CA) and an Optilab T-rEX differential refractometer. Two PLGel 5-μm MIXD-C columns were used for

Scheme A. Scheme of the synthesis of linear and star PLLA's

the separation. The samples were injected as a solution in methylene chloride. The volume of the injection loop was 0.1 cm³. Methylene chloride was used as a mobile phase at a flow rate of 0.8 cm³/min. The dn/dc increment of the refractive index (*RI*) equal to 0.035 was applied.

¹H NMR spectra were recorded in CDCl₃ using a Bruker Avance III 500 (11.7 T) spectrometer operating at 500 MHz.

DSC analysis was performed under nitrogen at a heating and cooling rate equal to 10 °C/min on DSC 2920 Modulated TA Instrument. Both temperature and heat flow were calibrated with indium.

TGA analysis was investigated under nitrogen flow by heating the samples from ambient temperature to 500 °C at a heating rate of 20 °C/min on Hi-Res TGA 2950 Thermogravimetric Analyzer, TA Instruments.

RESULTS AND DISCUSSION

In this work the thermal properties of high-molar-mass star-shaped poly(ʟ-lactide)s and their linear analogs with similar molar masses are discussed. The linear and 6-arm star-shaped PLLA's were synthesized in bulk at 130 °C by the coordination polymerization using Sn(Oct)₂ as a catalyst (Scheme A) according to the method previously described [30, 31].

In crude polymerization products, the content of unreacted ʟ-LA was usually below 0.50 %. The content of the residual amount of ʟ-lactide in the polymer was determined on the basis of the analysis of ¹H NMR spectra by comparison of the intensities of the respective signals (Fig. 1). After purification, the content of unreacted ʟ-LA decreased below of the sensitivity of using NMR equipment. During purification (precipitation) the catalyst [Sn(Oct)₂] was also removed. In Fig. 1 there are shown magnified fragments of ¹H NMR spectra derived from >CH- groups of the main chains (δ = 5.10 ppm) in crude and precipitated 6-arm star-shaped PLLA. In ¹H NMR spectrum of crude 6-arm star-shaped PLLA, there is marked a quartet (δ = 4.98 ppm) corresponding to the presence of residual ʟ-LA. In ¹H NMR spectrum of pre-
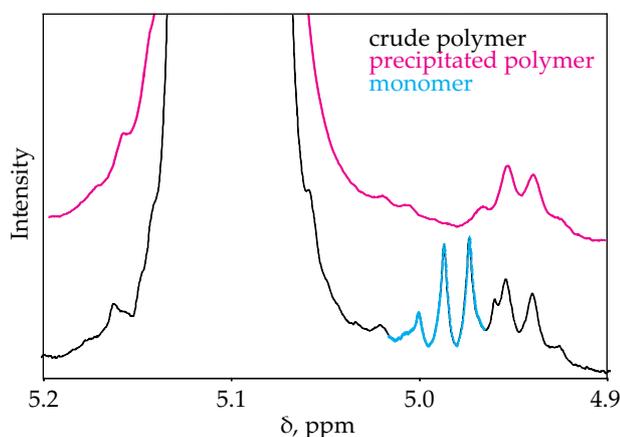
cipitated 6-arm star-shaped PLLA, this quartet was no longer observed.

The molar masses of the obtained star-shaped PLLA's (determined by ¹H NMR and SEC) were close to those calculated from the [M]₀/[I]₀ ratios, and their dispersity was in the range of typically observed for the ROP of lactides. To confirm the structure of obtained star-shaped polymers, the radii of gyration for linear and star macromolecules were compared (Fig. 2a), according to the Eq. (1):

$$g = \frac{\langle R_g \rangle_{br}^2}{\langle R_g \rangle_{lin}^2} \qquad (1)$$

where: g – branching index, R_g – radius of gyration for branch or linear polymers.

Star macromolecules have smaller radii of gyration than their linear analogs with the same molar masses. For example, the values of $g \approx 0.52$ was determined for our star-shaped polymers with 6 arms (Fig. 2b), that agrees with the literature data ($g = 0.50$–0.60) for stars with statistical distribution length of arms and dispersity near 1.50 [31]. The observed linear constant function for the relation between g factor and M_n denotes that obtained PLLA's have star-shaped structure in the whole interval of molar masses.

In Table 1 there are given characteristics of selected linear and star-shaped PLLA's studied in this paper.
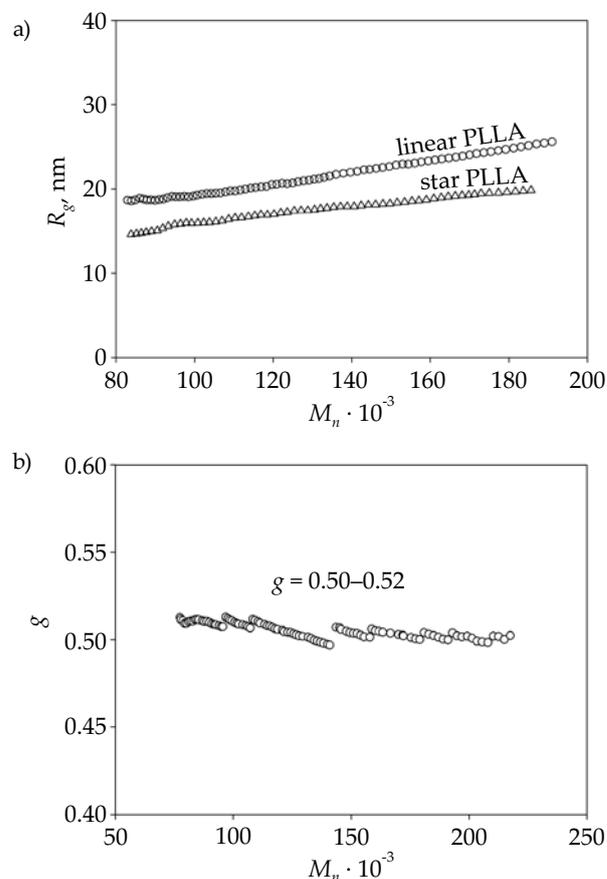

Fig. 1. ¹H NMR spectra of crude and precipitated 6-arm star-shaped PLLA, quartet in blue corresponds to the presence of residual ʟ-LA

Fig. 2. Dependence of: a) radii of gyration, b) branching index *vs* molar mass for 6-arm star PLLA

T a b l e 1. The characteristics of selected linear (L) and star-shaped PLLA's (6s – 6 arm)

PLLA[1]	SEC				DSC			TGA	
	M_n g/mol	M_w g/mol	Đ	M_n (arm) g/mol	T_m °C	ΔH_m J/g	T_g °C	T_o [2] °C	T_{max} [3] °C
1L-p	86 000	127 200	1.48	–	175.5	45.6	59.9	322.3	362.4
2L-p	142 500	168 600	1.18	–	179.6	45.3	61.7	322.3	338.0
3L-c	187 000	330 900	1.77	–	190.5	89.8	66.4	278.0	305.5
3L-p	235 600	321 700	1.37	–	179.7	44.7	60.9	302.4	325.9
4L-c	280 000	443 000	1.58	–	190.2	82.4	54.1	247.8	305.5
4L-p	336 900	498 000	1.48	–	177.9	41.3	70.0	319.7	343.8
6s-1p	6000	9000	1.50	1000	118.0	33.7	54.4	269.1	311.6
6s-2c	83 800	109 000	1.30	14 000	184.4	86.1	62.6	256.3	293.0
6s-2p	75 600	97 800	1.29	12 600	174.9	52.4	–	262.7	352.9
6s-3c	102 400	192 500	1.88	17 100	188.0	87.1	53.8	247.4	287.5
6s-4p	121 900	162 300	1.33	20 300	171.1	38.2	67.5	282.2	315.4
6s-5p	219 600	255 700	1.16	36 600	174.7	42.6	73.0	309.3	348.5

[1] c – denotes crude polymer; p – denotes precipitated polymer, [2] T_o – initial decomposition temperature (onset temperature), [3] T_{max} – temperature at maximum degradation rate.

In the most cases, the values of T_g for linear and star PLLA's were in the range of 54–67 °C, that agrees with the data published previously (55–63 °C) [37–39]. The high degree of crystallinity of the resulted crude PLLA's (up to ~ 96 %) was confirmed by the high melting temperatures (T_m) of 6-arm star-shaped PLLA's (184–188 °C) and for their linear analogs (~ 190 °C) and by the high melting enthalpy (ΔH_m) up to 90 J/g. That denotes the presence of polymers with an ordered structure of chains and without entanglements. The analogous high values of T_m and ΔH_m for PLLA were previously reported by Brzeziński *et al.* [40].

On the other hand, precipitated polymers exhibit typical behavior as polymers with entangled chains: T_m of 6-arm star PLLA's (for M_n > 50 000 g/mol) were ~ 175 °C, whereas for linear PLLA's were in the range of 175–180 °C. For both types of PLLA melting enthalpy was equal to ~ 45 J/g that corresponds to the degree of crystallinity ~ 55 %. The average molar mass of the segments between entanglements for PLLA's was reported to be equal $M_e \approx 4000$ g/mol [15, 41].

The values of the onset temperature (T_o) and T_{max} observed for linear and star PLLA's (Table 1) agree with the data reported in the literature [15].

DSC analysis of star-shaped PLLA's

Polymerization of L-LA at 130 °C in bulk proceeds mainly in the solid state and the high crystalline structure is formed without chain entanglements. This process is called polymerization with uniaxial crystallization [42] and/or crystallization during polymerization [43]. High values of T_m and ΔH_m in the 1st heating proved the significant crystallinity of the sample (Fig. 3). In the 2nd heating much lower T_m and ΔH_m were observed.

The dependence of T_m on the molar mass of the crude linear and 6-arm star PLLA's obtained at 130 °C and after precipitation is shown in Fig. 4. The melting temperatures decrease as the molar masses of
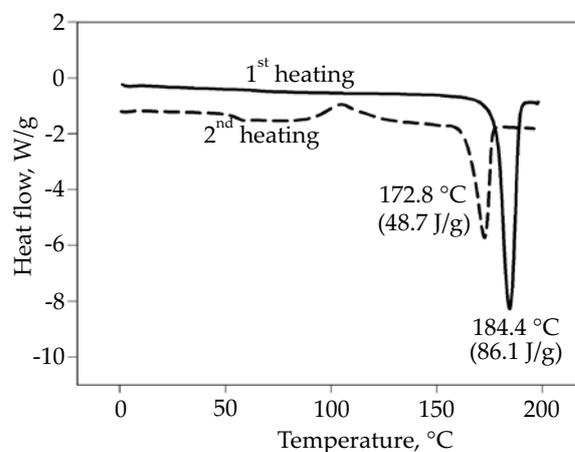

Fig. 3. DSC traces for the 1st and 2nd heating of the crude 6-arm star-shaped PLLA obtained at 130 °C (sample 6s-2c); in the graph the values of T_m and in brackets values of ΔH_m are given
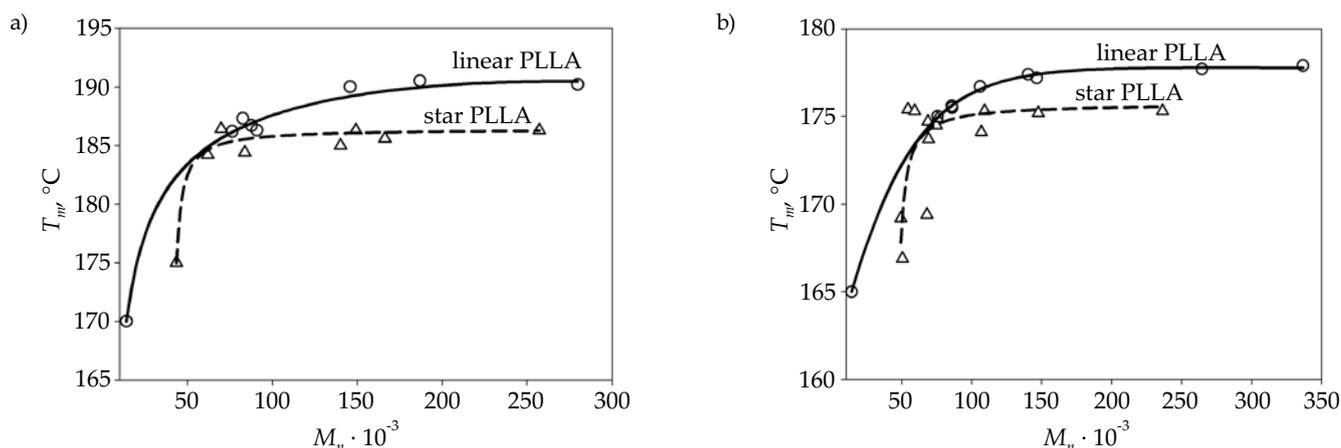
a)

b)

Fig. 4. Melting temperatures (T_m) for the linear and 6-arm star-shaped PLLA's: a) crude polymers obtained at 130 °C, b) precipitated polymers
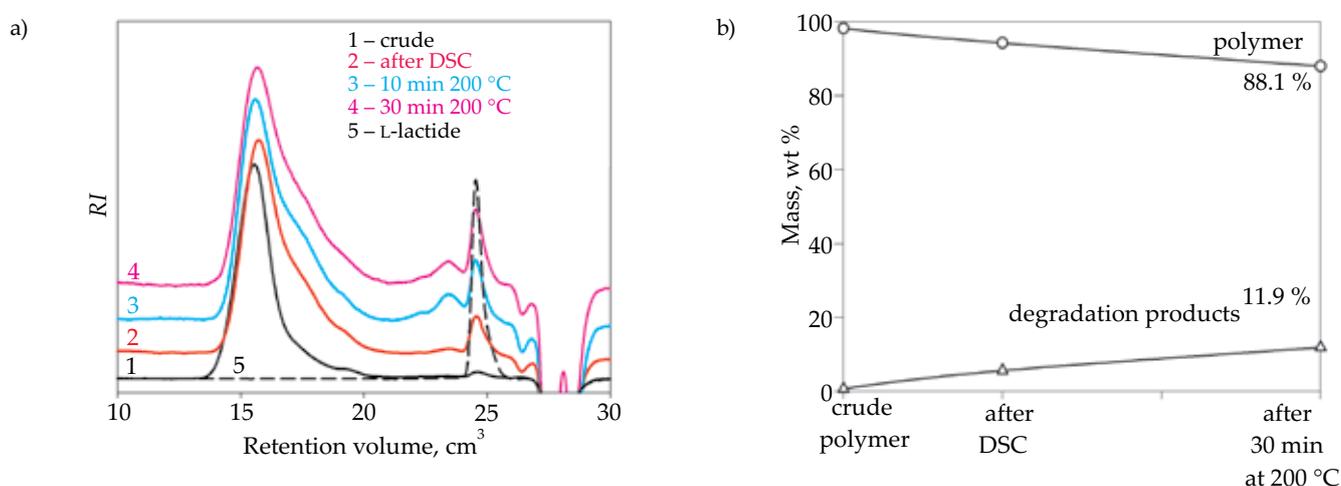
a)

b)

Fig. 5. The thermal stability of crude 6-arm star PLLA analyzed by SEC method (sample 6s-3c): a) numbers denote as follows: 1 – crude polymer, 2 – polymer after DSC analysis, 3 – polymer after DSC and after melt-annealing 10 min at 200 °C, 4 – polymer after DSC and after melt-annealing 30 min at 200 °C; the trace of ʟ-LA (5) is shown additionally, b) composition of the polymer sample during the degradation at 200 °C

PLLA's decrease. In both cases slightly lower T_m for 6-arm star-shaped PLLA's than for their linear analogs with the similar molar masses was observed. The different shape of curves for the star and linear polymers in the region of the smaller-molar-masses ($M_n < 50\ 000$ g/mol) is caused by the disturbance in the formation of the more regular crystalline structure in star polymers by the presence of the core and arms with end-groups.

Thermal stabilization of polymers

It is worth noting that the presence of many hydroxyl end-groups in star-shaped PLLA's accelerate their thermal degradation [44, 45]. The thermal degradation of crude 6-arm star PLLA at 200 °C was observed directly in SEC chromatograms. With the increase of the heating time, *RI* traces became wider with visible shoulders that were the result of the formation of lower-molar-mass compounds and/or oligomers. Additionally, the increase of the signal corresponding to ʟ-LA was also observed (Fig. 5).

Crude PLLA's and after purification without stabilization degrade easily at high temperature ~ 200 °C and their molar masses lowered up to ~ 70 % in 60 min (Fig. 6) with simultaneously increasing the dispersity (*Đ*) from 1.33 to 1.74. After
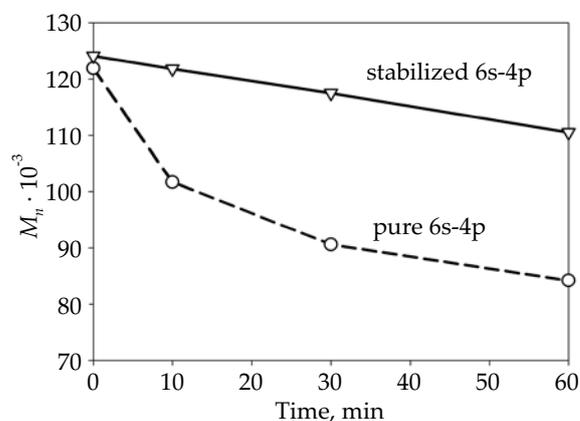

Fig. 6. The thermal stability at 200 °C of pure 6-arm star-shaped PLLA (6s-4p) before and after stabilization

addition of the thermal stabilizer (Irganox 1010, 0.2 wt %) and the catalyst deactivator (Irganox 1024, 0.2 wt %) polymers with high thermal stability were obtained. The only small decrease of molar masses (~ 10 %) was observed after keeping stabilized polymer 1 h at 200 °C, that is the longer time than usually applied in normal manufacturing. Addition of stabilizers has not the great influence on T_m, T_g and the degree of crystallinity of linear and star PLLA.

CONCLUSIONS

The synthesis and characterization of high-molar-mass 6-arm star-shaped and linear PLLA's with M_n in the range of 60 000 to 300 000 g/mol were described. Dipentaerythritol was used as initiator and Sn(Oct)$_2$ was applied as a catalyst in the ring-opening polymerization of L-lactide carried out at 130 °C. Polymerization at a relatively low temperature (130 °C), called as the solid phase polymerization resulted in the formation of polymers with an ordered structure of chains and a lack of entanglements. The high degree of crystallinity of the resulted crude PLLA's (up to ~ 96 %) was confirmed by the high melting temperatures (T_m) of 6-arm star-shaped PLLA's (184–188 °C) and for their linear analogs (~ 190 °C) and by the high melting enthalpy (ΔH_m) up to 90 J/g. The prepared high-molar-mass PLLA's were characterized by SEC, ^{1}H NMR, DSC, and TGA. The melting temperatures decrease as the molar masses of PLLA's decrease. The different shape of curves for the star and linear polymers in the region of the smaller-molar-masses (M_n < 50 000 g/mol) is caused by the disturbance in the formation of the more regular crystalline structure in star polymers by the presence of the core and arms with end-groups. Linear and star-shaped PLLA's after purification were additionally stabilized by adding the thermal stabilizer (Irganox 1010, 0.2 wt %) and the catalyst deactivator (Irganox 1024, 0.2 wt %). The thermal properties of stabilized PLLA's were discussed.

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Received 19 X 2017.