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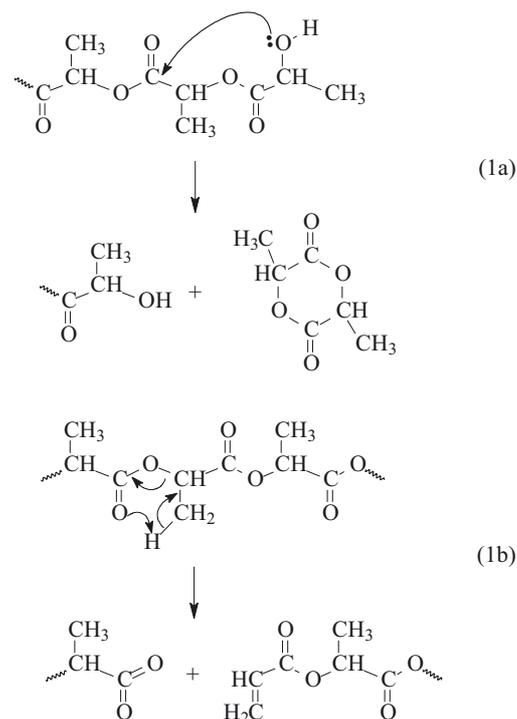
## Thermal stability of poly(L-lactide) prepared by polymerization of L,L-dilactide with Sn(II)-based initiators

**Summary** —  $\alpha$ -Ester- $\omega$ -hydroxy terminated poly(L-lactide) [ $C_4H_9OC(O)$ -PLA-OH] was prepared by the ring-opening polymerization of L,L-dilactide using tin(II) 2-ethylhexanoate [tin octoate,  $Sn(Oct)_2$ ]/BuOH system or tin(II) butoxide as initiators in a wide range of molecular weights ( $\bar{M}_n$ ): from  $10^3$  up to  $7 \cdot 10^5$ . Thermal degradation behavior of  $C_4H_9OC(O)$ -PLA-OH was then compared with that of its esterified counterpart [ $C_4H_9OC(O)$ -PLA-OC(O)CH( $C_2H_5$ ) $C_4H_9$ ]. Thermogravimetric measurements versus  $\bar{M}_n$  revealed, as a result of  $\bar{M}_n \rightarrow \infty$  extrapolation, the upper limit of thermal resistance of poly(L-lactide) (PLA). The onset temperature of the thermal degradation ( $OT$ ) and the temperature of maximum degradation rate ( $MDT$ ) of PLA are equal to 337 and 376 °C, respectively. Despite the deteriorating effect on the PLA molecular weight caused by *in situ* esterification of the hydroxyl chain ends with  $Sn(Oct)_2$ , largely unreacted in polymerization, certain improvement of PLA thermal stability due to this side reaction was also observed.

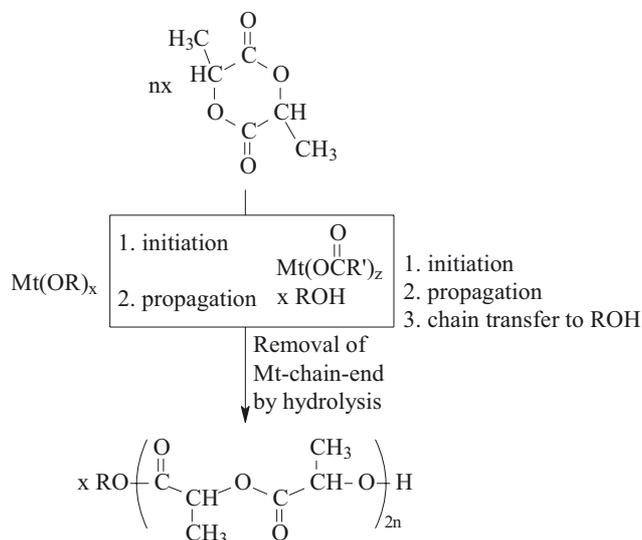
**Key words:** L,L-dilactide, poly(L-lactide), tin(II) butoxide, tin(II) octoate, polymerization mechanism, poly(L-lactide) esterification, thermal degradation.

Poly(lactide) (PLA) exhibits useful mechanical properties accompanied by a biocompatibility and ability to undergo controlled degradation in the natural environment. Due to these features PLA finds recently wide applications both as a speciality biomedical polymer and as an environmentally friendly commodity thermoplastic, and fiber-forming material [1–6].

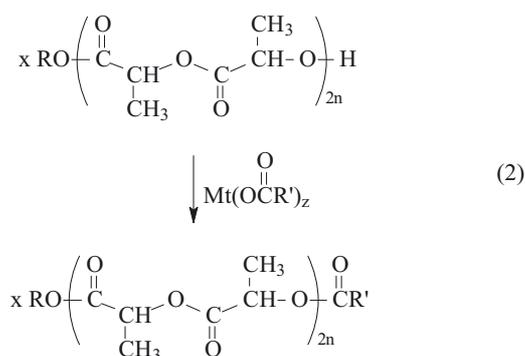
On the other hand, thermal stability of PLA is rather poor. For example, its temperature of the maximum rate of decomposition typically falls within the wide range from 240 to 370 °C and depends strongly on the end-groups structure, macromolecular architecture, molecular weight, and a purity of the sample [7–17]. It has been revealed that in the absence of  $O_2$  and  $H_2O$  thermal degradation of poly(aliphatic ester)s proceeds *via* two major mechanisms: back-biting (un-zipping), starting from the end-group reactive enough [equation (1a)], and/or main-chain carbon-oxygen bond [...-( $CH_3$ )HC-OC(O)-...] splitting *via cis*-elimination [equation (1b)] [9, 10, 14]. Moreover, radical random chain scission has also been taken into account [9].



In the controlled, covalent (coordination-insertion) polymerization of cyclic esters, macromolecules fitted with hydroxyl end-groups are eventually formed [18, 19]. This occurs both in the metal alkoxide  $[Mt(OR)_x]$  or metal carboxylate  $Mt[OC(O)R']_z$  (co)initiated processes (Scheme A).



However, as we report in the recently published papers [20–24], in the metal carboxylate cointiated polymerization some additional end-groups also appear, namely the ester groups  $\dots-OC(O)R'$ , formed by esterification of  $\dots-OH$  end-groups by the carboxylate ligands from  $Mt[O(O)CR']_z$  initiator [equation (2)].



In Scheme A and equation (2)  $Mt = Zn, Sn(II), Al, Y, Sn(IV), Ti$  (alkoxides) or  $Mt = Sn(II), Zn$  (carboxylates); ROH stands either for  $H_2O$ , alcohol or hydroxycarboxylic acid.

The present paper firstly aims at reporting on the thermal stability of  $\alpha$ -ester- $\omega$ -hydroxy terminated poly(L-lactide)  $[C_4H_9OC(O)-PLA-OH]$  prepared with tin(II) octoate and tin(II) butoxide in a wide range of molecular weights ( $\overline{M}_n$ ); from  $10^3$  up to  $\approx 7 \cdot 10^5$ . An additional effect, influencing thermal stability of the resulting PLA and related to the hydroxyl end-group esterification accompanying LA polymerization initia-

ted with the system tin(II) octoate/BuOH is also discussed.

## EXPERIMENTAL

### Materials

Tin(II) dibutoxide  $[Sn(OBu)_2]$  was prepared in the two step synthesis according to [25]. In the first step  $SnCl_2$  was reacted with  $CH_3OH$ , in the presence of  $(C_2H_5)_3N$  as HCl scavenger. Resulting  $Sn(OCH_3)_2$  was isolated and then reacted with  $C_4H_9OH$  in boiling toluene as a solvent. The  $Sn(OC_4H_9)_2$  formed was finally crystallized from toluene, dried in vacuum, and distributed into the thin-walled vials.

Tin(II) bis(2-ethylhexanoate) [tin octoate,  $Sn(Oct)_2$ ] purchased from Aldrich (95 wt. %) was purified as described in [20]. The amount of impurities ("acidic" protons) was decreased to 1.8 mol. % as determined from  $^1H$  NMR spectrum [20].

L,L-Dilactide (LA) ( $\geq 99\%$ , Boehringer, Ingelheim, Germany), crystallized consecutively from dry 2-propanol and toluene, was purified just before use by sublimation in vacuum ( $10^{-3}$  hPa,  $85^\circ C$ ). The purified monomer was distributed into the glass ampoules equipped with breakseals.

Butyl alcohol (BuOH) (99.4 %, Aldrich) was dried with Na metal and distributed by vacuum distillation into thin-walled vials and sealed off.

2-Ethylhexanoyl (octanoyl) chloride (98 %, Aldrich) was degassed and condensed under reduced pressure ( $3 \cdot 10^{-3}$  hPa) into the glass ampoule equipped with a break-seal and sealed off after freezing in liquid nitrogen.

Tetrahydrofuran (THF) (99 %, POCh, Gliwice, Poland) was kept over KOH for several days, then decanted and distilled from Na metal chips. Thus purified THF was stored over Na-K alloy and distilled under reduced pressure directly into the reaction vessel.

*o*-Dichlorobenzene (99 %, Aldrich) purified by distillation from  $CaH_2$  was stored over  $CaH_2$  and distilled under reduced pressure into the reaction vessel.

Pyridine (99 %, Aldrich) was kept over KOH for several days, then decanted and distilled under reduced pressure ( $80^\circ C$ , 1 hPa) from calcium hydride just before use.

Deuterated chloroform (99.5 % isotopic purity, Dr. Glaser, Basell, Switzerland) was stored over  $P_2O_5$  and distilled before use.

### Synthesis of hydroxy-terminated poly(lactides)

$\alpha$ -Ester- $\omega$ -hydroxy poly(lactides)  $[BuOC(O)-PLA-OH]$  were synthesized by the controlled ring-opening polymerization of LA initiated either with  $Sn(Oct)_2/BuOH$  ( $\overline{M}_n < 10^4$ ) or  $Sn(OBu)_2$  ( $\overline{M}_n > 10^4$ ), in THF as a solvent at  $80^\circ C$ . Polymerizing mixtures were prepared in sealed

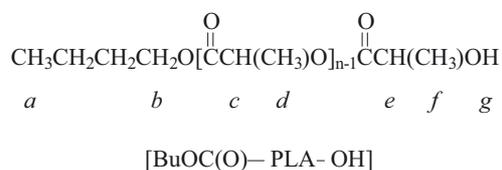
polarimetric cells using standard high vacuum technique. LA monomer conversion degree was followed by polarimetry. Molecular weight ( $\overline{M}_n$ ) of PLA formed was controlled by LA and BuO- concentrations in the feed:  $144.13 ([LA]_0 - [LA]) / [BuO-]_0 + 74.12$  (where 144.13 and 74.12 denote LA and BuOH molar masses, respectively). More detailed description of the polymerization procedure has been given in our previous works [26, 27].

### Esterification procedure

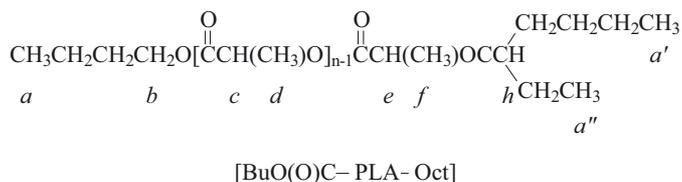
Poly lactide samples composed of the linear macromolecules fitted with one hydroxyl end-group [BuOC(O)-PLA-OH] were quantitatively esterified by a direct reaction with the octanoyl chloride at room temperature in dry pyridine used both as a solvent and HCl scavenger. A general procedure follows an example described below.

An ampoule containing 1 mL (0.95 g, *i.e.* 5.86 mmol) of octanoyl chloride and equipped with a breakseal was sealed to the reaction glass vessel ( $\approx 30$  mL) containing 0.501 g (0.175 mmol) of BuOC(O)-PLA-OH of  $\overline{M}_n = 2870$  (SEC — Size Exclusion Chromatography). Then it was evacuated below  $10^{-3}$  hPa and 5 mL of dry pyridine was distilled in. The whole reactor was sealed off, the breakseal was broken and all components were mixed at room temperature. After 1 hour the resulting BuO(O)C-PLA-Oct was precipitated into a cold methanol, separated by filtration, washed with distilled water (in order to remove pyridine hydrochloride) and then with methanol. After drying 0.4 g (80 % yield) of the polymer with  $\overline{M}_n$  (SEC) equal to 3050 was obtained.

Comparison of  $^1\text{H}$  NMR spectra ( $\text{CDCl}_3$ , 20 °C) of the starting BuOC(O)-PLA-OH and of the resultant BuO(O)C-PLA-Oct indicates complete transformation of the hydroxyl into the octoate ester end-groups [below in brackets are given chemical shifts ( $\delta$ , in ppm), multiplicities of signals and their relative intensities].



*a* (0.9, t, 2.46), *b* (4.12, m, 1.55), *c* (5.15, q, 32.12), *d* (1.58, d, 94.85), *e* (4.34, q, 0.82), *f* (1.47, d, 2.50), *g* (2.67, d, 0.85)



*a* + *a'* + *a''* (0.85—0.95, three t, 32.80), *b* (4.12, m, 6.53), *c* + *e* (5.03—5.20, two q, 136.74), *d* (1.58, d, 470.75), *e* (4.34, q, 0.82), *f* (1.51, d, 13.35), *h* (2.33, m, 3.79)

The corresponding  $\overline{M}_n$  values calculated from NMR spectra are equal to 2840 and 2950, being close to the given above values determined by SEC.

### Measurements

Polarimetric measurements were performed with Perkin Elmer 241 MC polarimeter. The optical rotations (*or*) of the living polymerization mixtures were measured at 578 nm at room temperature. The instantaneous monomer concentrations were determined assuming additivity of the optical rotations of LA (*or<sub>m</sub>*) and PLA (*or<sub>p</sub>*), *i.e.*:  $[LA] = [LA]_0 (or - or_p) / (or_m - or_p)$ .

SEC traces were recorded using LKB 2150 HPLC pump, two sets of TSK Gel columns (G 2000 H<sub>XL</sub> and G 6000 H<sub>XL</sub> or G 3000 H<sub>HR</sub> and G 6000 H<sub>HR</sub> with pore sizes  $2.5 \cdot 10^2$  and  $10^6$  or  $1.5 \cdot 10^3$  and  $10^6$  Å, respectively) at 20 °C. Wyatt Optilab 903 interferometric refractometer and MALLS Dawn F Laser Photometer, equipped with He-Ne laser emitting at 632.8 nm (both Wyatt Technology Corp., Santa Barbara, CA) were applied as detectors in series. The refractive index increments ( $dn/dc$ ) were determined with Wyatt Optilab 903 interferometric refractometer and using DNDC.EVE v 5.20 program (Wyatt Technology Corp., Santa Barbara, CA). For LA and PLA  $dn/dc = 0.0310$  and  $0.0256$  mL/g ( $\text{CH}_2\text{Cl}_2$ , 20 °C), respectively, were determined.

The number-average molecular weights  $\overline{M}_n$  of PLA were determined using a calibration method described previously for poly( $\epsilon$ -caprolactone) [27] and PLA standards prepared in our laboratory. The correct  $\overline{M}_n$  values of PLA can also be obtained after multiplying by 0.68 the  $\overline{M}_n$  determined with polystyrene standards, at least up to  $\overline{M}_n \approx 2 \cdot 10^4$  g/mol, for the set of G 2000 H<sub>XL</sub> and 6000 H<sub>XL</sub> columns with  $\text{CH}_2\text{Cl}_2$  as an eluent.

The actual number-average molecular weights ( $\overline{M}_n$ ) of the deactivated and isolated PLA were occasionally determined with Knauer vapour pressure or membrane osmometers for  $\overline{M}_n \leq 3.5 \cdot 10^4$  or  $\geq 3.5 \cdot 10^4$ , respectively, in dry methylene chloride.  $\overline{M}_w / \overline{M}_n$  ratios were determined from the SEC traces.

$\overline{M}_n$  higher than  $10^4$  was directly determined using MALLS Dawn F Laser Photometer and ASTRA v 4.70 program (Wyatt Technology Corp., Santa Barbara, CA).

$^1\text{H}$  NMR spectra were recorded in deuterated chloroform as a solvent using Bruker DRX 500 operating at 500 MHz. Chloroform was used as an internal standard ( $\delta = 7.26$  ppm).

Mass spectrometric measurements were performed using Voyager-Elite (PerSeptive Biosystems, USA) time of flight instrument equipped with a pulsed N<sub>2</sub> laser (337 nm, 4 ns pulse width) and time delayed extraction ion source. An accelerating voltage of 20 kV was used. Mass spectra were recorded in the reflector mode. The matrix, 2,5-dihydroxybenzoic acid, was dissolved in purified THF (10 mg · mL<sup>-1</sup>) and the solution was mixed with the polymerizing mixture (monomer concentration

in the feed: 2.0 or 1.0 mol · L<sup>-1</sup>) at 25:1 v/v ratio. NaI as cationizing agent was also added. The mixture was dried on a stainless steel covered by the gold metal target.

Molecular weights and their distributions were calculated from the recorded MALDI-TOF spectra by means of the computer program: Grams 386™ — version 3.4 (Galactic Industries Inc.).

Thermal stability measurements were performed using Hi-Res TGA 2950 Thermogravimetric Analyser (TA Instruments, USA), in a nitrogen atmosphere and heating rate of 10 °C/min.

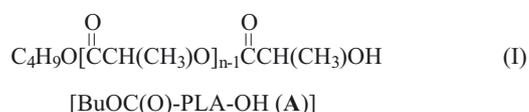
## RESULTS AND DISCUSSION

In the earlier works we have revealed, that in polymerization of ε-caprolactone (CL) [20, 21, 24] and LA [22] initiated by Sn(Oct)<sub>2</sub>/ROH systems there is a variety of the end-groups in the resulting polyester macromolecules. Then we have shown [22, 23], that if the ratio of [Sn(Oct)<sub>2</sub>]<sub>0</sub>/[coinitiating alcohol]<sub>0</sub> is high enough, the large proportion or even almost all of the originally present ...-OH end-groups can be converted into the octoate esters. Indeed, if for example in bulk polymerization of LA the final molecular weight ( $\overline{M}_n$ ) of PLA is equal to 10<sup>5</sup>, the complete conversion of -OH groups into ester groups will require 730 ppm (equivalent to 6.4 · 10<sup>-3</sup> mol · L<sup>-1</sup>) of Sn(Oct)<sub>2</sub>, provided, that all of the available octoate groups in Sn(Oct)<sub>2</sub> are converted into the octoate end-groups. Thus, it could in principle be possible directly in the polymerization process to obtain the macromolecules of ROC(O)-PLA-Oct structure, where RO comes from the coinitiating alcohol.

### Comparison of the thermal stability of esterified and non-esterified PLA-OH chains

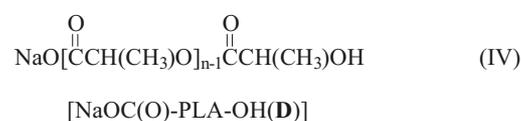
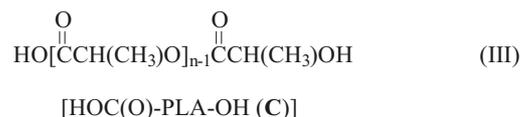
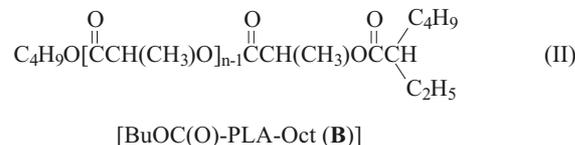
In order to establish how ...-PLA-OH → ...-PLA-Oct conversion could influence thermal stability of the polyester, we prepared PLA macromolecules of BuOC(O)-PLA-Oct structure by esterification of BuOC(O)-PLA-OH macromolecules with C<sub>4</sub>H<sub>9</sub>CH(C<sub>2</sub>H<sub>5</sub>)C(O)Cl. After purification of the resulting polymer by a series of dissolutions and precipitations this sample was studied by MALDI-TOF mass spectrometry.

Figure 1a shows MALDI-TOF spectrum of the starting PLA prepared with Sn(Oct)<sub>2</sub>/BuOH initiating system. According to the results of <sup>1</sup>H NMR analysis given in the Experimental part this sample consists exclusively of BuOC(O)-PLA-OH macromolecules:



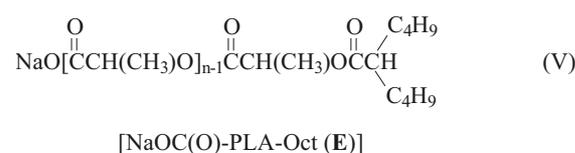
Indeed, in MALDI-TOF spectrum the signals (marked by **A**), coming from this population of PLA,

dominate. However, expanded fragment of the spectrum reveals a power of MALDI-TOF method in polymers' analysis. Signals of the lower intensities were identified as corresponding to the following PLA macromolecules:



Mechanism of formation of **B** and **D** populations has been already discussed in our previous papers [21, 22, 24]. Population **D** appears as a result of proton and Na<sup>+</sup> exchange. A qualitative estimation gives more than 90 mol % of macromolecules showing BuOC(O)-PLA-OH (**A**) structure.

<sup>1</sup>H NMR analysis of BuOC(O)-PLA-OH esterified with octanoyl chloride shows the presence of predominantly one population of macromolecules, namely BuO(O)C-PLA-Oct (**B**) (cf. Experimental part). In MALDI-TOF spectrum (Fig. 1b) the signals coming from **A** and **E** macromolecules are also seen.



Their concentration (assuming proportional response) is below 10 mol %. Apparently, population **E** is a product of esterification of populations **C** and **D**. The presence of signals coming from chains **A** indicates that esterification was non-quantitative. Moreover, comparison of MALDI-TOF traces presented in Fig. 1 shows that the molecular weights and their distributions of non-esterified and esterified PLA samples do not differ appreciably.  $\overline{M}_n$  and  $\overline{M}_w/\overline{M}_n$  values calculated from these spectra are equal to 2680 and 2860, and to 1.33 and 1.31, respectively.

Finally, samples analyzed above, being composed predominantly either of macromolecules BuOC(O)-PLA-OH or of BuOC(O)-PLA-Oct were studied by thermogravimetry. Result is shown in Fig. 2 — the difference in thermal stability is remarkable. Esterified sample is

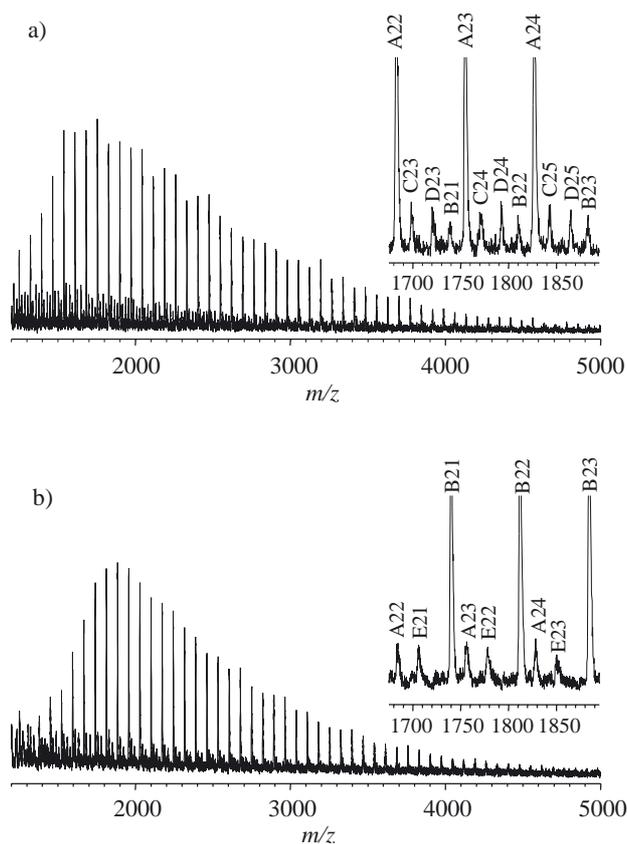


Fig. 1. MALDI-TOF spectra (linear mode, NaI added) of: (a) poly(L-lactide) prepared by L,L-dilactide polymerization initiated with tin octoate/butyl alcohol system, (b) poly(L-lactide) prepared as indicated above and esterified with octanoyl chloride. All marked signals correspond to macromolecules cationized with  $\text{Na}^+$ ; the numbers following A, B, C, D, and E denote the degrees of polymerization of the poly(L-lactide) chains, the meanings of A, B, C, D and E — see text. Polymerization conditions:  $[\text{LA}]_0 = 1.40 \text{ mol} \cdot \text{L}^{-1}$ ,  $[\text{Sn}(\text{Oct})_2]_0 = 0.04 \text{ mol} \cdot \text{L}^{-1}$ ,  $[\text{BuOH}]_0 = 0.1 \text{ mol} \cdot \text{L}^{-1}$ ; THF solvent,  $80^\circ\text{C}$

much more resistant and exhibits the onset temperature of the thermal degradation (OT) and the temperature of maximum degradation rate (MDT)  $115^\circ\text{C}$  and  $112^\circ\text{C}$  higher, in comparison with these determined for the hydroxy-terminated PLA.

This result agrees with observation of Ikada who has already shown that acetylation of the hydroxyl end-group in PLA-OH increases its thermal stability [7]. Although the reasons of such enhanced stability have not yet been studied in detail, it is highly possible that this phenomenon has the same origin as in polyacetals [28]. Blocking of terminal ...-OH group eliminates the possibility of the depropagation from the chain end by the unzipping mechanism [cf. equation (1a)]. In the case of PLA with the esterified hydroxyl chain ends thermal degradation proceeds most probably *via* the *cis*-elimination [equation (1b)], requiring much higher activation energy in comparison to that of the back-biting depolymerization from equation (1a). Neither unsaturated nor carbo-

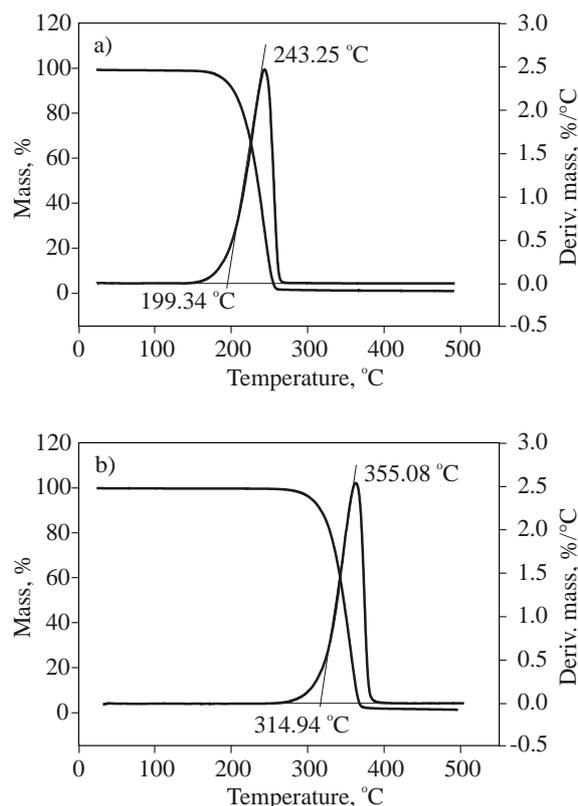


Fig. 2. TGA and DTA traces of thermal degradation of: (a) poly(L-lactide) prepared by L,L-dilactide polymerization initiated with tin octoate/butyl alcohol system, (b) poly(L-lactide) prepared as indicated above and esterified with octanoyl chloride. For polymerization conditions see Fig. 1

xylic acid chain ends formed could start depropagation *via* back-biting. Therefore for the esterified samples OT and MDT are shifted into the considerably higher values range.

Results of thermogravimetric analyses performed for a series of  $\text{BuOC}(\text{O})\text{-PLA-OH}$  samples differing in  $\overline{M}_n$  show that their thermal stability increases with increasing molecular weight (Fig. 3a). Interestingly enough, above  $\overline{M}_n \approx 4 \cdot 10^5$  dependencies of OT and MDT *vs.*  $\overline{M}_n$  tend to level off. Similar behavior of the thermal resistance of the hydroxy-terminated PLA has been reported by  $\underline{\text{Cam}}$  [12]. Extrapolation of these plots into a direction of  $\overline{M}_n \rightarrow \infty$  (*i.e.*  $1/\overline{M}_n \rightarrow 0$ ) results in OT =  $337^\circ\text{C}$  and MDT =  $376^\circ\text{C}$  (Fig. 3b). On the other hand, OT and MDT determined for the esterified polylactide  $[\text{BuOC}(\text{O})\text{-PLA-Oct}]$  do not change practically with  $\overline{M}_n$  (Fig. 3c) and are equal to  $\approx 330^\circ\text{C}$  and  $370^\circ\text{C}$ , respectively. Thus, the values obtained by extrapolation ( $\overline{M}_n \rightarrow \infty$ ) for  $\text{BuOC}(\text{O})\text{-PLA-OH}$  give an upper limit of PLA thermal resistance since for the infinite long chains the only possible mechanism of thermal degradation involves the main chain breaking [as for example depicted in equation (1b)]. The same mechanism operates for the esterified PLA chains  $[\text{BuO}(\text{O})\text{C-PLA-Oct}]$  leading to the similar values of OT and MDT.

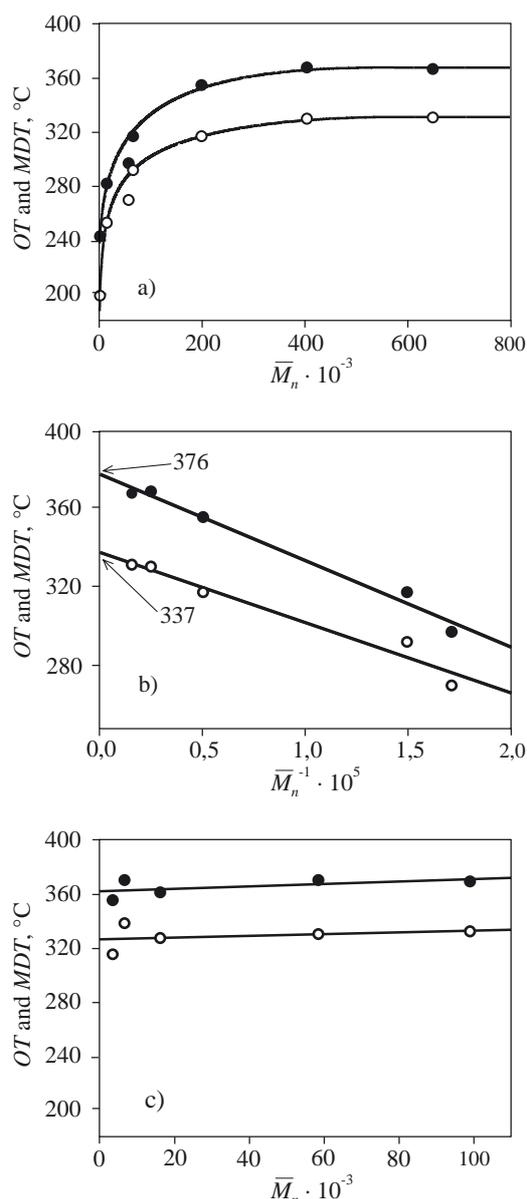


Fig. 3. Effect of molecular weight ( $\bar{M}_n$ ) on PLA decomposition temperatures: onset temperature of thermal decomposition [OT, (o)] and temperature of the maximum rate of thermal decomposition [MDT, (●)]. Dependencies for BuOC(O)-PLA-OH (a, b) and for BuOC(O)-PLA-Oct (c)

### Influence of PLA-OH esterification in LA/Sn(Oct)<sub>2</sub>/BuOH polymerizing system on its thermal stability

In order to check how direct esterification, by Sn(Oct)<sub>2</sub>, of the hydroxyl end-group in the growing BuO(O)C-PLA-OH influences the microstructure and thermal stability of the resultant polymer, polymerization of LA was studied in a model system with a high starting concentration of Sn(Oct)<sub>2</sub> equal to 1.0 mol · L<sup>-1</sup>. Analysis of MALDI-TOF spectrum of the corresponding reaction revealed complete esterification of ...-PLA-OH end-groups (Fig. 4).

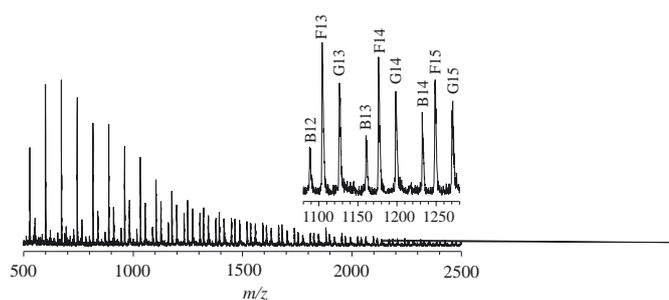
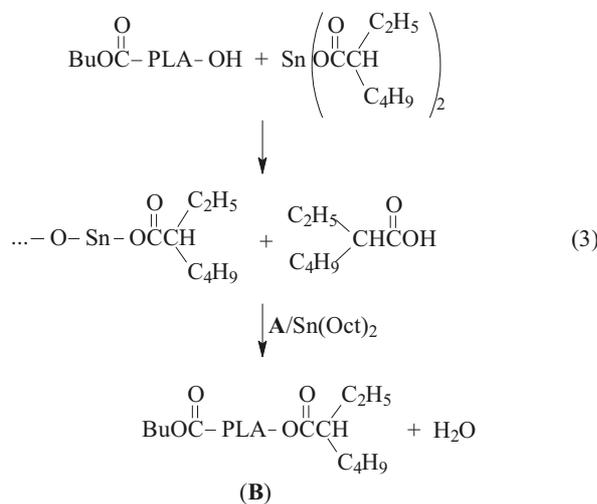
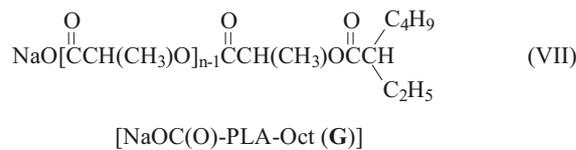
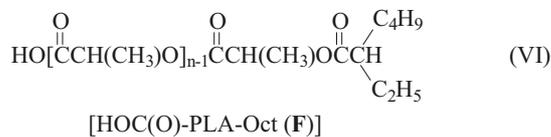


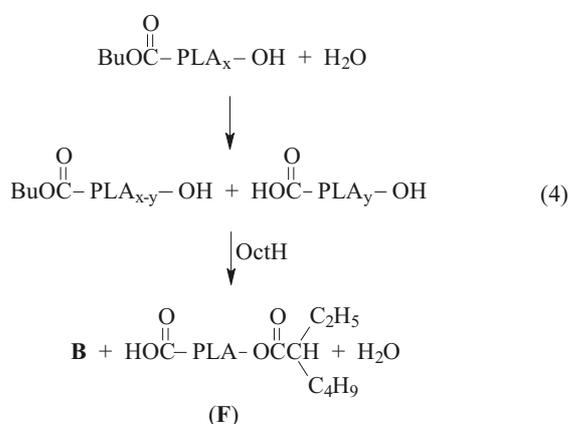
Fig. 4. MALDI-TOF spectra (linear mode, NaI added) of poly(L-lactide) prepared by L,L-lactide polymerization initiated with tin octoate/butyl alcohol system. All marked signals correspond to macromolecules cationized with Na<sup>+</sup>; the numbers following B, F, and G denote the degrees of polymerization of the corresponding poly(L-lactide) chains, the meanings of B, F and G — see text. Polymerization conditions: [LA]<sub>0</sub> = 1.1 mol · L<sup>-1</sup>, [Sn(Oct)<sub>2</sub>]<sub>0</sub> = 1.0 mol · L<sup>-1</sup>, [BuOH]<sub>0</sub> = 4.1 · 10<sup>-2</sup> mol · L<sup>-1</sup>, *o*-dichlorobenzene solvent, 140 °C, polymerization time 5 h

In the spectrum presented in Fig. 4 three populations of periodically repeating signals, marked by B, F, and G, can clearly be distinguished. All of them correspond to PLA chains fitted with octanoate ester end-groups.



As reported in our previous papers [21, 22, 24], the population of chains **B** results from the reaction depicted in equation (3). Octanoic acid (OctH), formed in the alkoxide-carboxylate ligands exchange at tin atom in  $\text{Sn}(\text{Oct})_2$ , acts then as an esterification agent giving in reaction with **A** esterified chains **B**.

Water, being a by-product of the esterification, acts further as the chain transfer/chain splitting agent giving rise of PLA chains fitted with the hydroxyl and carboxylic end-groups [HO(O)-PLA-OH]. Esterification of HO(O)C-PLA-OH macromolecules, proceeding in the next step, results in formation of the population **F** [equation (4)]. The latter is then partially transformed during MALDI-TOF measurement into the population **G** *via*  $\text{H}^+ \rightarrow \text{Na}^+$  exchange.



The expected molecular weight of PLA, formed in the conditions given in the caption for Fig. 4, calculated on the basis of the starting LA and BuOH concentrations,  $\overline{M}_n = 144.13 ([\text{LA}] - [\text{LA}]_{\text{eq}})/[\text{BuOH}]_0 + 74.12$  where:  $[\text{LA}]_{\text{eq}} = 0.15 \text{ mol} \cdot \text{L}^{-1}$  at  $140^\circ\text{C}$  [29] is equal to  $3.4 \cdot 10^3$ , whereas determination on the basis of MALDI-TOF spectrum in Fig. 4 gives  $\overline{M}_n = 1.2 \cdot 10^3$  ( $\overline{M}_w/\overline{M}_n = 1.24$ ). This result can be explained by means of equations (3) and (4) — appearance of  $\text{H}_2\text{O}$  followed by chain transfer and chain splitting reactions directly leads to PLA molecular weight depression.

Despite the deteriorating effect of the *in situ* esterification on the molecular weight, certain improvement in PLA thermal stability could be expected. DTA trace recorded for PLA composed of two populations of macromolecules: BuOC(O)-PLA-Oct (**B**) and HO(O)-PLA-Oct (**F**) formed during *in situ* esterification from the BuOC(O)-PLA-OH (**A**) chains shows a bimodal shape. The broader signal of lower intensity is characterized by  $OT = 198^\circ\text{C}$  and  $MDT = 241^\circ\text{C}$ , and the sharper, more intensive peak by  $OT = 269^\circ\text{C}$  and  $MDT = 283^\circ\text{C}$  (Fig. 5). For BuO(O)C-PLA-OH of the assumed  $\overline{M}_n = 3.4 \cdot 10^3$  the following thermal decomposition temperatures could be expected:  $OT = 204^\circ\text{C}$  and  $MDT = 246^\circ\text{C}$  (as read from a plot in Fig. 3a), which are close to the thermal decomposition temperatures determined from the

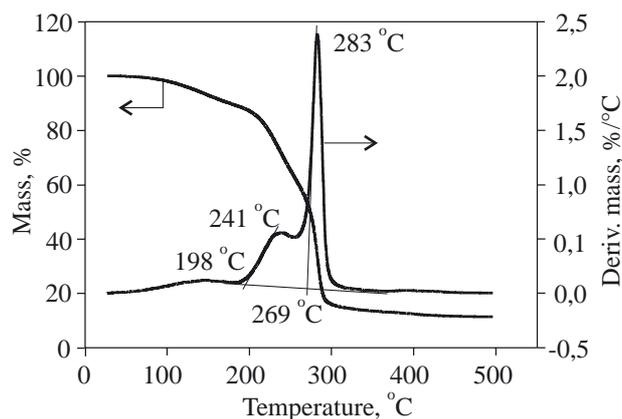


Fig. 5. TGA and DTA traces of thermal degradation of poly(L-lactide) prepared by L,L-dilactide polymerization initiated with tin octoate/butyl alcohol system. For polymerization conditions see Fig. 4

broader, lower temperature signal in Fig. 5. However, approximately 50 wt. % of PLA sample shows slightly improved thermal resistance reflected in  $OT = 269^\circ\text{C}$  and  $MDT = 283^\circ\text{C}$ .

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