Synthesis and characterization of star-shaped copolymers obtained from lactic acid and heterocyclic monomers

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Dedicated to the late Professor Andrzej Duda

Abstract: In this paper we report a two-step method of synthesis of star-shaped copolymers of lactic acid and heterocyclic monomers. Firstly, the branched cores with hydroxyl end groups have been obtained by the polycondensation of L or D-lactic acid with pentaerythritol. Then we carried out ring opening polymerization of trimethylenecarbonate or L-lactide in the presence of star-shaped poly(lactic acid) cores and tin(II) 2-ethylhexanoate as a catalyst. We proved that setting the polymerization temperature at 130 °C provides a block structure of obtained copolymers. However, increasing temperature could cause transesterification and consequently changes in the chain structure. The results of the DSC analysis indicate that the block copolymer, consisting of the poly(lactic acid) and the polytrimethylenecarbonate segments, forms a homogeneous amorphous phase, whereas stereoblock poly(lactic acid) forms a crystalline phase which has a melting point between 180 and 190 °C.

Keywords: lactic acid copolymers, star-shaped polymers, stereocomplexes.

Synteza i charakterystyka kopolimerów o kształcie gwiazdy otrzymanych z kwasu mlekowego i monomerów heterocyklicznych

Streszczenie: Opisano dwustopniową metodę syntezy gwieździstych kopolimerów kwasu mlekowego z monomerami heterocyklicznymi. Na pierwszym etapie w wyniku kondensacji kwasów o konfiguracji L lub D w obecności pentaerytrytu otrzymano rozgałęzione rdzenie zakończone grupami hydroksylowymi. Na etapie drugim do rdzeni dobudowywano mery węglanu trimetylenu lub L-laktydu w reakcji polimeryzacji katalizowanej 2-etyloheksanianem cyny(II). Stwierdzono, że polimeryzacja prowadzona w temp. 130 °C skutkuje powstaniem kopolimerów o budowie blokowej, natomiast w wyższej temperaturze struktura ramion może się zmieniać wskutek procesów transestryfikacji. Badania DSC kopolimerów blokowych wykazały, że segmenty poli(węglanu trimetylenowego) i poli(kwasu mlekowego) tworzą jednorodną fazę amorficzną, a segmenty zawierające mery kwasu mlekowego o różnej konfiguracji tworzą krystaliczne stereokompleksy o temperaturze topnienia w zakresie 180–190 °C.

Słowa kluczowe: kopolimery kwasu mlekowego, polimery gwieździste, stereokompleksy.

Star-shaped polylactides (SPLA) have recently attracted considerable attention due to their unique chemical and physical properties and potential applications in drug delivery systems, tissue engineering, and nanotechnology [1–3]. Various practically important properties of SPLA such as melt viscosity, thermomechanical parameters, morphology, and degradation rate can be adjusted by the number of arms, stereochemistry of monomeric units, structure of end groups, and molar mass [4–10]. Moreover, the stereoregular SPLA form crystalline stereocomplexes with linear and branched polylactides of opposite configuration, which exhibit structural memory after melting and cooling cycles [11]. This kind of specific interaction between segments of different configuration gives rise to materials of better mechanical and thermal performance and allows to control the morphology of micro- and nanobiomaterials based on SPLA assemblies [11–13]. The most commonly used method for synthesis of SPLA is ring opening polymerization of lactide in the presence of a multifunctional component which plays the role of coinitiator or chain transfer reagent [1, 14]. This approach leads to the formation of macromolecular stars with secondary –OH end groups, which could be used in constructing more complicated architectures. SPLA can be also obtained directly from lactic acid (LAc) by means of polycondensation using polyols or polycarboxyl compounds as branching agents [15–17]. We have found that thus prepared polymers may serve as useful building blocks in the synthesis of biodegradable polyesters of

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molecular masses in the range of 15–60 kg/mol containing a stiff SPLA core combined with more elastic segments made by ring opening polymerization of ε-caprolactone, and copolymerization of oxiranes with cyclic anhydrides or carbon dioxide [17–19].

In this paper we describe the synthesis and characterization of two new kinds of star-shaped copolymers based on the products of lactic acid polycondensation. The first one is composed of L-lactyl and trimethylenecarbonate (TMC) monomeric units whereas the second type of copolymer constitutes the combination of D-lactyl and L-lactyl segments. We report here also some preliminary data concerning their phase structure particularly the ability of forming stereocomplexes by star-shaped macromolecules containing segments of opposite configuration in the same arm.

EXPERIMENTAL PART

Materials

L-lactide (L-LA) (Aldrich) was recrystallized from dry isopropanol, then toluene and vacuum dried before polymerization. Toluene and isopropanol were dried with sodium and distilled. L-SPLA and trimethylenecarbonate (TMC) were prepared according to the procedures described in refs. [17–20]. The D-SPLA were obtained in a similar way as L-SPLA using D-lactic acid (DLAc) (Avison, 80 % aqueous solution). Tin(II) 2-ethylhexanoate [Sn(EH)$_2$] (Aldrich, 95 %), dichloromethane, and methanol were used without purification.

Polymerization

ROP (ring opening polymerization) of TMC or L-LA in the presence of SPLA were catalyzed by 0.01 wt % of Sn(EH)$_2$ (with respect to the batch). The reactants and catalyst were placed in a three-necked round-bottom flask equipped with magnetic stirrer and condenser. After polymerization completion, the reaction mixture was cooled to room temperature and dissolved in dichloromethane and then poured into an excess of methanol. The precipitated product was filtered off, washed with methanol and dried in a vacuum oven at 40 °C for 48 h.

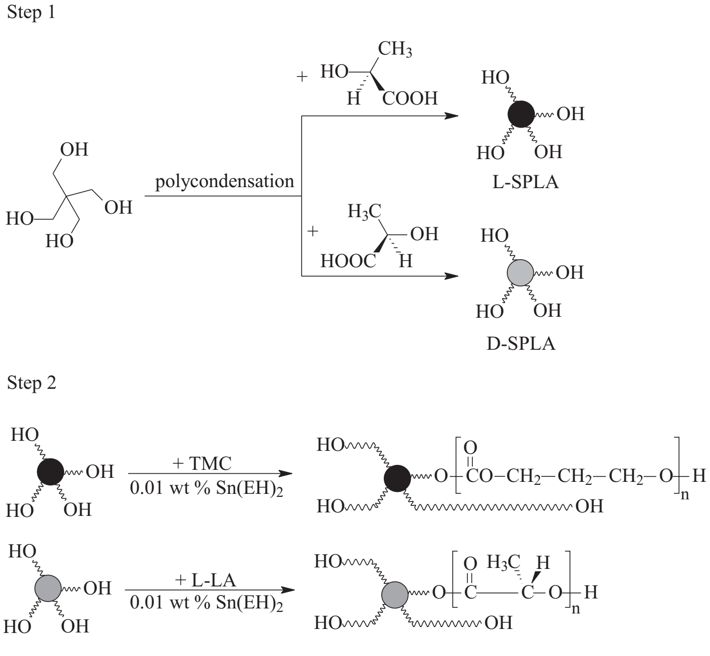
Methods of testing

^{1}H NMR and ^{13}C NMR measurements were performed on Varian Mercury 400 MHz spectrometer using DMSO-d_6 or CDCl$_3$ as solvent. The molar mass and molar mass distribution were determined by GPC using RI detector and polystyrene (PS) calibration on a Viscotek TDA 305 apparatus equipped with one guard and two DVB Jordi gel columns (10^2–10^7, linear mix bed) in dichloromethane as eluent at 30 °C at a flow rate of 1.0 cm^3/min. The DSC measurements were performed using DSC Q200 V24.2 Build 107 apparatus. The first heating run from 0 °C to 200 or 250 °C was performed at a heating rate of 10 °C/min in order to study the crystallinity, then cooling and the second heating run at the rate of 20 °C/min were applied to follow crystallization and determine the glass transition temperature.

RESULTS AND DISCUSSION

Description of synthetic approach and characterization of SPLA cores

A general idea of the star-shaped lactic acid copolymers formation employing the synthetic approach described in this paper is shown in Scheme A. Thus, in the first step SPLA core bearing either L-lactyl (L-SPLA) or D-lactyl (D-SPLA) monomeric units were obtained by polycondensation of corresponding lactic acid isomers in the presence of pentaerythritol as primary core molecules and zinc acetylacetone monohydrate as the catalyst. Starting from these cores, the star-shaped copolymers were synthesized by the ring opening polymerization of TMC in the presence of L-SPLA or L-lactide polymerization in the presence of D-SPLA with tin(II) 2-ethylhexanoate [Sn(EH)$_2$] as the catalyst.



Scheme A

Theoretically, the polycondensation of lactic acid in the presence of branching agents leads to a mixture of star-shaped and linear polymers. However, the concentration of linear macromolecules is decreasing with elapse of time since they are gradually attached to the stars. This process was monitored by ^{1}H NMR measurements (in DMSO-d_6) and the proportion between linear polymers and SPLA was estimated from the ratio of the signals of the methine proton of the hydroxyl [~C$\underline{\text{H}}$(CH$_3$)OH; δ = 4.20 ppm] and carboxyl [~C$\underline{\text{H}}$(CH$_3$)COOH, δ = 4.95 ppm] terminal units. In isolated final products the content of the residual lin-

T a b l e 1. Characteristics of the products of the TMC polymerization in the presence of lactic acid branched oligomers terminated with hydroxyl groups[a)], extending in different temperature

No.	Temp.[b)] °C	[TMC]/ [Olig.][b)] mol/mol	$M_{p,\,GPC}$ kg/mol	$M_{w,\,GPC}$ kg/mol	*DI*	Units content mol %[c)]		Efficiency wt %
						LAc	TMC	
1	130	110	11.0	12.9	1.37	89.8	10.2	15.0
2	150	110	11.3	13.3	1.91	71.1	28.9	17.6
3	170	110	21.1	36.2	3.61	49.9	50.1	46.1
4	130	140	10.9	12.4	1.36	83.8	16.2	22.6
5	130	170	11.6	16.1	1.51	77.8	22.2	8.7

[a)] LAc oligomer with hydroxyl end groups, characterized by M_p = 8.4 kg/mol, M_w = 9.5 kg/mol, *DI* = 1.53 (obtained from GPC measurements registered in dichloromethane with PS calibration and RI detection).

[b)] Temp. – temperature, Olig. – oligomer.

[c)] LAc and TMC units content determined from ^{1}H NMR spectra.

ear macromolecules was below 5 mol %. The ^{1}H NMR technique was applied also for estimation of number average molar mass (M_n) of L-SPLA (M_n = 6.2 kg/mol) and D-SPLA (M_n = 10.9 kg/mol), by end group analysis (from the ratio of signals of methine protons in the δ range 4.95–5.25 ppm and O<u>H</u> protons at 5.45 ppm). The values of weight average molar masses (M_w), determined by GPC with RI based on PS standards were significantly higher (M_w L-SPLA = 9.4 kg/mol; M_w D-SPLA = 31.0 kg/mol) and the dispersity index (*DI* = M_w/M_n) was equal to 2.1 and 2.4, respectively. Both SPLA obtained were semicrystalline materials which revealed melting transition in the rage 90–110 °C and glass transition around 50 °C.

The ring opening polymerization step is often also not fully selective, because in reactions catalyzed by Sn(EH)$_2$ part of heterocyclic monomers may undergo polymerization, since traces of water or other protolytic impurities may act as a coinitiator that compete with hydroxyl group in SPLA [21, 22]. Therefore, the star-shaped copolymers are typically contaminated by a small amount of linear or cyclic polymers.

Synthesis and characterization of L-LA-TMC copolymers

Ring opening polymerization of TMC was carried out in bulk in the presence of L-SPLA and Sn(EH)$_2$ as catalysts in order to obtain products rich in star-shaped fraction. In Table 1 we present the composition of the starting reaction mixture, reaction temperature and yield, as well as composition and molar mass of precipitated fraction.

Initially, we decided to carry out the reactions at temperature as low as possible to avoid secondary transesterification reactions and obtain polymers with block structure. We found that copolymers containing 10–20 mol % of TMC monomeric units can be obtained with moderate yield (10–20 %) when carrying out the reaction in bulk at 130 °C for 24 hours. GPC curve of isolated product had a monomodal character (Fig. 1) and the dispersity was narrow in the range 1.4–1.5, while the weight average molar masses were in the range 12–16 kg/mol. The MALDI TOF spectra of these products were extremely rich in signals coming from a number of copolymer populations. Unfortunately, they were difficult for precise interpretation due to the overlapping of the signals of different isomers. However, it is worth to note that spectra did not reveal residual signals that could be assigned neither to SPLA nor to TMC homopolymers.

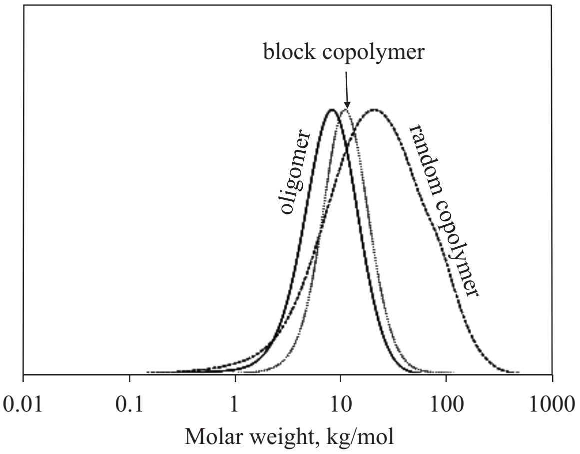


Fig. 1. GPC curves of oligomer of L-lactic acid and copolymer of L-lactic acid and trimethylenecarbonate, obtained at 130 °C (block copolymer) and at 170 °C (random copolymer); registered in dichloromethane with PS calibration and RI detection

Figure 2a shows a ^{1}H NMR spectrum of SPLA and Fig. 2b shows a ^{1}H NMR spectrum of the copolymer obtained at 130 °C. In the copolymer spectrum signals characteristic for LAc (b – C<u>H</u> quartet at 5.2 ppm; c – C<u>H</u>$_3$ doublet at 1.45 ppm) and TMC (d, f – triplet at 4.15 ppm, e – multiplet at 1.9 ppm) monomeric units have the same shape and position as that in the spectra of homopolymers which indicates that long segments of TMC and L-LA are present in the resulting products. One should also notice that these products still contain residual signals assigned to terminal OH groups (o – doublet at 5.5 ppm) which shows that at 130 °C some arms of the star-shaped core are not combined with TMC segments.

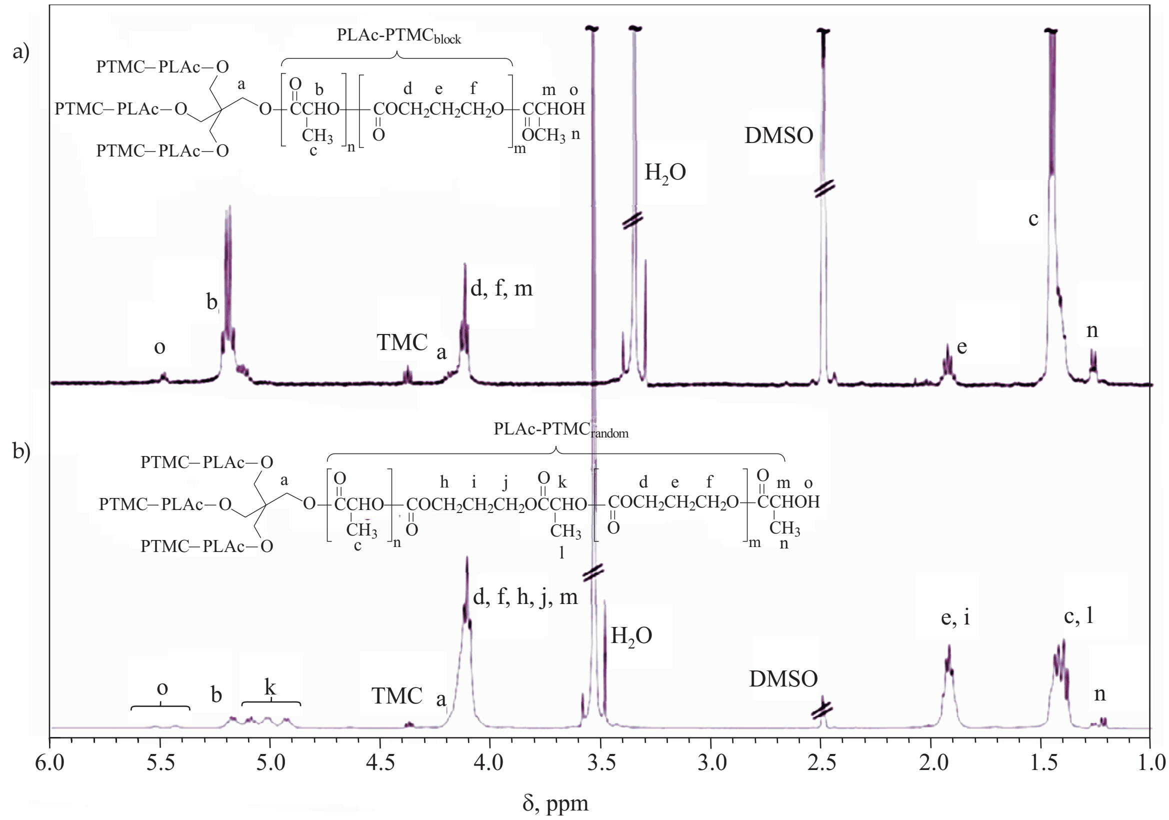
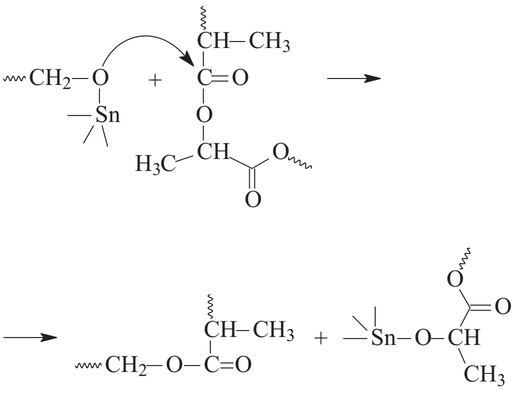


Fig. 2. ^{1}H NMR spectrum (DMSO-d_6) of: a) L-SPLA, b) star-shaped copolymer obtained from L-SPLA and TMC

Next, polymers characterized by higher concentration of TMC monomeric units were obtained in reactions carried out at 150 °C and 170 °C. These polymers were characterized by the broader molar mass distribution (*DI* 1.9–3.6) and GPC traces were tailed in the range of low molar masses (Fig. 1). It suggests that star-shaped copolymers are probably contaminated by short linear chains or cyclic macromolecules. The analysis of ^{1}H NMR spectrum of products obtained at 170 °C leads to the conclusion that lactic acid monomeric units do not form long sequences. This is clearly indicated by the splitting of the signal of methine protons into the set of four signals around 5 ppm. They can be assigned to the randomly distributed triad: LLL, LLC, CLL and CLC (L – lactic acid monomeric unit, C – TMC monomeric unit), whereas in the block copolymers the signal of LLL triad predominates. The high concentration of heterotriads indicates that at elevated temperature segmental exchange occurred which gave rise to the formation of random copolymers. Moreover, despite the relatively high M_w values (36 kg/mol), the weak signals at 5.5 ppm of O$\underline{\mathrm{H}}$ protons in terminal lactic acid monomeric units can be observed. This type of chain ends are expected to be formed after nucleophilic attack of growing TMC chains onto carbonyl groups in lactic acid segments leading to the isomerization of active species [decay of active primary ~CH$_2$O–Sn centers and restoration of more stable secondary ~CH(CH$_3$)O–Sn derivatives – Scheme B].



Scheme B

The SPLA-TMC copolymer containing approximately 50 mol % of L-LAc and TMC monomeric units obtained at 170 °C was completely amorphous and showed one T_g at 5 °C (Fig. 3a). This value is slightly higher than the theoretical one predicted by the Fox equation (-10 °C) for the random copolymers of L-LAc and TMC of the same composition. The heating trace for the block copolymer obtained at 130 °C showed melting transition at 100 °C and one T_g at about 30 °C (Fig. 3b). It indicates that LAc segments in the copolymer are long enough to form crystalline domains and suggests the miscibility of TMC and LAc segments in amorphous phase.

Synthesis and characterization of L-LA-D-LA copolymers

L-lactide polymerization reactions in the presence of D-SPLA and Sn(EH)$_2$ were carried out in bulk at temperature ranging from 130 °C to 190 °C in order to obtain co-

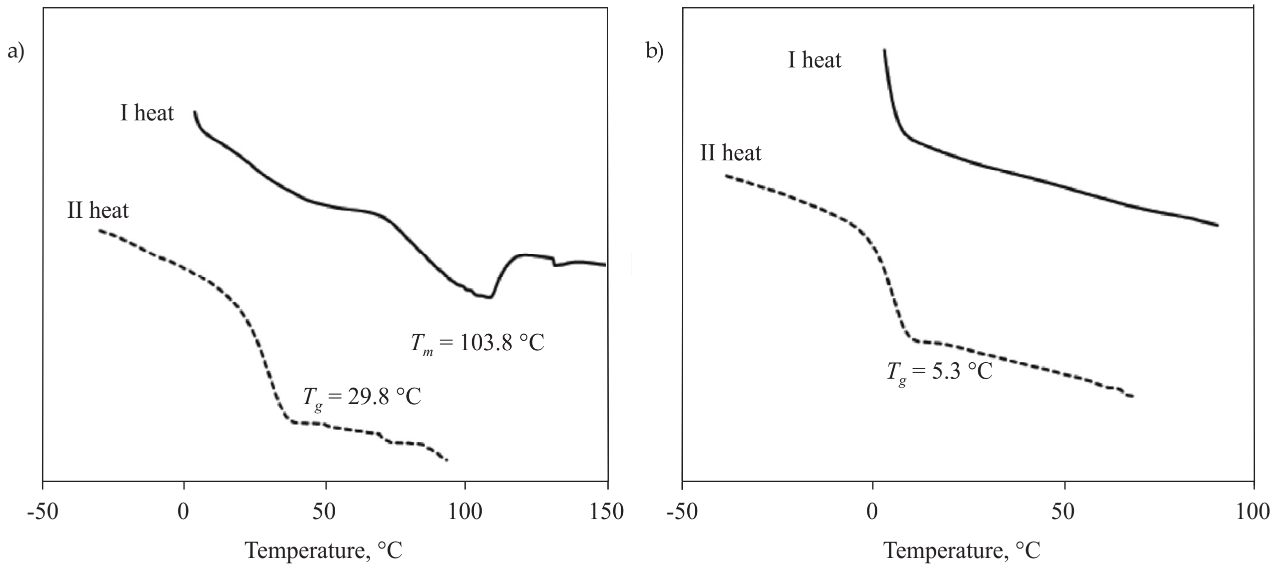


Fig. 3. DSC thermogram of the product of TMC polymerization in the presence of L-SPLA as a ROP coinitiator at: a) 170 °C, b) 130 °C

polymers of both stereoisomers. Table 2 summarizes the conditions, results and characterization of the polymerization products. The reaction mixture obtained at 190 °C formed a glassy transparent material which was soluble in dichloromethane and was purified in a similar manner as TMC copolymers. The yield of precipitated fraction calculated with respect to the sum of masses of D-SPLA and L-LA was about 50 %.

The GPC traces of this fraction revealed monomodal mass distribution (Fig. 4) with a small tail similarly as in the case of TMC copolymers. Weight average molar mass (M_w = 49.0 kg/mol) and dispersity index (*DI* = 2.8) determined by GPC analysis were higher than those for D-SPLA.

DSC traces of this material (Fig. 5) showed clear glass transition at around 50 °C and does not exhibit peaks that can be attributed neither to crystallization nor to melting of crystalline phases. To elucidate why the copolymers obtained at 190 °C have no ability to crystallize, we studied the microstructure of chains by means of ^{13}C NMR. Figure 6 shows the fragment of copolymer spectrum in the range of methine carbon (around 69 ppm) and carbonyl carbon (169–170 ppm) which are commonly used for the analysis of stereoisomeric tetrads and hexads in polylactides. The assignments for the lines observed were made according to the analysis described in the Kasperczyk and Bero articles [23, 24]. One can distinguish two lines that can be assigned to the tetrads. The less intensive one at 69.2 ppm is attributed to the *isi* sequence, whereas the second resonance at 69.0 ppm can be attributed to *iii*, *sis*, *sii*, and *iis* tetrads. In the region of carbonyl resonance the most intensive signal at 169.6 ppm may correspond to *iiiii*, *iiiis*, *siiii*, and *siiis* hexads. Two other lines at 169.3–169.4 ppm are attributed to *iiisi*, *isiii*, *iisii*, *sisii* hexads. It is important to note that neither lines corresponding to the tetrads and hexads containing *ss* sequences nor signal of alternating hexads *isisi* are present. It means that chains preserve a "predominantly isotactic structure" but probably the length of isotactic sequences is too short to form crystalline domains. The forma-

Table 2. Characteristics of the products of the L-LA polymerization in the presence of lactic acid branched oligomers terminated with hydroxyl groups[a)], extending in different temperature

No.	Temp.[b)] °C	[L-LA]/ [Olig.][b)] mol/mol	Main fraction			*LMW* fraction[c)]	T_m °C	T_g °C	T_c °C	Efficiency wt %
			$M_{p,\,GPC}$ kg/mol	$M_{w,\,GPC}$ kg/mol	*DI*	$M_{p,\,GPC}$ kg/mol				
1	130	110	41.0	52.0	1.7	4.8	184.7	52.9	99.9	72.6
2	130	220	35.0	48.0	1.6	7.0	–	–	–	61.6
3	150	110	44.0	71.5	1.9	3.9	189.9	62.0	106.0	62.9
4	170	110	32.0	89.0	2.1	1.8	–	–	–	59.3
5	190	110	37.0	49.0	2.8	–	–	54.0	–	51.1

[a)] LAc oligomer with hydroxyl end groups, characterized by M_p = 22.0 kg/mol, M_w = 12.5 kg/mol, *DI* = 2.5 (obtained from GPC measurements registered in dichloromethane with PS calibration and RI detection).

[b)] Temp. – temperature, Olig. – oligomer.

[c)] Low molar weight fraction, which could be observed by GPC.

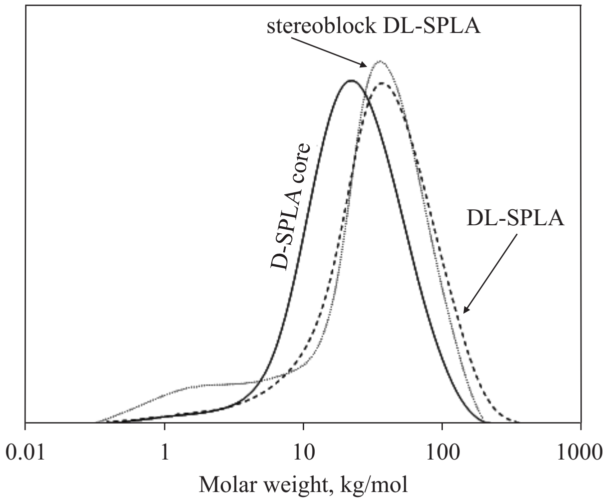


Fig. 4. GPC curves of D-SPLA (D-SPLA core), product of L-LA polymerization in the presence of D-SPLA as a ROP coinitiator at 190 °C (DL-SPLA) and at 130 °C (stereoblock DL-SPLA); registered in dichloromethane with PS calibration and RI detection

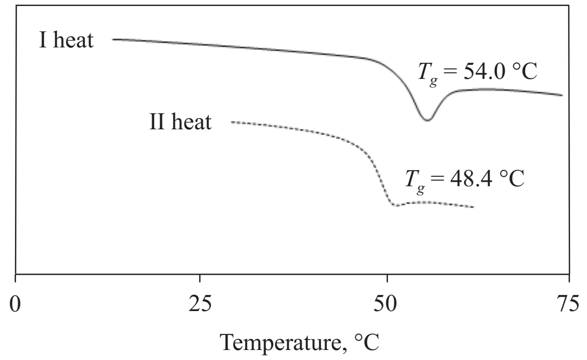


Fig. 5. DSC thermogram of the product of L-LA polymerization in the presence of D-SPLA as a ROP coinitiator at 190 °C

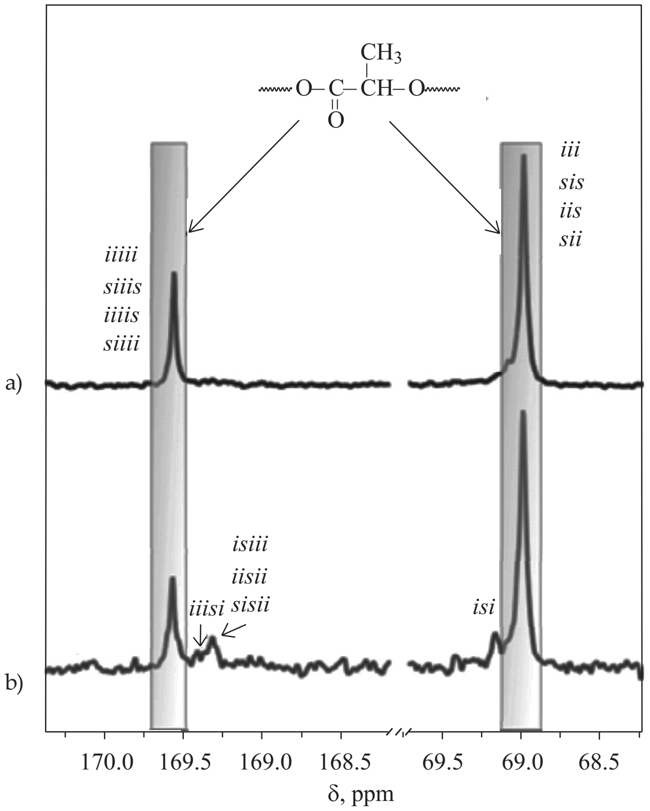


Fig. 6. ^{13}C NMR ($CDCl_3$) spectrum of the product of L-LA polymerization in the presence of D-SPLA as a ROP coinitiator at: a) 130 °C, b) 190 °C

tion of syndiotactic links may results from the addition of L-LA to stars terminated by D-LA monomeric units, segmental exchange reactions and racemization of monomeric units. However, this last possibility is rather unlikely since the polymerization of L-LA carried out under similar condition yielded fully a isotactic polymer [24].

Polymerization reactions carried out at lower temperature afforded white solids, which were hardly soluble in common organic solvents. The fraction that was subjected for further studies was isolated by making colloidal dispersion in dichloromethane, which was then coagulated by excess of methanol. The yield of products isolated in this way was in the range of 60–70 %. Exemplary DSC traces of this fraction are shown in Fig. 7 and the results of the DSC analysis for all products are collected in Table 2. All copolymers obtained at a temperature ranging from 130 to 170 °C turned out to be semicrystalline materials of glass transition temperature 50–60 °C and melting transition in the range 180–190 °C which is 30–40 °C higher than that reported for isotactic polylactides (150–170 °C). Therefore, we believe that these materials contain segments built of monomeric units of opposite configuration capable of forming stereocomplexes. However, the melting peaks are rather broad which suggests that homochiral crystallites are also formed in the studied systems. We observed that formation of crystalline domains can be impeded by fast cooling and cold crystallization occurs effectively at about 100 °C. The samples of fast cooled materials proved to be well soluble in $CDCl_3$ and CH_2Cl_2 which allow

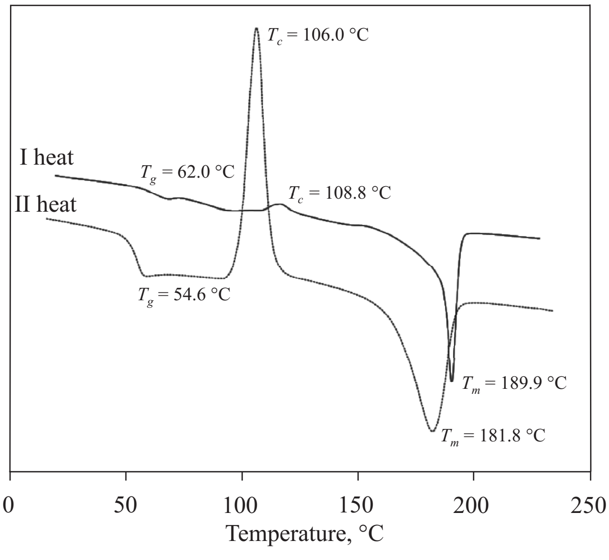


Fig. 7. DSC thermogram of the product of L-LA polymerization in the presence of D-SPLA as a ROP coinitiator at 150 °C

the studies of their tacticity by means ^{13}C NMR and molar masses distribution by means of GPC. Fig. 6a shows the fragment of a spectrum of the sample obtained at 130 °C, which clearly indicates that in this materials the segmental exchange was negligible and both segments preserve an isotactic structure. The GPC traces of this product revealed typically bimodal distribution with the main signal corresponding to the M_w in the range 48–89 kg/mol. Molar mass of the second population is significantly lower than that of D-SPLA which suggests the presence of the segments which are not attached to the core (Fig. 4).

CONCLUSIONS

We have shown that catalytic polymerization of TMC in the presence of L-SPLAs carried out at 130 °C allows to obtain star-shaped block copolymers with moderate rate. Although the content of TMC monomeric units does not exceed 20 mol %, they significantly reduce the glass transition temperature of resulting polymers in comparison with lactic acid polymers. In reaction carried out at 170 °C the transesterification reactions effectively competed with propagation, which lead to a complicated mixture of random copolymers which one can consider as potential plasticizers of PLA. The polymerization of L-LA in the presence of D-SPLA carried out in temperature ranging from 130 to 170 °C results in the formation of block copolymers containing segments built of monomeric units of opposite configuration which formed *in situ* crystalline stereocomplexes with melting temperature in the range 180–190 °C. The way in which the star-shaped macromolecules bearing segments of opposite configuration in the same arm interact with each other is not clear yet and requires further studies using cores of different number of arms and different length of blocks. The polymerization carried out at higher temperature gives rise to amorphous "predominately isotactic" star-shaped copolymers of moderate molar masses.

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