

Stereocomplexation of polylactides containing ionic liquid end-groups

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Dedicated to the memory of Professor Andrzej Duda

Abstract: Linear and cyclic oligomers of epichlorohydrin were synthesized and converted by reaction with *N*-methylimidazole into linear or cyclic derivatives fitted with imidazolium ionic liquid groups. These oligomers containing hydroxyl groups were used as macroinitiators of cationic polymerization of L- and D-lactide. Two types of products were obtained: linear polylactides (PLA's) containing a few ionic liquid groups at the chain end and star PLA's containing a few ionic liquid groups at the core. The enantiomeric forms of PLA, poly(L-lactide) (PLLA) and poly(D-lactide) (PDLA) were used for stereocomplexation studies following earlier observation that if PLLA and PDLA containing one imidazolium ionic liquid group at the chain end are mixed in 1,4-dioxane solution, stereocomplex precipitates spontaneously in form of uniform microspheres. In a present contribution it is shown that if more than one ionic liquid group is introduced at the chain ends of PLLA and PDLA, morphology of precipitated stereocomplex is similar to that observed for PLA's fitted with one ionic liquid group but microspheres are slightly less regular. When few ionic liquid groups are present at the core of star PLLA no specific morphology is observed for precipitating stereocomplex with linear PDLA fitted with C₄H₉O- group. Only when end-groups able to interacting with each other are introduced, specific morphology appears. With ionic liquid end-groups in linear component, stereocomplex precipitates in form of irregular granules while with strongly interacting ureidopyrimidine end-groups, microspheres, although not very regular, are formed. These results indicate that well defined morphology (regular spherical particles) is observed when interacting groups are present at the freely moving chain ends but not, when the same groups are embedded and immobilized at the core of star polymers and through it probably are hidden inside polymer random coil.

Keywords: polylactide, stereocomplex, epichlorohydrin, interacting end-groups, microspheres.

Stereokompleksowanie polilaktydów zawierających ciecze jonowe jako grupy końcowe

Streszczenie: Otrzymano liniowe i cykliczne oligomery epichlorohydryny, następnie grupy chlorometylowe przekształcono – w reakcji z *N*-metyloimidazolem – w imidazoliowe, analogiczne do grup występujących w cieczach jonowych. Oligomery zawierające grupy hydroksylowe zastosowano jako makroinicjatory kationowej polimeryzacji L- i D-laktydu, w wyniku której uzyskano dwa rodzaje produktów: liniowe polimery laktydu (PLA) z udziałem kilku grup cieczy jonowej na jednym z końców łańcucha oraz gwiazdziste polimery laktydu zawierające kilka grup cieczy jonowej w centrum gwiazdzistej makrocząsteczki. Enancjomeryczne formy PLA: poli(L-laktyd) (PLLA) i poli(D-laktyd) (PDLA) zastosowano do wytworzenia stereokompleksów. Wykazano, że jeśli na końcu łańcucha znajduje się więcej niż jedna grupa cieczy jonowej, morfologia wytrącającego się stereokompleksu jest zbliżona do morfologii obserwowanej w wypadku obecności tylko jednej grupy cieczy jonowej, ale mikrosfery są mniej jednorodne. Wyniki wskazują, że regularne mikrosfery powstają jeśli grupy zdolne do wzajemnych oddziaływań znajdują się na końcach liniowych makrocząsteczek, nie powstają natomiast wtedy, gdy grupy te znajdują się w centrum gwiazdzistej makrocząsteczki i są otoczone jej ramionami.

Słowa kluczowe: polilaktyd, stereokompleks, epichlorohydryna, wzajemnie oddziałujące grupy końcowe, mikrosfery.

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Polymers that contain chiral carbon atoms within the chain show optical activity if the majority of chiral centers have identical configuration. It has been established some time ago that if polymers with opposite configuration of chiral centers are mixed, stereocomplex is formed that differs from both enantiomers with respect, *e.g.*, to solubility or melting temperature [1–4].

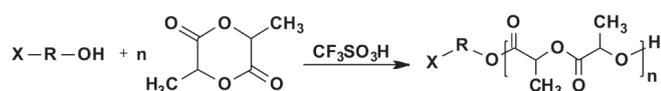
Among pairs of polymers that may form stereocomplexes, polylactide occupies special position. Polylactide (PLA), biodegradable polymer obtained from renewable resources is generally recognized as safe by the US Food and Drug Administration (FDA), and is considered as potential replacement for petroleum based commodity plastics as well as for more specialized applications such as drug delivery systems.

Polylactide is manufactured either by condensation of lactic acid or by ring-opening polymerization (ROP) of cyclic dimer of lactic acid, *i.e.*, lactide (LA). Because biochemical processes (fermentation of various natural carbohydrates) may, depending on enzyme used, lead to either L- or D-lactic acid, both enantiomers are easily available. It has been found, that stereocomplexation of PLLA and PDLA leads to significant increase of melting point (by about 50 °C) and this property, important from practical point of view, raised still growing interest in studies of PLA stereocomplexation and stereocomplex properties [5–8].

Stereocomplexation is mainly studied for high molecular weight polymers. It has been established, however, that for stereocomplexation to occur it is sufficient to have chains composed of at least seven repeating units thus also medium molecular weight PLA may form stereocomplexes [9].

In our group, synthesis of medium molecular weight lactide polymers containing functional group at one of chain ends (functional PLA's) has been studied. For LA polymerization mainly coordination polymerization with metal containing catalysts (tin octoate being most typical example) is applied [10]. LA may also be polymerized by cationic mechanism although this process is less studied [11–13]. We have found, however, that cationic polymerization proceeding by Activated Monomer (AM) mechanism with -OH containing compounds as initiators and protic acids as catalysts is especially suitable for the synthesis of medium molecular weight functional PLA's [14–16].

This process, discussed in several reviews, proceeds according to Scheme A:



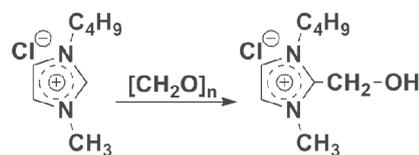
Scheme A

thus if X- is functional group, this group is introduced as a head-group to polymer while polymer molecular weight is controlled by [monomer]/[-OH] ratio [10, 17–18].

Among different factors that affect PLA stereocomplexation the nature of end-groups is generally not considered. It is justified because in high molecular weight polymers the effect of end-groups may be neglected. Situation may be, however, different for stereocomplexation of medium molecular weight PLA's, when contribution of end-groups is not insignificant.

Indeed, in a recently published papers we have shown that the nature of end-groups may have profound effect on morphology of precipitated stereocomplex particles [15, 16, 19].

In the course of our earlier works concerning application of ionic liquids (IL) in polymer chemistry, we developed convenient way of fitting typical ionic liquid: 1-butyl-3-methyl imidazolium tetrafluoroborate (bmimBF₄) with -CH₂OH group in 2-position of imidazolium ring by simple reaction of bmimCl with paraformaldehyde, according to Scheme B [20].



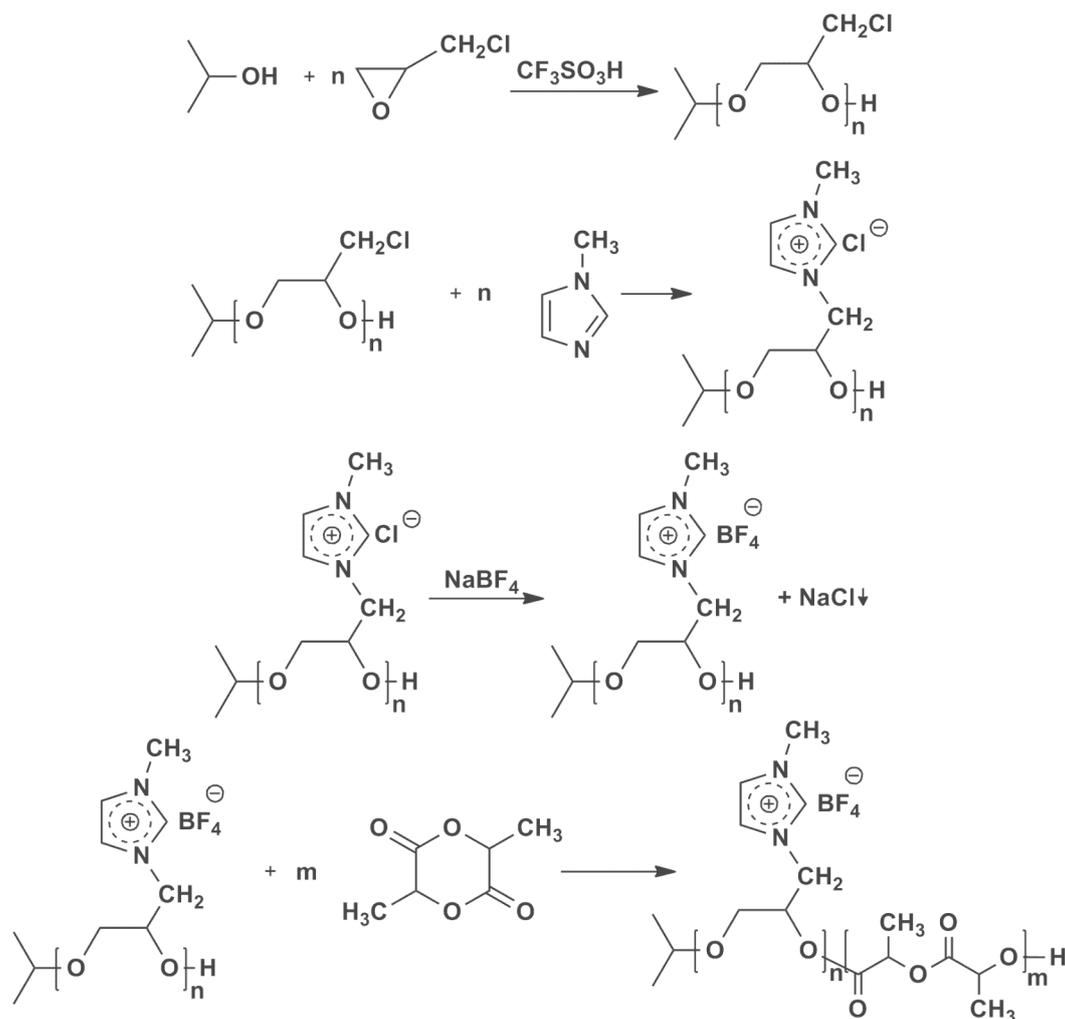
Scheme B

The product (abbreviated as bmim-OH), after replacing Cl⁻ anion with BF₄⁻ anion, may be used as initiator for cationic AM polymerization of LA leading to PLA with M_n controlled in the range between few hundreds to few thousands fitted with IL derived head-group [14].

The IL derived functional group will be further in the text designated as ionic liquid (IL) group although polymers containing this group are no longer liquid. Groups derived from imidazolium ionic liquids are not simple ionic groups interacting only through electrostatic (thus not directional) interaction but due to directional interaction resulting from hydrogen bonding show higher order of self-organization. Thus it is common in the literature to use expression “polymeric ionic liquids” to distinguish it from simple ionic polymers.

When 1,4-dioxane solutions of medium molecular weight (M_n ~ 2500) PLLA and PDLA with IL head-groups were mixed in 1 : 1 molar ratio spontaneous precipitation of stereocomplex occurred. Scanning electron microscopy (SEM) analysis revealed that stereocomplex spontaneously precipitated in a form of uniform (diameter ~ 2.5 μm), perfectly spherical particles (microspheres). This was in marked contrast to morphology of stereocomplexes precipitated in identical conditions from mixtures of PLLA and PDLA of the same molecular weight but fitted with another kind of end-groups (*e.g.*, HO-, C₄H₉O- or CF₃- groups) which precipitated in form of particles with no definite shape or size [15].

Although the exact mechanism of spontaneous formation of nearly ideal microspheres from mixture of PLLA-IL with PDLA-IL is not clear, there are indications



Scheme C

that preorganization of macromolecules resulting from interaction between IL end-groups is a prerequisite for a formation of regular microspheres on macro scale.

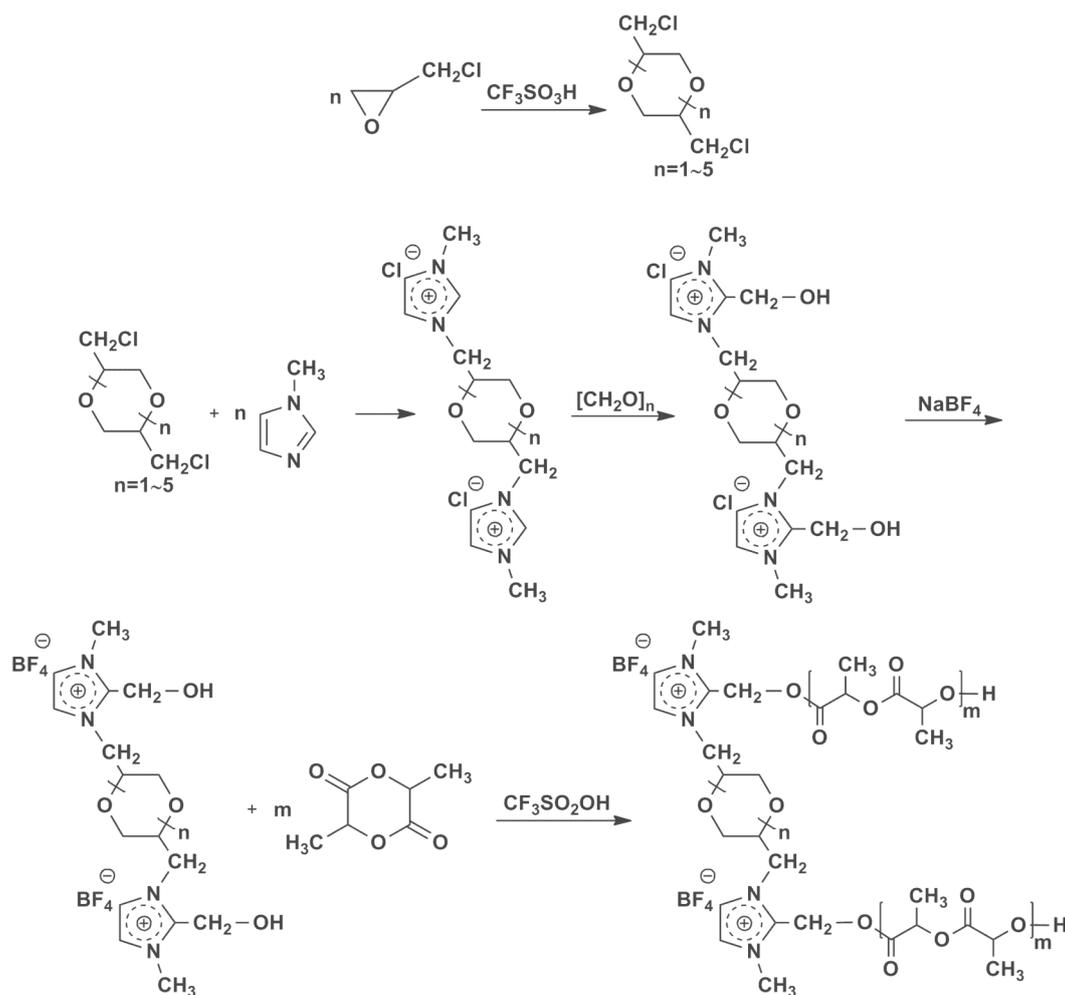
This observation prompted us to study whether enhancing interaction between IL end-groups would affect the morphology of precipitated stereocomplex particles. Such enhancement could be achieved by placing more than one IL group at the end of PLA macromolecule. To introduce a few IL groups as head-groups in PLA macromolecules we chose the approach based on preparation of macroinitiator starting from oligomer containing epichlorohydrin (ECH) units followed by reaction of $-\text{CH}_2\text{Cl}$ groups in ECH units with N -methylimidazole, thus converting each ECH unit into unit containing IL group. This approach is outlined in Scheme C.

Depending on conditions polymerization of ECH may lead either to linear oligomers or predominantly cyclic oligomers [21].

Linear oligomers are formed if cationic polymerization is conducted in the presence of alcohols or diols, *i.e.*, by AM mechanism (as shown in Scheme C). Polymerization degree may be regulated by adjusting $[\text{ECH}]/[\text{ROH}]$ ratio. On the other hand, if polymerization is conduct-

ed in the absence of HO- containing compounds, it proceeds by Active Chain End (ACE) mechanism and due to extensive back-biting it leads predominantly to cyclic oligomers. Reaction of $-\text{CH}_2\text{Cl}$ groups of cyclic oligomers with N -methylimidazole leads to cyclic structure decorated with a few ionic liquid groups which may be fitted with $-\text{CH}_2\text{OH}$ groups by reaction with formaldehyde as shown in Scheme D.

Both approaches were employed to synthesize linear or cyclic macroinitiators containing HO- group(s) and a few IL groups. These macroinitiators were used to initiate cationic polymerization of both L- and D-lactide, respectively, and stereocomplexation of resulting polymers was performed. Morphology of spontaneously precipitating particles formed from stereocomplexes composed of PLLA and PDLA containing several IL groups (either at the chain end of linear macromolecules or at the core of star macromolecules) was studied in order to compare it with morphology of stereocomplex particles composed of PLLA and PDLA containing single IL group at the chain end described earlier [15, 16] and to determine whether increasing of a number of IL groups favors self-organization leading to well defined morphology.



Scheme D

EXPERIMENTAL PART

Materials

Epichlorohydrin (Sigma Aldrich) was dried with calcium hydride and distilled collecting fraction boiling at 116–118 °C. *N*-methylimidazole (Aldrich) was purified by distillation under reduced pressure. L-lactide and D-lactide (both from Purac) were crystallized first from 2-propanol and then from toluene and purified before use by sublimation. Paraformaldehyde (Aldrich) was used as supplied.

Trifluoromethanesulfonic acid (Aldrich) was distilled under reduced pressure, $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (Aldrich) was distilled (b.p. 126–128 °C), NaBF_4 (Aldrich) was used as supplied.

Methylene dichloride (Stanlab), dichloroethane (Chempur), 1,4-dioxane (Chempur) were dried with CaH_2 (Aldrich, used as supplied) and distilled, butanol (Aldrich) and isopropanol (Eurochem) were distilled.

Synthesis of linear oligomers of epichlorohydrin

To a mixture of 11.23 g (0.121 mol) of epichlorohydrin and 2.42 g of isopropanol (0.04 mol) (attempted $DP_n \sim 3$) 2 drops of $\text{BF}_3 \cdot \text{Et}_2\text{O}$ were added (after addition of cata-

lyst temperature of reaction mixture raised spontaneously to ~ 60 °C and then the mixture cooled to room temperature). Reaction mixture was kept for 24 h. After this time ~ 1 g of CaO was added to neutralize the catalyst and resulting suspension was filtered to remove CaO. The viscous liquid was distilled in vacuum (40 Pa). Fractions boiling up to 120 °C [composed of unimer and dimer as determined by ^1H NMR on the basis of integration of $(\text{CH}_3)_2\text{CH}$ - end-group signal and signals of ECH unit] were discarded and residue was analyzed. ^1H NMR analysis indicated that it contained on the average 4.0 ECH units. This fraction was used for functionalization with *N*-methylimidazole.

Reaction of linear oligomer of epichlorohydrin with *N*-methylimidazole

0.70 g (0.00163 mol) of ECH oligomer was dispersed in 2 cm³ of water and with stirring 1.62 g (0.0197 mol) of methylimidazole was added. The aqueous suspension was heated to 100 °C and kept under reflux for 48 h. The aqueous phase was washed three times with 2 cm³ of ethyl acetate to remove unreacted excess of *N*-methylimidazole and water was evaporated.

Anion exchange

Because Cl⁻ counterion may interfere with cationic polymerization, anion exchange was performed prior to applying the macroinitiator for polymerization of lactide. 0.79 g of macroinitiator was dispersed in 3 cm³ of acetone and 0.807 g of NaBF₄ was added. The mixture was heated to 50 °C and kept at this temperature with stirring for 24 h. During this time NaCl precipitated as white crystals. Clear solution was separated by decantation from solid precipitate and acetone was evaporated. Remaining NaCl was still precipitating from viscous liquid and was removed by filtration.

Polymerization of lactide with linear macroinitiator

0.493 g (0.000513 mol) of macroinitiator with BF₄⁻ anion and 1.52 g of L-lactide (0.0105 mol) were dissolved in 5 cm³ of CH₂Cl₂ under vacuum and an ampoule containing 0.105 g of triflic acid (0.0007 mol) was broken. Solution was stirred at room temperature for 48 h. The sample was then taken for ¹H NMR analysis and LA conversion was determined as >95%. 0.5 g of CaO was added at this stage to neutralize acid catalyst and, after filtration, solvent was evaporated. 1.80 g of PLLA was obtained (some product was lost during filtration).

Polymerization of D-lactide was conducted in the same way.

Synthesis of cyclic oligomers of epichlorohydrin

33.0 g of epichlorohydrin was dissolved in 15 cm³ of 1,2-dichloroethane. Separately solution of 1.3 g of BF₃ · Et₂O was dissolved in 12.6 cm³ of 1,2-dichloroethane. Solution of ECH was placed in a flask equipped with magnetic stirrer, cooled to 0 °C and solution of BF₃ · Et₂O was added dropwise over 3 h. The solution of reaction product was then washed with 50 cm³ of 5 mol % NaOH aqueous solution and finally with distilled water until pH = 7. Solvent was then removed using rotary evaporator. Products were analyzed by NMR, GPC, and MALDI TOF. MALDI TOF analysis with lithium salt as cationizing agent indicated that main components of the mixture were cyclic tetramer (observed at *m/z* = 376.9, calculated 4 · 92.5 + 7 = 377) and pentamer (observed at 468.9, calculated 5 · 92.5 + 7 = 469.5). GLC analysis indicated also the presence of cyclic dimer.

Crude product was distilled in high vacuum using Büchi Glas Oven B-585 Kugelrohr apparatus. Three fractions were collected boiling, respectively, up to 165 °C (fraction 1), between 165 °C and 190 °C (fraction 2) and between 190 °C and 205 °C (fraction 3) all at 66.7 Pa. Fraction 1 was a mixture of cyclic tetramer and cyclic pentamer, fraction 2 was almost pure pentamer, fraction 3 was highly colored and was not analyzed. Fraction 2 was used for further reaction.

Reaction of cyclic pentamer of epichlorohydrin with *N*-methylimidazole

6.12 g (0.0132 mol) of cyclic oligomer of epichlorohydrin was mixed with 6.07 g (0.074 mol) of *N*-methylimid-

azole and 9.73 cm³ of water. Reaction mixture was heated to boiling and kept at this temperature under reflux for 10 days. After cooling to room temperature additional 3 cm³ of water was added and resulting aqueous solution was washed 6 times with 5 cm³ of ethyl acetate to remove unreacted excess of *N*-methylimidazole. Product obtained after solvent evaporation using rotary evaporator was analyzed. ¹H NMR analysis indicated that >95% of -CH₂Cl groups were converted into -CH₂-imidazolium groups. Product was a viscous liquid.

Reaction of pentameric cyclic ionic liquid with formaldehyde in order to introduce -CH₂OH group in 2-position of imidazolium ring

5.457 g (0.0392 mol) of pentameric cyclic ionic liquid (PCIL) was mixed with 1.35 g (0.045 mol) of paraformaldehyde and the mixture was heated in closed reaction vessel to 100 °C with stirring for 48 h. The vessel was then connected to vacuum line and an excess of paraformaldehyde was removed (in form of formaldehyde) by prolonged heating to 80 °C in vacuum. By ¹H NMR analysis the degree of substitution with -CH₂OH (PCIL-OH) was determined as >95%. Exchange of anions (Cl⁻ to BF₄⁻) was performed as described for linear oligomer.

Polymerization of lactide with cyclic macroinitiator (PCIL-OH)

0.373 g of cyclic macroinitiator (0.00033 mol) and 3.91 g of L-lactide (0.0273 mol) were mixed in 15 cm³ of CH₂Cl₂ under vacuum. Cyclic macroinitiator was not dissolved thus the mixture was kept for 24 h at room temperature to dissolve it. Part of macroinitiator was still not dissolved. Nevertheless an ampoule containing 0.16 g of triflic acid (0.00105 mol) was broken and the solution was stirred at room temperature for 96 h. The mixture was inhomogeneous. 0.5 g of CaO was added at this stage to neutralize acid catalyst and, after filtration, solvent was evaporated. 2.82 g of PLLA was recovered corresponding to ~66% yield. SEC analysis showed relatively broad molecular weight distribution. *M_n* value determined by polystyrene calibration (*M_n* ~ 6000 considering correction factor) differed considerably from absolute molecular weight determined by MALS (*M_n* ~ 40 000). This strongly indicates non-linear structure of the product.

Methods of testing

The number average molar masses *M_n* of polymers were determined by size exclusion chromatography (SEC) using two different equipment.

First: Agilent Pump 1100 Series (preceded by an Agilent G1379A Degaser), equipped with a set of two PLGel 5μ MIXED-C columns. Wyatt Optilab Rex differential refractometer and a DawnEOS (Wyatt Technology Corporation) laser photometer were used as detectors. Dichloro-

methane was used as eluent at a flow rate of 0.8 cm³/min at room temperature.

Second: Knauer K-501 HPLC pump, LDC RI detector and Malvern 270 Dual detector (Light scattering RALS+LALS; Dilute Solution Viscometry), equipped with a set of two PLGel 5 μ MIXED-C columns.

¹H NMR spectra were recorded in CDCl₃ using a Bruker Avance III 500 spectrometer operating at 500 MHz. Traces of the nondeuterated chloroform were used as an internal standard.

Scanning electron microscopy (SEM) images were obtained with a Nova Nano SEM 230 instrument (FEI company) equipped with SE Detector at HV L 15 kV and low vacuum (40 Pa) with high resolution in lens detector Helix (resolution approximately 2 nm). The electron micrographs were recorded with a resolution of 1024 x 768 pixels. The samples were prepared by fixing onto carbon adhesive tape and covering with a conductive gold layer, and studied in low vacuum.

RESULTS AND DISCUSSION

Synthesis and stereocomplexation of linear polylactide containing a few ionic liquid group at the chain end

Polymerization of ECH in the presence of isopropyl alcohol led to oligomers containing terminal HO- group. Polymerization was conducted at [ECH]/[ROH] = 3.3 with BF₃ · Et₂O as catalyst with slow feeding of ECH as described in Experimental and followed by quantitative conversion of -CH₂Cl groups into -CH₂-imidazolium groups and anion exchange. Linear macroinitiator com-

posed of 4 (on the average) units and containing terminal HO- group was used to initiate polymerization of L- and D-lactide. Polymerization, as described in Experimental, proceeded with practically complete conversion. Polymers with M_n = 2300 (polystyrene calibration) and 1800, respectively, were obtained.

Stereocomplexation was performed by mixing 5 wt % solutions of poly-L-lactide and poly-D-lactide at room temperature without stirring. After few hours stereocomplex started to precipitate. The mixture was kept for 24 h and solid precipitate was separated by decantation and dried. The amount of stereocomplex recovered corresponded to ~ 90 wt % of the sum of both components used for stereocomplex formation.

The morphology of spontaneously precipitating stereocomplex was studied by scanning electron microscopy (SEM). Typical SEM images are shown in Fig. 1.

Stereocomplex precipitates in form of spherical particles with diameter ~ 1 μ m. The microspheres are less regular in size but significantly smaller as compared to previously described microspheres from stereocomplex of PLA containing only one IL group as head-group (diameter ~ 2.5 μ m) [15]. Thus, it may be concluded that introduction of more than one IL group at one chain end of PLA chain does not have beneficial effect on the tendency for self-organization during formation of stereocomplex as compared to PLA's containing only one such group.

Synthesis of star polylactide containing a few ionic liquid groups at the core

Cationic polymerization of epichlorohydrin was performed in the absence of HO- containing compound as described in Experimental at conditions when mainly cyclic oligomers are formed. The mixture of cyclic oligomers was formed. The crude reaction product was separated into individual oligomers, reacted with *N*-methylimidazole and functionalized with -CH₂OH group as described in Experimental and shown in Scheme D. The resulting cyclic macroinitiator was used for polymerization of L-lactide with trifluoromethanesulfonic acid as initiator. Two independent SEC analysis using refractive index (RI) and MALS detectors and separately Tri-SEC detection (RI, RALS, Viscometer) strongly indicated that the product has indeed compact structure as expected for star polymer. Thus, M_n value calculated on the basis of RI detection with polystyrene calibration was equal to $7.8 \cdot 10^3$ while real M_n was considerably higher ($4.15 \cdot 10^4$ by MALS, $3.1 \cdot 10^4$ by Tri-SEC).

It has been shown previously, that if one component of stereocomplex is a star PLA and the other is a linear polymer (with length comparable to a length of one arm) the tendency for self-organization is enhanced and regular microspheres are further aligned to structures resembling colloidal crystals [16].

Thus, we used star polymer of L-lactide containing a few IL groups at the core and HO- groups as end-groups

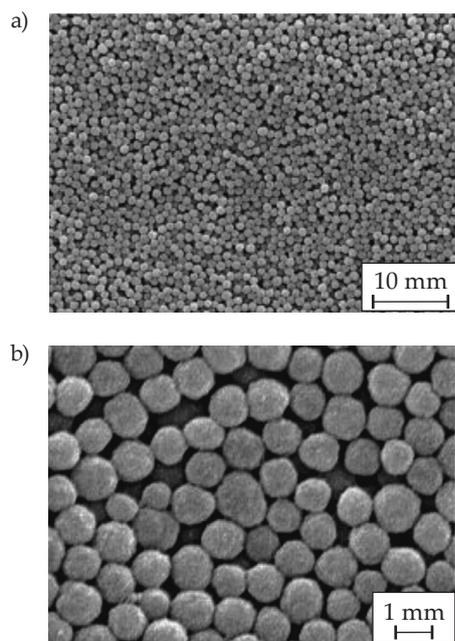


Fig. 1. SEM images of particles of stereocomplex between PLLA and PDLA containing a few ionic liquid head-groups: a) magnification 2000x, b) magnification 10000x

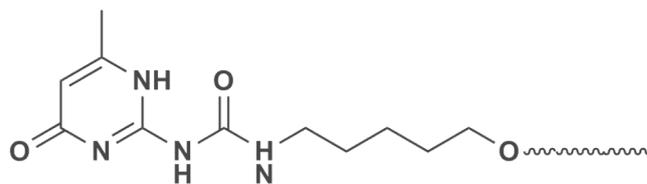
for stereocomplexation with linear poly-D-lactide containing BuO- head-group and HO- end-group. Stereocomplexation was performed by mixing 5 wt % solutions of components in 1,4-dioxane as in the case of linear PLA's, but it took much longer, stereocomplex started to precipitate after ~ 48 h therefore the mixture was kept for 7 · 24 h to complete the process. Precipitated stereocomplexes were isolated by decantation and dried. SEM analysis of star PLLA and BuO-PDLA stereocomplexes showed no specific morphology with only a few irregular particles as shown in Fig. 2a.

This indicate that IL groups present in the core of star macromolecules do not promote self-organization leading to specific particles morphology.

Self-organization of stereocomplex leading to perfectly spherical morphology was observed earlier for stereocomplexes of linear PLA's of moderate molecular weight containing ionic liquid (IL) end-groups. In linear macromolecules IL end-groups can move freely which enables their aggregation leading to self-organization of macromolecules. In star macromolecules containing IL groups in the core, apparently this mobility and accessibility of IL groups is restricted.

To check this hypothesis, BuO- end-groups of linear counterpart were replaced with groups able to interact with each other. Linear PDLA with IL head-groups was prepared as described earlier [15]. Stereocomplexation of this product with star PLLA containing a few IL groups in the core led to particles showing granular but not regular morphology as shown in Fig. 2b. When still stronger interacting head-groups, *i.e.*, ureidopyrimidine (UPy) groups (see Scheme E) (sample of PDLA-UPy prepared according to method described earlier [19] was generously provided by dr. Brzeziński) were introduced to linear counterpart of stereocomplex with star PLA, stereocomplex micro-particles precipitated in form of relatively large (~ 5 μm) but not very regular spherical particles.

These results indicate that IL groups present at the core of star polymer do not promote spontaneous self-organization of the stereocomplex with polymer of opposite configuration which contain end-groups such as BuO- and -OH. IL groups, which were shown to promote such self-organization when present as head-groups in linear



Scheme E

PLA, do not show such effect when present at the core of star polymer, probably because they are embedded by arms of star polymers and thus are not able to interact one with other. Only when BuO- head-group in linear component is replaced by groups able to interact one with other the tendency for self-organization appear. This tendency is still weak when end-group is IL group but is enhanced with more strongly interacting UPy groups. Thus tendency for self-organization is related to interaction groups in linear component and not to IL groups in star polymer.

CONCLUSIONS

The presence of a few ionic liquid groups at the chain end of linear medium molecular weight polylactide did not lead to significant changes of morphology of spontaneously precipitating stereocomplex as compared to described earlier stereocomplexation of polylactide fitted with one ionic liquid group at the chain end. Stereocomplex precipitated in form of microspheres similar to that described earlier, although smaller and less regular. Thus, intuitive prediction that introducing more than one ionic liquid group at the chain end would enhance preorganization of macromolecules did not prove true. One of the possible explanation is that when a few ionic liquid groups are located in close proximity, interactions between them (electrostatic, hydrophobic, hydrogen bonding) are mainly intramolecular and this reduces the possibility for enhanced intermolecular interactions.

Synthesis of star polymers of lactide using cyclic macro-initiator led to star polymer with a few ionic liquid groups at the core. Although cationic polymerization of lactide initiated by bmim-OH proceeded to high conversion and poly-

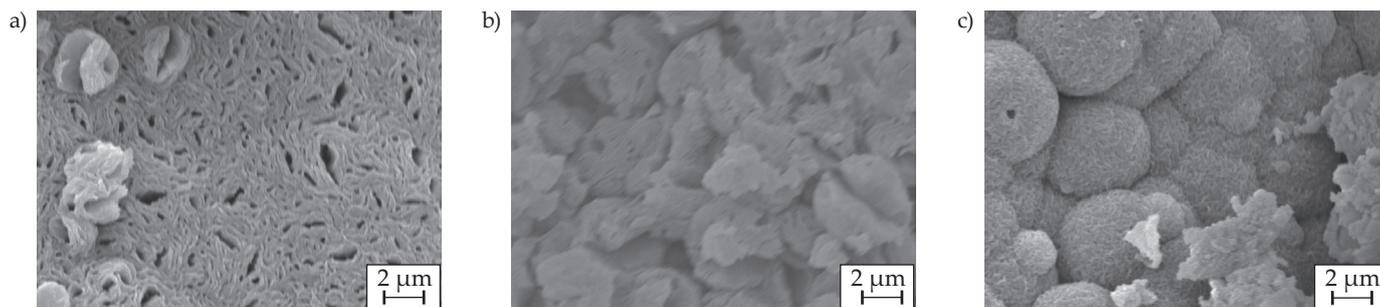


Fig. 2. SEM images of stereocomplex of star PLLA containing a few IL groups at the core with linear PDLA containing: a) BuO-groups, b) IL groups, c) UPy groups (magnification 6000x)

mers with expected degree of polymerization were formed, if several similar groups are connected to cyclic structure, polymerization proceeds slowly and full conversion could not be reached within reasonable time. Polymerization was poorly controlled, molecular weight was considerably higher than expected on the basis of [monomer]/[initiator] ratio. One of the reasons may be limited solubility of macroinitiator in reaction medium. Nevertheless, application of this cyclic functionalized ionic liquid as initiator of cationic polymerization of lactide led to star PLLA containing a few ionic liquid groups at the core. Application of such star PLA as the component of stereocomplex with linear PLA containing BuO- and -OH end-groups did not lead to any specific morphology. Only when linear PLA was fitted with head-groups able to interact (IL, UPy groups), self-organization could be observed and in the case of strongly interacting UPy groups stereocomplex precipitated in form of spherical particles (although rather irregular). Thus the presence of UPy groups in linear PLA rather than the presence of IL groups at the core of star polymer seems to be responsible for self-organization to specific morphology.

Synthesized cyclic macroinitiator was used as initiator of the cationic polymerization of lactide but it may be interesting by itself. The ring is composed of sequence of -C-C-O- units, the same as in crown-ethers (although there is substituent at one carbon atom). Crown-ethers are known to strongly bind certain cations, forming complexes [22]. Synthesized cyclic ionic liquids (CIL), not reported till now in the literature, with skeleton resembling crown-ether structure are decorated with several imidazolium ionic liquid moieties.

Combination of crown-ether like cyclic structure and imidazolium ionic liquid groups at the periphery of the cyclic structure may thus offer interesting perspective for extraction of metal ions.

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