Stereocomplexes formation from enantiomeric star-shaped block copolymers of ε-caprolactone and lactide

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(Received: 19 January, 2010; published: 07 August, 2010)

Abstract: Enantiomeric star-shape block copolymers of ε-caprolactone and lactide with different molar masses and compositions were synthesized using pentaerythritol/tin(II) 2-ethylhexanoate as initiating system. Stereocomplex formation between pair of enantiomeric blocks of star arms was investigated. Thermal properties of both copolymers and obtained stereocomplexes were examined. A rise of above 50 °C of melting temperature of polylactide phase was observed as a consequence of stereocomplex creation.

Introduction

Synthetic homo- and copolymers of ε-caprolactone (CL) and lactide (LA) are increasingly investigated world-wide for biomedical, pharmacological, environmental and ecological applications because of their excellent biodegradability and biocompatibility [1-3]. Star-shaped polyesters have attracted even more attention because of their interesting physical properties. As all stars they exhibit smaller hydrodynamic radius, hence lower melt and solution viscosity if compared to linear analogues. It was shown that star-shaped polyesters have lower crystallinity, increased elasticity and they exhibit higher end-group functionality than linear polymers of the same molar mass and composition [4-8].

Most practical applications of mentioned polyesters require high molar mass polymers. The effective method to synthesize polymers of required mass is ring opening polymerization (ROP) of cyclic esters [9, 10].

Many organometallic derivatives have been successfully used as catalyst for ROP of lactones and lactides, among them inter alia tin, zircon, zinc, calcium and aluminium derivatives [11, 12]. One of the most widely used catalysts in ROP of CL or/and LA is tin(II) 2-ethylhexanoate (SnOct2) [13] due to its high efficiency and other advantages. It produces in high yield polycaprolactone (PCL) with relatively small dispersity and enables molar mass control. Moreover, due to coordination-insertion mechanism of the reaction, SnOct2 can reduce or eliminate side reactions like inter- and
intramolecular transesterification [14]. Additional advantages of SnOct$_2$ catalyst are:
good solubility in common organic solvents and cyclic esters and the fact that the
American FDA has accepted it as biocompatible compound [12, 15, 16], which is
important for potential biomedical applications of synthesized polymers.

In the past decades a large number of studies have been performed for homo- and
copolymers of LA and CL, mainly because of their known advantages but also
because of the possible formation of stereocomplexes between D-lactide (DLA) and
L-lactide (LLA) unit sequences [17-19].

Polymer stereocomplex results from stereoselective interaction (mainly hydrogen
bonds, van der Waals interactions) between two complementing stereoregular
polymers that interlock and form a new composition. Stereocomplexes can be formed
by macromolecules having opposite stereoregular configuration [19]. They may
belong to the same or different polymer families, like polyesters and polyamides.
Generally, the stereocomplex crystallites can be formed when the interaction
between two polymer chains having different configurations is stronger than between
those having the same configuration. Therefore mechanical properties and thermal
transitions of stereocomplexes differ from enantiomeric parent polymers
(intermolecular complexes usually form crystalline structures that melt at higher
temperatures ($T_m$) than that of the corresponding homochiral component crystalline
phase [19, 20]. The formation of complexes can be observed between for example R- and S-poly(γ-benzylglutamate, poly(α-methyl-α-ethyl-β-propiolactone) and, as
mentioned, between poly(D-lactide) (PDLA) and poly(L-lactide) (PLLA) chains (Fig.
1) [19].

Fig. 1. Stereocomplex formation by the PLLA and PDLA chains.

There are many publications relevant to stereocomplexes obtained from linear
polyesters based on D- and L-lactide - both homo- and copolyesters. The formation
of stereocomplexes from star-shaped PDLA and PLLA was also described [20].

Here we report about stereocomplexes formed by star copolymers of ε-caprolactone
and lactide (D- or L-lactide). The aim of this work was the synthesis and
characterization of four-arm polymer stars with arms built of block copolymers of CL
and LA (racemic, D- or LLA) of different molar masses and compositions and the
evaluation of the possibility of formation of stereocomplexes from enantiomeric block copolymers.

Results and discussion

Synthesis of star-shaped block copolymers of CL and LA

4-arms star-shaped hydroxyl-terminated block copolymers of CL and LA (racemic, D- or LLA) were synthesized through two-stage sequential ROP of CL and LA in the presence of SnOct$_2$ as a catalyst and multifunctional initiator - pentaerithritol (PTOL) (Scheme 1). In the first step of the synthesis star-shaped PCL prepolymer (4-PCL) was obtained. The monomer/catalyst ratio ([M$_1$]$_0$/[C], where M$_1$=CL) in the syntheses was maintained as 1000. Then, in second step LA was introduced to the system and bonded to “living” ends of 4-PCL, creating expected copolymer (4-P(CL–b–LA)). The composition and the arm lengths of copolymers were varied by controlling monomer to hydroxyl end-groups molar ratios ([CL]$_0$/[OH]; [LA]$_0$/[OH]).

![Scheme 1](image)

Scheme 1. Scheme of the synthesis of 4-arms star-shaped hydroxyl-terminated block copolymer of CL and LA.

After each step of the process constitutions and molar masses of synthesized both pre- and copolymers were checked. Expected structure of polyesters obtained was confirmed by NMR and IR spectroscopy. Their molar masses and dispersities were measured using size exclusion chromatography system with light scattering detector (SEC-MALLS). To obtain absolute molar masses the values of refractive index increments were measured separately for investigated polymers. Thermal properties of the polyesters were investigated using DSC method.

The $^1$H NMR spectrum of PCL obtained in the first step of syntheses is shown in Fig. 2. PCL characteristic signals of CL units can be identified: triplets at 4.06 ppm (E) and at 2.31 ppm (A) assigned to methylene groups adjacent to carboxyl and carbonyl group respectively, two multiplets at 1.60-1.71 ppm (B, D) and at 1.35-1.43 ppm (C) characteristic for methylene groups which are not directly connected to carboxyl or carbonyl groups. There are also signals of methylene protons of reacted initiator at 4.10 ppm (X) and that of methylene groups connected to hydroxyl end-groups of 4-PCLs at 3.65 ppm (Y). These signals confirm that polymers with PCL chains were obtained. The evidence for expected structure of prepolymers is lack of signals of protons from methylene groups adjacent to unreacted free hydroxyl groups in initiator.
The structure of the synthesized prepolymers was also confirmed by IR spectroscopy. Representative FT-IR spectrum of 4-PCL is shown in Fig. 3.

Bands characteristic for functional groups can be identified. A narrow strong band at 1730 cm$^{-1}$ is assigned to stretching vibrations of C=O group. In the C-H stretching region (3100-2800 cm$^{-1}$) bands characteristic for $\nu$(CH$_2$) are observed. Bands $\nu$(C–O), $\nu$(O–H) and coming from $\delta$CH$_2$, are also identified, thus confirming expected structure of 4-PCL.

On the basis of $^1$H NMR spectra, number average molar masses of prepolymers ($M_{n\text{ NMR 4-PCL}}$) were calculated using following equations:

$$M_{n\text{ NMR 4-PCL}} = 4 \cdot M_{CL} \cdot n_{\text{NMR}} + M_{PTOL}$$  \hspace{1cm} (1)
\[ n_{\text{NMR}} = \frac{l_A}{l_Y} \]  

where: \( M_{\text{CL}} \) – molar mass of CL; \( n_{\text{NMR}} \) – number of CL units in one arm of 4-PCL; \( M_{\text{PTOL}} \) – molar mass of initiator (PTOL) used; \( l_A \) – intensity of signal A characteristic for protons of methylene groups adjacent to carbonyl group; \( l_Y \) – intensity of signal Y characteristic for protons of methylene group connected to hydroxyl end-group.

Number average molar masses and number of CL units in one arm of 4-PCL were determined by \(^1\)H NMR spectroscopy (\( M_n \) \(_{\text{NMR}}\) 4-PCL and \( n_{\text{NMR}} \), respectively).

All chromatograms of 4-PCL stars were monomodal. The mass dispersities of the stars did not exceed 1.13. Absolute molar masses and degree of polymerization of arm for obtained PCL stars (\( M_n \) \(_{\text{SEC}}\) 4-PCL, and \( n_{\text{SEC}} \), respectively) determined using SEC–MALLS are contained in Table 1.

Theoretical values of molar masses of prepolymer (equation 3) and theoretical number of CL units in star arms (\( M_{n \text{theor.}} \) 4-PCL and \( n_{\text{theor.}} \), respectively) were calculated from composition of reaction mixture.

\[ M_{n \text{theor.}} 4\text{-PCL} = 4\cdot(114,14[\text{CL}]:[\text{OH}]+M_{\text{PTOL}}) \]  

All values are collected in Table 1.

**Tab. 1. Basic characteristics of 4-PCL prepolymer.**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>([M_1]_0/ [I]_0^*)</th>
<th>( M_n ) (_{\text{theor.}})</th>
<th>( M_n ) (_{\text{NMR}})</th>
<th>( M_n ) (_{\text{SEC}})</th>
<th>( n_{\text{theor.}})</th>
<th>( n_{\text{NMR}})</th>
<th>( n_{\text{SEC}})</th>
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<tr>
<td>4-PCL1</td>
<td>122.7/ 14 000</td>
<td>12 000</td>
<td>11 400</td>
<td>30.7</td>
<td>26.3</td>
<td>24.7</td>
<td></td>
</tr>
<tr>
<td>4-PCL2</td>
<td>87.6/ 10 000</td>
<td>9 400</td>
<td>9 000</td>
<td>21.9</td>
<td>20.7</td>
<td>19.4</td>
<td></td>
</tr>
<tr>
<td>4-PCL3</td>
<td>157.7/ 18 000</td>
<td>18 800</td>
<td>15 800</td>
<td>39.4</td>
<td>41.2</td>
<td>34.3</td>
<td></td>
</tr>
<tr>
<td>4-PCL4</td>
<td>192.7/ 22 000</td>
<td>18 600</td>
<td>16 400</td>
<td>48.2</td>
<td>40.7</td>
<td>35.6</td>
<td></td>
</tr>
<tr>
<td>4-PCL5</td>
<td>122.7/ 14 000</td>
<td>15 000</td>
<td>13 500</td>
<td>30.7</td>
<td>32.8</td>
<td>29.3</td>
<td></td>
</tr>
<tr>
<td>4-PCL6</td>
<td>87.6/ 10 000</td>
<td>10 400</td>
<td>9 800</td>
<td>21.9</td>
<td>22.8</td>
<td>21.2</td>
<td></td>
</tr>
<tr>
<td>4-PCL7</td>
<td>157.7/ 18 000</td>
<td>16 300</td>
<td>15 400</td>
<td>39.4</td>
<td>35.7</td>
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<tr>
<td>4-PCL8</td>
<td>192.7/ 22 000</td>
<td>21 200</td>
<td>17 200</td>
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<td>37.4</td>
<td></td>
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<tr>
<td>4-PCL9</td>
<td>122.7/ 14 000</td>
<td>14 100</td>
<td>14 700</td>
<td>30.7</td>
<td>30.9</td>
<td>31.9</td>
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<td>4-PCL10</td>
<td>122.7/ 14 000</td>
<td>12 800</td>
<td>12 200</td>
<td>30.7</td>
<td>28.0</td>
<td>26.4</td>
<td></td>
</tr>
<tr>
<td>4-PCL11</td>
<td>87.6/ 10 000</td>
<td>9 900</td>
<td>9 100</td>
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<tr>
<td>4-PCL12</td>
<td>122.7/ 14 000</td>
<td>10 700</td>
<td>11 800</td>
<td>30.7</td>
<td>23.5</td>
<td>25.6</td>
<td></td>
</tr>
<tr>
<td>4-PCL13</td>
<td>87.6/ 10 000</td>
<td>8 500</td>
<td>8 500</td>
<td>21.9</td>
<td>18.7</td>
<td>18.7</td>
<td></td>
</tr>
</tbody>
</table>

\(^*\) \([M_1]_0 = [\text{CL}]_0; [I]_0 = [\text{PTOL}]_0\)

Thermal properties of synthesized 4-PCLs stars were examined using DSC. For all polymers in the temperature range of measurements (-50 to 250 °C) only one transition can be observed at about 60 °C. It is related to the melting temperature (\( T_m \)) of PCL chains. It was noticed that \( T_m \) increased to some extent with increasing chain length. Unfortunately limited temperature range of measurements did not allow observation of expected glass transition temperature (\( T_g \)) of PCL which is below -60 °C [2, 7, 16].

Polycaprolactone stars listed in Table 1 were used for the polymerization of lactides. Block 4-arm star hydroxyl-terminated copolymers of CL and LA (4-P(CL–b–LA))
obtained by sequential ROP of both cyclic esters (Scheme 1) were characterized in the same way as prepolymers.

In the $^1$H NMR spectra of 4-P(CL–b–LA)s (Fig. 4) signals characteristic for protons of CL units, with similar chemical shift like in the $^1$H NMR spectra of 4-PCLs, can be identified. Additionally signals characteristic for LA units are also observed: those of protons of methyl group (G) overlapping with (B') and (D') at $\delta = 1.45 - 1.75$ ppm and signal of methine proton adjacent to ester group at $\delta = 5.1 - 5.3$ ppm (F). There are also signals characteristic for protons of methylene groups from built-in initiator at $\delta = 4.10$ ppm (X') and of methine protons next to hydroxyl end groups at $\delta = 4.25 - 4.45$ ppm (Z'). Lack of signal coming from protons of methylene group connected to hydroxyl end group (–CH$_2$–OH) which was present in the spectra of homopolymer (see Fig. 2, $\delta = 3.65$ ppm (Y)) suggests that LA molecules were connected to all arms of CL homopolymer and copolymer of expected star-shaped structure was obtained.

**Fig. 4.** 300 MHz $^1$H NMR spectrum of 4-P(CL–b–LA)$_5$ (25 °C, CDCl$_3$).

Structure of 4-P(CL–b–LA)s was investigated not only with $^1$H NMR but also $^{13}$C NMR spectroscopy. The example of $^{13}$C NMR spectrum for 4-P(CL–b–LA) is shown in Fig. 5. In the $^{13}$C NMR spectra of copolymers signals characteristic for both CL and LA units can be identified. Peaks with chemical shift equal to 24.6 ppm (c), 25.5 ppm (b), 28.4 ppm (d), 34.1 ppm (a), 64.1 ppm (e), 173.5 ppm (h) come from carbon atoms of PCL blocks and those at $\delta = 16.7$ ppm (g), 69.1 ppm (f), and 169.1 – 169.7 ppm (i) are characteristic for carbon atoms in PLA blocks.

$^{13}$C NMR spectra of 4-P(CL–b–LA)s enables characterization of the sequences of LA and CL units on the basis of the carbonyl carbon atom signals that are sensitive to structural and conformational changes in their neighborhood. Polymerization of racemic LA (DLLA) gives polymer that is “predominantly isotactic” (lack of “ss”
sequences, where “s” means that two neighboring units are of opposite configuration (DL or LD)), while during polymerization of one of the enantiomers, isotactic polymer is received. According to the literature [21] when neither the stereoelection (privileged selection of one of monomers) nor transesterification processes are observed during polymerization of DLLA, it is possible to foresee addition of monomer to growing LA chain.

![Diagram of polymer structure]

**Fig. 5.** 75 MHz $^{13}$C NMR spectrum of 4-P(CL-b-LA)$_5$ (25 °C, CDCl$_3$).

In Fig. 5 ($^{13}$C NMR spectrum of copolymer of CL and DLLA) group of signals ascribed to carbonyl carbon atom in LA unit (i, 169.1 – 169.7 ppm) is a result of the use of both enantiomeric forms of lactide (DLA and LLA) that can form different sequences. Comparison of theoretical intensities of lines with experimental ones make possible to assign spectral lines in carbonyl range to hexades (iiiii, iiisi, iiisi, iiiii, iiiii, iiisi, iiisi, iiiii, iiiii, where “i” means that two neighboring units are of the same configuration (DD or LL). Signals of all those hexades are present in the spectra.

In case of copolymer of CL and one of lactic enantiomers (Fig. 6), in carbonyl carbon atom range there is only one signal around 169.6 ppm assigned to “iiiii” hexade, which means that isotactic structure of LA block is confirmed.

In the $^{13}$C NMR spectra of copolymers of CL and DLLA between signals ascribed to carbonyl carbon of CL (h) and LA blocks (i) no signals (or of very small intensity) belonging to sequences formed by transesterification were found. This confirmed that transesterification reactions were eliminated (or reduced to small extent) and 4-P(CL-b-LA)s of intended block structure were obtained.

IR spectroscopy provided additional evidences for expected constitution of synthesized copolyesters.
Fig. 6. 75 MHz $^{13}$C NMR spectrum of 4-P(CL-b-LLA)$_{11}$ (25 °C, CDCl$_3$).

In the exemplary FT-IR spectrum of copolymer (Fig. 7) bands characteristic for given functional groups can be identified and they are analogous to that in the FT-IR spectra of homopolymers i.e PCLs (Fig. 3). The only difference is in the band characteristic for stretching vibrations of carbonyl group. In Fig. 7 absorption band at 1760 cm$^{-1}$ characteristic for ester carbonyl group (–CHC(O)–) of LA block and absorption band at 1730 cm$^{-1}$ belonging to the ester carbonyl group (–CH$_2$C(O)–) of
CL block are observed. For homopolymers (4-PCLs), there was only one strong single band around 1700 cm\(^{-1}\). This difference is a supplementary proof of the formation of block structure of 4-P(CL-b-LA)s.

On the basis of \(^1\)H NMR spectra of copolymers, LA contents (weight percentage, PLA\(_{\text{NMR}}\)) and number average average molar masses (M\(_n\)_NMR) of synthesized copolyesters were calculated using following equations:

\[
\text{PLA}_{\text{NMR}} = \frac{[(m+1)\cdot M_{LA}] / [(m+1)\cdot M_{LA} + 2 \cdot n_{NMR} \cdot M_{CL}]} \cdot 100\%
\]

\[
m_{\text{NMR}} = \frac{(2 \cdot I_F \cdot n_{\text{NMR}})}{I_A}
\]

\[
M_n_{\text{NMR}} = \frac{(100 \cdot M_n_{\text{NMR} \cdot 4\text{-PCL}})}{(100 - \text{PLA}_{\text{NMR}})}
\]

where:

- M\(_{LA}\) – molar mass of LA; n\(_{NMR}\) – number of caprolactone units in one arm of 4-P(CL-b-LA) equal to number of CL units in one arm of initial 4-PCL; m\(_{\text{NMR}}\) – number of lactide units in one arm of 4-P(CL-b-LA); I\(_A\) – intensity of signal A\(^{\prime}\) characteristic for protons of methylene group adjacent to carbonyl group in CL unit; I\(_F\) – intensity of signal F characteristic for methine proton in LA repeating unit.

LA contents and M\(_n\) values determined by \(^1\)H NMR spectroscopy for obtained block copolymer stars, theoretical molar mass (M\(_n\)_theor.) and absolute molar masses of stars (M\(_n\)_SEC) determined using SEC–MALLS are collected in Table 2.

**Tab. 2.** Basic characteristics of 4-P(CL-b-LA) star copolymers.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>LA</th>
<th>M(_n)_theor.</th>
<th>M(_n)_NMR</th>
<th>M(_n)_SEC</th>
<th>m(_NMR)</th>
<th>PLA(_{\text{NMR}})</th>
<th>Yield %</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-P(CL-b-LA)(_1)^*</td>
<td></td>
<td>35 000</td>
<td>18 800</td>
<td>20 400</td>
<td>22.5</td>
<td>36</td>
<td>37</td>
</tr>
<tr>
<td>4-P(CL-b-LA)(_2)^*</td>
<td></td>
<td>25 000</td>
<td>14 000</td>
<td>14 300</td>
<td>14.7</td>
<td>32</td>
<td>30</td>
</tr>
<tr>
<td>4-P(CL-b-LA)(_3)^*</td>
<td></td>
<td>45 000</td>
<td>33 700</td>
<td>26 600</td>
<td>50.5</td>
<td>44</td>
<td>52</td>
</tr>
<tr>
<td>4-P(CL-b-LA)(_4)^*</td>
<td>Racemic LA</td>
<td>55 000</td>
<td>44 300</td>
<td>37 300</td>
<td>88.2</td>
<td>58</td>
<td>58</td>
</tr>
<tr>
<td>4-P(CL-b-LA)(_5)^*</td>
<td>DLLA</td>
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<td>39 100</td>
<td>29 500</td>
<td>82.5</td>
<td>62</td>
<td>63</td>
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<tr>
<td>4-P(CL-b-LA)(_6)^*</td>
<td></td>
<td>25 000</td>
<td>21 100</td>
<td>17 900</td>
<td>36.0</td>
<td>51</td>
<td>50</td>
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<tr>
<td>4-P(CL-b-LA)(_7)^*</td>
<td></td>
<td>45 000</td>
<td>37 300</td>
<td>32 900</td>
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<td>29 800</td>
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<td>4-P(CL-b-LLA)(_9)^*</td>
<td></td>
<td>35 000</td>
<td>29 800</td>
<td>26 200</td>
<td>64.9</td>
<td>52</td>
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<tr>
<td>4-P(CL-b-LLA)(_10)^*</td>
<td>LLA</td>
<td>35 000</td>
<td>28 200</td>
<td>23 400</td>
<td>52.5</td>
<td>55</td>
<td>79</td>
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<tr>
<td>4-P(CL-b-LLLA)(_11)^*</td>
<td></td>
<td>25 000</td>
<td>19 600</td>
<td>14 300</td>
<td>32.9</td>
<td>50</td>
<td>57</td>
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<tr>
<td>4-P(CL-b-DLA)(_12)^*</td>
<td>DLA</td>
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<tr>
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<td></td>
<td>25 000</td>
<td>19 300</td>
<td>17 100</td>
<td>36.4</td>
<td>56</td>
<td>72</td>
</tr>
</tbody>
</table>

*24 h; **48 h

Obtained results indicate that PLA\(_{\text{NMR}}\) in 4-P(CL-b-LA)s is usually lower than expected, probably due to the fact that not all LA introduced to the system reacted. It can be observed that the control of synthesis was better when duration of second step of process was elongated from 24 to 48 hours. For stars with racemic LA blocks the best results were obtained for copolymers with theoretical M\(_n\) from 25 000 to 35 000, theoretical content of LA equal 60 % and 48 h reaction time of second step.
So these conditions were used in the synthesis of enantiomeric LA blocks in the copolymers of CL with LLA or DLA (4-P(CL-b-LLA)\textsubscript{9} + 4-P(CL-b-DLA)\textsubscript{13}). Unfortunately in almost all copolyesters LA contents (PLA\%\textsubscript{NMR}) was lower than that calculated from feed ratio, i.e. 60\%. It was probably due to the sublimation of a part of LA collecting on the walls of reaction vessel.

For better characterization of synthesized polymers, their thermal properties were examined as for 4-PCLs. Thermal analyses were performed for temperature range from -50 to 250 °C, at a heating rate of 10 °C/min. Characteristic temperatures were determined from the peak positions at first heating run. Fig. 8 shows the DSC curves of selected stars with different lactides: DLLA (4-P(CL-b-LA)\textsubscript{8}), LLA (4-P(CL-b-LLA)\textsubscript{11}) and DLA (4-P(CL-b-DLA)\textsubscript{13}). It can be seen that copolymerization has a radical impact on thermal properties. For copolymers of CL and DLLA the only thermal transition temperature observed is the T\textsubscript{m} of PCL blocks because LA blocks are fully amorphous. In case of copolymer of CL and enantiomeric forms of LA (LLA) both T\textsubscript{m} of PCL and PLLA blocks are observed due to the phase microseparation and presence of crystalline structures of PCL and PLLA blocks. For copolymers of CL and DLA only one transition connected with T\textsubscript{m} of PDLA blocks is observed. For 4-P(CL-b-DLA)\textsubscript{13} star T\textsubscript{m} of PCL disappeared, probably due to the presence of PLA segments long enough to disturb formation of crystalline structure of PCL.

![Fig. 8. DSC thermograms of selected copolymers.](image)

According to results of DSC analyses carried out the thermograms of copolymers of CL and LLA or DLA show two melting temperatures (T\textsubscript{m} of PCL and PLLA or PDLA phase) when the value of LA content is around 50 % w/w, as it is shown for LLA in Fig. 8, 9 (4-P(CL-b-LLA)\textsubscript{11}).

No glass transition is visible on thermograms of stars. T\textsubscript{g} of PCL block (~ -60 °C) is not observed because it is out of the measuring range of the apparatus. T\textsubscript{g} of PLA block also cannot be identified probably due to the fact that it lies close to the region...
characteristic for $T_m$ of PCL block and is not visible as separate change on DSC curve.

**Preparation of stereocomplexes**

Formation of stereocomplexes was performed using synthesized star copolymers of similar molar masses and compositions. For comparison stereocomplexes of linear LLA and DLA homopolymers both of similar molar masses 3300 g/mol were also prepared (stereo₁ and stereo₂, Table 3). Applied method makes use of different solubility of stereocomplex and parent polymers from which it was formed, in acetonitrile. Advantage of this method is easy removal of non-complexed polymers.

To confirm formation of stereocomplexes DSC analyses of obtained materials were performed.

Enantiomeric PDLA or PLLA blocks in 4-arm star copolymers melt at about 115-135 °C, while synthesized linear homopolymers (PDLA or PLLA) shows $T_m$ between 170-180 °C (Table 3, Fig. 9). According to the literature, as a consequence of stereocomplex formation, a rise of approximately 50-55 °C of the $T_m$ of PLA phase should be observed [18]. Fig. 9 shows exemplary thermograms of selected 4-P(CL–b–LA)s and stereocomplexes based on these (Stereo₆).

Fig. 9. DSC thermograms of 4-P(CL-b-LLA)₁₁, 4-P(CL-b-DLA)₁₃ and their stereocomplexes.

In case of both parent polymers (4-P(CL-b-LLA)₁₁ and 4-P(CL-b-DLA)₁₃), $T_m$ of LA blocks is around 115-120 °C. In the stereocomplex thermogram a broad peak at 178 °C can be seen, which can be considered as an evidence of stereocomplex formation.

The melting temperatures of parent polymer used for stereocomplex formation ($T_m$ of LA blocks in case of stars), temperature of stereocomplexing process ($T_{\text{process}}$) and the phase transition temperature for stereocomplexes ($T_{mS}$) are collected in Table 3.
**Tab. 3.** Thermal properties of parent polymers and obtained stereocomplexes.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Polymer A</th>
<th>$T_{mA}$ [°C]</th>
<th>Polymer B</th>
<th>$T_{mB}$ [°C]</th>
<th>$T_{\text{process}}$ [°C]</th>
<th>$T_{ms}$ [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stereo1</td>
<td>PDLA*</td>
<td>175</td>
<td>PLLA*</td>
<td>177</td>
<td>40</td>
<td>218</td>
</tr>
<tr>
<td>Stereo2</td>
<td>4-P(CL-b-DLA)$_{12}$</td>
<td>133</td>
<td>4-P(CL-b-LLA)$_{9}$</td>
<td>130</td>
<td>40</td>
<td>205</td>
</tr>
<tr>
<td>Stereo3</td>
<td>4-P(CL-b-DLA)$_{13}$</td>
<td>121</td>
<td>4-P(CL-b-LLA)$_{11}$</td>
<td>116</td>
<td>40</td>
<td>179</td>
</tr>
</tbody>
</table>

* $M_{n\text{NMR PDLA}} = 3300$ g/mol, $M_{n\text{NMR PLLA}} = 3300$ g/mol;*

The observed increase of melting temperature of PLA segments in the case of stereocomplexes compared to the parent polymers (Polymer A and Polymer B) indicates that the stereocomplexes were formed for all cases (Stereo$_1$ + Stereo$_6$). In case of formation of complexes from linear homopolymers PDLA and PLLA (Stereo$_1$, Stereo$_2$) increase of $T_m$ is observed, but it is lower than in case of formation of complexes by star-shaped copolymers of CL and LA. This difference may result from low molar mass of linear polymers as well as be caused by the topology of stars with enantiomeric LA blocks. Stereocomplexes obtained from 4-P(CL-b-LA)s showed lower $T_{ms}$ than these from linear PLLA and PDLA. Results like these can be connected with both composition of polyesters (presence of PCL phase in 4-P(CL-b-LA)s) and their star structure. The temperature of the process plays a meaningless role in stereocomplex formation but higher temperature improve the solubility of parent polymers which is important especially in case of high molar mass polymers.

**Conclusions**

Sequential bulk polymerization of CL and LA in the presence of SnOct$_2$ and multifunctional initiator (PTOL) produced star-shaped hydroxyl-terminated block copolymers with 4 arms. Relatively good control of molar mass of synthesized polymers in range 25000 to 35000 was observed. Considerable difficulties in preparation of high molar mass 4-P(CL-b-LA)s probably results from the presence of other carriers of hydroxyl groups in reaction mixture such as trace of water, silanol groups on surface of glass walls of reaction vessel etc. Relatively effective control of copolymer composition was obtained when polymerization was performed for 72 h with LA content in the reaction mixture equal to 60 % w/w.

Influence of constitution and molar masses on the thermal transition of synthesized polymers was observed. The DSC measurements showed that in the star copolymers of CL and racemic polylactide blocks were fully amorphous, as it was expected according to literature [22, 23] and the only observed temperature was the $T_m$ of PCL. In case of copolymers of CL and enantiomeric LA, thermograms showed one or two characteristic thermal transition temperatures. Two characteristic thermal transition temperatures were observed only when LA content was approximately 50 % w/w (both $T_m$ of PCL and $T_m$ of PLA blocks were observed). Higher LA content disturbed crystalline structure of PCL blocks, which results in disappearance of its $T_m$ in DSC thermograms.
Stereocomplexes were prepared between enantiomeric star copolymers with similar molar masses and compositions. Additionally the stereocomplex formation was investigated for synthesized enantiomeric linear polylactides (PDLA, PLLA) with similar molar masses and compositions. The comparison of the thermal behaviour of stereocomplexes of stars with stereocomplexes of linear homopolymers showed the influence of the star architecture on the changes of phase transition temperature of complex formed. A rise of melting temperature of polylactide phase (T_{mS}) of above 50 °C was observed as a consequence of stereocomplex creation from star copolymers 4-P(CL-b-LA)s while for stereocomplexes of linear polylactides it was significantly lower. On the other hand stereocomplexes obtained from 4-P(CL-b-LA)s showed lower T_{mS} than those from linear PLAs. This can be a result of both presence of PCL phase in 4-P(CL-b-LA)s and star structure itself. The temperature of the stereocomplexation process plays a meaningless role in stereocomplexes formation.

Experimental part

Materials

Pentaerythritol (PTOL, Aldrich) was purified by sublimation under vacuum. DL-, D- and L-Lactide (DLLA, LLA, Aldrich; DLA PURAC biomaterials) were purified by sublimation under vacuum too. ε-Caprolactone (CL, Fluka) was dried over CaH₂ at room temperature for 48 h and then distilled under vacuum. Ti(II) 2-ethylhexanoate (SnOct₂, Aldrich) was dried by heating at 150 °C under vacuum for 12 hours. Xylene (POCh Gliwice) was dried over CaH₂ at room temperature for 48 h and then distilled under vacuum at 138 °C. Acetonitrile (ACN, POCh) was purified by distillation at 81 °C. Methanol (MeOH), tetrahydrofuran (THF) and methylene chloride, all from POCh Gliwice, were used as received.

Instrumentation

Polymers obtained were characterized by means of NMR and IR spectroscopy. NMR spectra were recorded with UNITY/INOVA (Varian) spectrometer operating at 300 MHz (¹H NMR) and at 75 MHz (¹³C NMR). CDCl₃ and tetramethylosilane (TMS) were used as a solvent and internal standard, respectively.

The IR spectroscopy was conducted with BIORAD FTS 175L spectrophotometer at room temperature after dissolving samples in dichloromethane and coating potassium bromide (KBr) tablets with this solution to form films.

Absolute molar masses of polyesters were determined using size exclusion chromatography system equipped with differential refractive index (Δn-1000 RI WGE Dr. Bures) and multiangle laser light scattering (MALLS; DAWN EOS, Wyatt Technologies) detectors. Measurements were performed in THF using SDV 1 x 10⁵ Å+1x10³ Å+2x10² Å columns (Polymer Standard Service). The specific refractive index increment (dn/dc) of polymer samples was measured for all polymer samples in separate measurements. SEC results were collected and evaluated by ASTRA software from Wyatt Technologies.

DSC analysis of polymers and stereocomplexes were made using differential scanning calorimeter (METTLER-TOLEDO, DSC822e). Analyses were performed in temperature range from -50 to 250 °C, at a heating rate of 10 °C/min. Characteristic temperatures were determined from the first heating run.
Synthesis of 4-P(CL-b-LA)

Calculated amount of CL was introduced into freshly silanized and dried round bottom flask under argon atmosphere. SnOct₂ as a solution in dry xylene was added (2.9 mL of SnOct₂ in 70 mL of xylene), monomer to catalyst molar ratio ([M₁]/[C], where M₁ = CL) was maintained as 1000. Addition was followed by solvent removal by vacuum distillation. After that exhausting-refilling processes with argon were repeated three times. Initiator (PTOL) was introduced into reaction vessel. Reaction mixture was purged with dry argon and kept for 24 h in oil bath pre-heated to 120 °C. The products, precursors for next step of synthesis, are described as 4-PCLₓ where x is the number of synthesis and 4 is the number of star arms.

After that sample of the polymerization mixture was collected and desired amount of LA monomer was charged into flask (assumed theoretical content of LA part in copolymer of 60 %). Vessel was left for 24 or 48 h at 120 °C again. The product was cooled, dissolved in dichloromethane and precipitated in methanol. The solid was isolated by filtration and dried under reduced pressure at 60 °C to constant weight. Star block copolymers are described as 4-P(CL-b-LA)ₓ, where x is the number of precursor.

Synthesis of linear PLA (PDLA and PLLA)

Method of polymerization and equipment used were analogous to that applied in the synthesis of 4-PCLₓ precursors. Given amounts of LA (DLA or LLA) and initiator (MTEG) were introduced into freshly silanized and dried round bottom flask under argon atmosphere and dried in a vacuum (∼ 5⋅10⁻² mmHg) for 1 hour at room temperature. Then SnOct₂ as a solution in dry xylene was added (2.9 mL of SnOct₂ in 70 mL of xylene), molar ratio of monomer to catalyst was [LA]/[SnOct₂] = 1000. Addition was followed by solvent removal by vacuum distillation. After that exhausting-refilling processes with argon were repeated three times and reaction mixture purged with argon was kept for 24 h in oil at 130 °C. Product of reaction was cooled, dissolved in dichloromethane and precipitated in methanol. PLA was isolated by filtration and dried under reduced pressure at 60 °C to constant weight.

Preparation of stereocomplexes

For the preparation of stereocomplexes from synthesized polymers, equal amounts of enantiomeric LA homo- or star copolymers of similar molar masses (and compositions in case of copolymers) were dissolved in acetonitrile. Solutions were separately prepared to have a polymer concentration of 1 g/dL and then mixed together under vigorous stirring with mixing ratio equal 1:1 and left for 7 days at 40 or 60 °C, depending on the solubility of the polymers. The stereocomplexes started to precipitate within several hours or days (depending on the polymer structure and molar mass). The precipitate formed was separated and washed with fresh acetonitrile to remove non-complexed polymers and with methanol to remove acetonitrile, and then dried at room temperature.

Acknowledgements

The authors appreciate the Lady Davis Foundation support for Jan Łukaszczyk sabbatical period at Hebrew University.
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