Macromol. Symp. **2005**, *224*, 71-83

Thermodynamic and Kinetic Polymerizability of Cyclic Esters

Andrzej Duda, Adam Kowalski, Jan Libiszowski, Stanisław Penczek**

Department of Polymer Chemistry, Center of Molecular and Macromolecular Studies, Polish Academy of Sciences, Sienkiewicza 112, 90-363 Lodz, Poland
Fax: (+48) 42 684 7126; E-mail: anduda@bilbo.cbmm.lodz.pl;
spenczek@bilbo.cbmm.lodz.pl

Summary: Recent advances in the controlled ring-opening polymerization (ROP) of cyclic aliphatic esters are reviewed with a particular attention to thermodynamics and kinetics of the polymerization of industrially important monomers, namely: lactide (LA), 1,4-dioxan-2-one (DX), and ε-caprolactone (CL). For comparison, polymerization of β-lactones is discussed. Progress in stereocontrolled polymerization of monomers bearing centers of chirality [LA and β-butyrolactone (BL)] is also briefly reviewed.

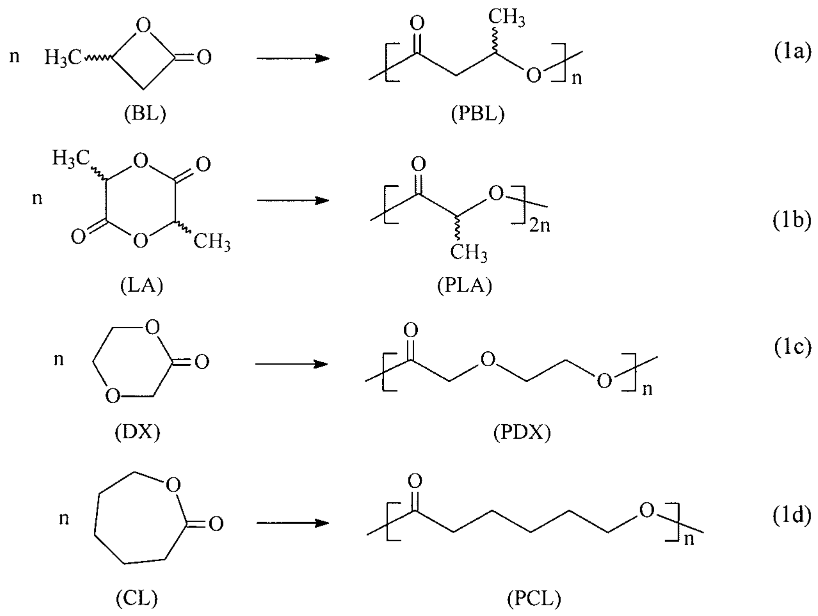
Keywords: covalent (pseudoanionic) polymerization; cyclic aliphatic esters; kinetics (polym.); ring-opening polymerization; stereocontrolled polymerization; thermodynamics (polym.)

Introduction

Poly(aliphatic ester)s (PAE) have recently become an important class of polymers as both specialty biomedical materials and large-scale production commodity thermoplastics. These applications are mainly related to their biocompatibility and ability to "spontaneously" degrade in the natural environment, after the required time of exploitation, combined with useful mechanical and thermal properties. There are two large classes of PAE being extensively developed: bacterial poly(β-hydroxyalkanoate)s and the polymers prepared by a ring-opening polymerization (ROP) of cyclic aliphatic esters. Moreover, polymerization of these monomers provides convenient model systems for studying mechanisms of ROP initiated with classical chemical initiators and more recently by enzymes.[1]

In the present contribution, the recent progress in the controlled ROP of cyclic aliphatic esters is reviewed with a particular attention to thermodynamics and kinetics of β-butyrolactone (BL), lactide (LA), 1,4-dioxan-2-one (DX), and ε-caprolactone (CL) polymerization (Scheme I).

DOI: 10.1002/masy.200550607



Scheme I.

Polymerization is possible only when a free enthalpy of this process (ΔG_p) is negative (Equation 2).[2,3]

$$\Delta G_p = \Delta H_p - T\Delta S_p \qquad (2)$$

Table 1. Thermodynamic parameters of cyclic esters polymerization (at 100 °C).

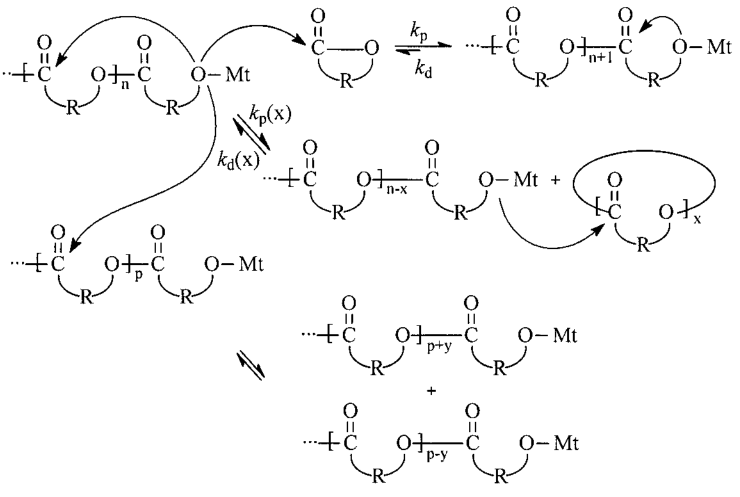
Monomer	Ring size	Monomer Polymer States[a)]	ΔH_p kJ/mol	ΔS_p^0 J/mol K	$[M]_{eq}$ mol/L	$[\Sigma xM(x)]_{eq}$ mol/L
PL[11]	4	ll	-74.4	-51	2.45×10^{-7} b)	≈0 c)
LA[12]	6	ss	-22.9	-41	0.09 c)	≈0 c)
DX[13]	6	ll	-13.8	-45	2.5 c)	0.95 c)
CL[14]	7	ll	-13.9	-10.4	0.37 b) (≈0) c)	0.25 d)

[a)] l – liquid, s-solution
[b)] calculated from equation 4
[c)] observed experimentally
[d)] estimated from data in ref.[15]

Polymerization of the four-, six-, and seven-membered cyclic esters is accompanied by an entropy decrease ($\Delta S_p < 0$) and therefore the only driving force of the monomer-polymer conversion is the negative enthalpy of polymerization (ΔH_p) mostly related to the release of the monomer ring strain (Table 1).

Moreover, the applied initiating/catalytic system should give reasonable polymerization times [i.e., rate constants of propagation (k_p) should be high enough] and allow controlling of the polymer chain growth with regard to its molar masses (M_n), molar masses distribution (M_w/M_n) and end-groups structure. This goal can be achieved only when the termination and transfer side reactions are eliminated or at least considerably depressed. In the ROP of aliphatic cyclic esters the best control was observed for the covalent metal [e.g.: Sn(II), Zn, Al, La, Y, Sn(IV), Ti] alkoxides as initiators; [4] when carboxylates are used, then a coinitiator is needed giving, eventually, the alkoxide structure.[5,6]

Since the resulting polyester repeating units contain an ester group, in the general scheme of cyclic esters polymerization, apart from propagation (3a), intra- (3b) and inter-molecular (3c) transesterification have also to be taken into account.



(3a)

(3b)

(3c)

The extent of these side reactions conforms to the Reactivity-Selectivity Principle. Thus, for the initiators providing less reactive active species (e.g., covalent versus ionic ones) bearing additionally bulky substituents at the metal atom, transesterification can be almost eliminated. Therefore at the kinetic control conditions the covalent metal based initiators lead to polyesters devoid of macrocyclics and having narrow molar masses distribution (see the corresponding review papers[4,7-9]).

Thermodynamics of Cyclic Esters ROP

Monomer equilibrium concentration. Cyclic esters of various ring sizes, including β-propiolactone (PL), LA, DX, and CL, are able to provide high molar mass polymers. For example, in LA polymerization initiated by $Sn(OBu)_2$ PLA with M_n approaching 10^6 has been prepared in a controlled manner.[10] However, the six- and seven-membered cyclic monomers exhibit only moderate ring strain. This leads to the relatively high equilibrium monomer concentration ($[M]_{eq}$), resulting from the pronounced reversibility of propagation ($k_p[M] \approx k_d$). $[M]_{eq}$ and the thermodynamic parameters of polymerization are interrelated, according to Dainton and Ivin's equation:[2]

$$\ln[M]_{eq} = \Delta H_p / RT - \Delta S_p^0 / R \tag{4}$$

Thus, in the case of $\Delta H_p < 0$ and $\Delta S_p^0 < 0$, the less strained the monomer (i.e., the less negative is ΔH_p) and the higher the polymerization temperature, the higher the $[M]_{eq}$ is.

Indeed, results of the measurements by means of size exclusion chromatography (SEC) of the position of the monomer-polymer equilibria, carried out directly in the reacting mixtures, revealed high $[LA]_{eq}$ and $[DX]_{eq}$, particularly at elevated temperatures (Table 1).[12,13]

Since polymerizations of LA and DX are conducted often in the monomer/polymer melt, relatively high temperatures are required. It is therefore important to find conditions to force these monomers, being in a relatively high equilibrium concentration, to enter into the polymer chains. If lowering of the polymerization temperature cannot be applied, copolymerization looks to be the only way to achieve this goal. Indeed, polymer crystallization at a lower temperature would decrease the amount of monomer at equilibrium,[16] but remelting of the system at a higher temperature would restate the previous conditions of equilibrium. When copolymerization is applied, the repeating units, derived from a comonomer, will appear at the polymer chain-end, altering the final polymer properties in a certain way. Thus, the comonomer structure has to be chosen in a way to keep the deterioration of the properties to as little as possible.

For the latter purpose copolymerization of L,L-lactide (LA) with CL, after the homopolymerization system: living poly(L,L-lactide)/L,L-lactide reached equilibrium, has been recently applied.[17] The copolymerization was initiated by living PLA, bearing at its growing chain-end aluminum alkoxide species decorated with a bulky ligand - Schiff's base derivative, (*S*)-(+)-2,2'-[1,1'-binaphtyl-2,2'-diylbis(nitrylomethilidyne)]-diphenolate, in order to at least decrease the extent of transesterification. At these conditions LA was completely converted into the polymer repeating units. A block copolymer resulted with the first block composed of PLA and the second block of LA/CL copolymer.

Analysis of the pertinent kinetic scheme:

$$\text{...-la* + LA} \underset{k_{\mathrm{lala}}}{\overset{k_{\mathrm{laLA}}}{\rightleftharpoons}} \text{...-la-la*} \qquad (k_{\mathrm{laLA}}\,[\text{...-la*}][\mathrm{LA}] \ll k_{\mathrm{lala}}\,[\text{...-la-la*}]) \tag{5a}$$

$$\text{...-la* + CL} \underset{k_{\mathrm{lacl}}}{\overset{k_{\mathrm{laCL}}}{\rightleftharpoons}} \text{...-la-cl*} \qquad (k_{\mathrm{laCL}}\,[\text{...-la*}][\mathrm{CL}] > k_{\mathrm{lacl}}\,[\text{...-la-cl*}]) \tag{5b}$$

$$\text{...-cl* + LA} \underset{k_{\mathrm{clla}}}{\overset{k_{\mathrm{clLA}}}{\rightleftharpoons}} \text{...-cl-la*} \qquad (k_{\mathrm{clLA}}\,[\text{...-cl*}][\mathrm{LA}] > k_{\mathrm{clla}}\,[\text{...-cl-la*}]) \tag{5c}$$

$$\text{...-cl* + CL} \underset{k_{\mathrm{clcl}}}{\overset{k_{\mathrm{clCL}}}{\rightleftharpoons}} \text{...-cl-cl*} \qquad (k_{\mathrm{clCL}}\,[\text{...-cl*}][\mathrm{CL}] \gg k_{\mathrm{clcl}}\,[\text{...-cl-cl*}]) \tag{5d}$$

led eventually to Equation 6 relating $[\mathrm{LA}]_{\mathrm{eq}}$ in homo- and copolymerization.

$$([\mathrm{LA}]_{\mathrm{eq}})_{\mathrm{co}} = \frac{1}{1+\dfrac{[\ldots-\mathrm{cl}-\mathrm{la}^*]_{\mathrm{eq}}}{[\ldots-\mathrm{la}-\mathrm{la}^*]_{\mathrm{eq}}}} \times ([\mathrm{LA}]_{\mathrm{eq}})_{\mathrm{homo}} \tag{6}$$

Equation 6 shows that, with the exception of [...-cl-la*] = 0, the equilibrium concentration of LA in copolymerization $[([\mathrm{LA}]_{\mathrm{eq}})_{\mathrm{co}}]$ would always be lower than that in homopolymerization $[([\mathrm{LA}]_{\mathrm{eq}})_{\mathrm{homo}}]$. Thus, the research should be directed towards comonomers giving as high as possible ratios of active centers resulting from cross- and homopropagations: [...-cl-la*]/[...-la-la*] and $k_{\mathrm{laCL}} < k_{\mathrm{clLA}}$.

For highly strained four-membered lactones such as PL or BL, which are expected to polymerize almost completely, $[\mathrm{M}]_{\mathrm{eq}}$ cannot be determined by a direct analysis of the reacting mixtures. However, it is possible to calculate $[\mathrm{M}]_{\mathrm{eq}}$ by employing ΔH_{p} and $\Delta S_{\mathrm{p}}^{0}$ determined by means of thermochemical measurements (see, e.g., $[\mathrm{M}]_{\mathrm{eq}}$ for PL and CL in Table 1). It has to be stressed, however, that the calculated values have to be taken with reserve, as shown by the example of CL. Thermochemical data give the value of 0.37

mol/L at 100 °C, whereas according to our experience $[CL]_{eq}$ is close to 0 under these conditions.

Cyclic oligomers equilibrium concentration. Themodynamically equilibrated polymerizing mixtures of some cyclic esters reveal the presence of the undesired macrocyclic side products, formed via intramolecular transesterification (equation 3b). This phenomenon is particularly pronounced in DX and CL polymerization (cf. $\Sigma x[M(x)]_{eq}$ values in Table 1) whereas for BL, PL, and LA, formation of cyclic oligomers was reported only rarely (see e.g. ref.[18]). A series of various ring sizes is formed and, as it was shown for CL polymerization, these cyclic oligomers are usually strainless[15,19] and therefore their equilibrium concentration can be predicted by the Jacobson-Stockmayer theory:[20]

$$[M(x)]_{eq} = Ax^{-5/2} \tag{7}$$

where x is the number of repeating units and A is a constant characteristic for a given polymer chain.

According to detailed kinetic and thermodynamic studies, a total equilibrium concentration of the CL macrocyclics (in terms of concentration of the PCL repeating units) is equal to 0.25 mol/L and is approximately independent on the polymerization temperature.[15,19]

Cyclic oligomers are usually considered as undesirable contamination of the high polymer, and the polymerization control with regard to molar masses and end groups may be lost this way. Therefore, polymerization methods were elaborated, at least for CL, allowing elimination of the back-biting by a kinetic control,[7,8] as has been already mentioned in the Introduction.

Formation of cyclic oligomers in DX polymerization have been detected only recently by means of a combination of SEC and MALDI TOF mass spectrometry.[13] Their concentration $[\Sigma x[DX(x)]_{eq}]$ increased with increasing temperature and monomer concentration in the feed, and reached a maximum value equal approximately to 1 mol/L for the polymerization in bulk. On the other hand, the mass fraction (f) of cyclic oligomers, after passing a maximum (f = 40% at $[DX]_0 \approx 4.0$ mol L^{-1}, 100 °C), decreased with increasing $[DX]_0$ and eventually for bulk polymerization $f < 10\%$ ($f = 8\%$ at 80 °C) was reached.

Kinetics of Cyclic Esters ROP Initiated with Covalent Alkoxides

The majority of aliphatic cyclic ester/covalent metal alkoxide systems leads to living polymerization and therefore provides almost perfect control of the overall polymerization process and serves as a valuable model system for detailed studies of the polymerization mechanism. [4,21]

Kinetic data available for anionic polymerization have already shown that thermodynamic polymerizability cannot be taken as a direct measure of monomer reactivity. A similar conclusion can be drawn for the covalent (pseudoanionic) process (Table 2).

Table 2. Rate constants of propagation in cyclic esters polymerization initiated with $Al(O^iPr)_3$.

Monomer	BL[22]	LA[23]	DX[24]	CL[23]
Ring size	4	6	6	7
Temperature / °C	80	80	80	20
Solvent	toluene	THF	bulk	THF
k_p / L/mol s	3.9×10^{-5}	4.7×10^{-3}	2.6×10^{-2}	0.5

In spite of the high ring strain, the four-membered lactones propagate much slower than the six- and seven-membered ones. The significant differences between the reactivities of alkoxides reactivities with PL, BL and with DX, LA, and CL can be attributed to stereoelectronic and steric factors, similarly to the anionic polymerization.[25] Namely, in the intermediate formed on the attack of the alkoxide species on the carbonyl carbon atom of the β-lactone molecule, the lone electron pairs on the endocyclic oxygen atom and the polar carbon-oxygen bonds are in the unfavorable synperiplanar position. In the case of the larger, folded larger rings, the lone electron pairs and the carbon-oxygen bonds are in the much more favorable gauche position.

Moreover, there are suggestions that an attack of the anion on the carbonyl carbon atom in the planar β-lactone, occurring with the initial part of the trajectory along the dipole moment of the monomer molecule (along the C=O bond), can be hindered by the hydrogen atoms and/or larger substituents. Such restrictions are much less significant in the case of puckered LA, DX, and CL molecules.

More recently, however, the kinetics of polymerization of the 6-, 7-, 9-, 12-, 13-, 16, and 17-membered lactones initiated with zinc 2-ethylhexanoate/butyl alcohol system has been studied.[26] The following relative rates have been measured: 2500, 330, 21, 0.9, 1, 0.9, 1, respectively (bulk polymerization, 100 °C). Since active species operating in the polymerization of various lactones in this systen are structurally identical, *viz.* ...-$C(O)(CH_2)_{m-1}CH_2O$-Zn-..., the order of the resulting polymerization rates is equivalent to the order of lactones reactivities. Comparison of the lactone ring sizes with the relative polymerization rates shows that the larger the lactone ring, the lower is its reactivity (reactivities of the 12-, 13-, 16-, and 17-membered lactones are practically identical, taking into account experimental error). It can be expected that in the transition state of propagation the ring strain is partially released and the resulting enthalpy of activation ($\Delta H_p^{\neq}$) is lower for strained monomers in comparison with the non-strained ones. Probably this is the main reason why the reactivity of lactones decreases with increasing their sizes and eventually reaches a constant value for larger rings.

Interestingly, the order of rates of the enzymatic polymerization shows an inverted dependence on the ring size, namely: 0.10 : 0.13 : 0.19 : 0.74 : 1.0 for the 7-, 12-, 13-, 16-, and 17-membered lactones, respectively. This kinetic behavior can be explained assuming that in enzymatic polymerization, the rate-determining step involves formation of the lactone-enzyme complex. The latter reaction is promoted by the hydrophobicity of the lactone monomer, which is higher for the larger lactone rings.

On the other hand, the rate of polymerization of a given monomer depends strongly both on the metal atom and on the number of (macro)alkoxide chains growing from this atom in the involved active centers (Table 3).

Table 3. Rate constants of propagation for L,L-LA polymerization initiated with covalent metal alkoxides.[a)][10]

Initiator	Bu_3SnOMe	$Bu_2Sn(OEt)_2$	$Sn(OBu)_2$	$Al(O^iPr)_3$	$Y(OR)_3$[27]
k_p / L/mol s	3.5×10^{-4}	1.5×10^{-2}	5×10^{-1}	4.7×10^{-3}	10[b)]

[a)] Polymerizations carried out in THF as solvent at 80°C if not otherwise indicated.

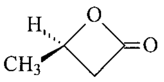
[b)] CH_2Cl_2 as solvent, 22 °C; R = 2,6-di-*tert*-butylphenoxide group, polymerization conducted in the presence of $(CH_3)_2CHOH$.

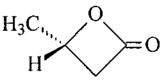
Higher reactvity of the Sn(II) compounds in comparison with their Sn(IV) counterparts may be explained by the better steric accessibility of the tin atom in the divalent derivative as well as its more pronounced ability to coordinate the approaching monomer molecule. The positive induction effect of the alkyl groups on Sn(IV) additionally decreases its reactivity towards nucleophilic agents. The large difference of the reactivities between Sn(II) dialkoxides and Al trialkoxides [10^2 times in favor of Sn(II)] comes mostly from the difference of the ionic radii of both metal atoms resulting in a stronger polarization of the tin-oxygen bond.

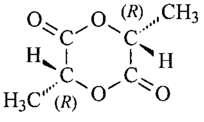
However, the highest rates of LA polymerization reported till now were found for even more polarized yttrium alkoxides. For example, polymerization initiated with a *tris*(2,6-di-*tert*-butylphenoxy)yttrium/isopropanol mixture reveals a k_p as high as 10 mol/L s at 20 °C. It would be of interest to compare this rate constant with the corresponding value for anionic polymerization, but reliable data are not yet available.

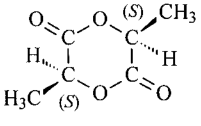
Stereocontrolled Polymerization of Cyclic Esters

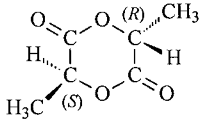
Stereoregular polyesters consisting of macromolecules bearing centers of chirality in the main chain provide highly ordered materials with unusual mechanical and thermal properties. Moreover, strong dependence of (bio)degradability on the polyesters stereostructure was observed.[1] Two of the monomers discussed in the present review bear centers of chirality, namely BL and LA (see structures below).


(*R*)-BL


(*S*)-BL

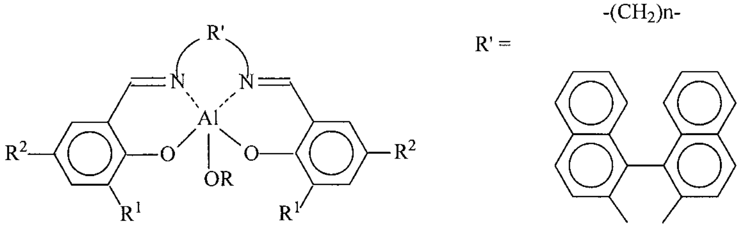

(*R*,*R*)-LA


(*S*,*S*)-LA


(*R*,*S*)-LA

In the case of BL polymerization the main problem is still related to slow polymerization with the covalent initiators, whereas anionic polymerization, although much faster, suffers from the chain transfer to monomer, disabling controlled synthesis of the high polymer.[29] Nonetheless, it has been shown that in *rac*-BL polymerization initiated with Et_3Al/H_2O mixtures, PBL containing short poly(*R*) and poly(*S*) stereoblocks is formed,[30,31] whereas initiation with some alumoxanes, stannoxanes or tin carboxylates leads to the syndiotactic PBL sequences.[32-35] Polymerization with the enantiomerically pure initiator, e.g., $(C_2H_5)_2Zn/(R)\text{-}(CH_3)_3CCH(OH)CH_2OH$, proceeded with a low stereoelection coefficient (k_{RR}/k_{RS}) not higher than 1.7.[36] Similar results were obtained with the Al-alkoxide initiators bearing chiral bidendate phenoxy Schiff’s bases.[37,38]

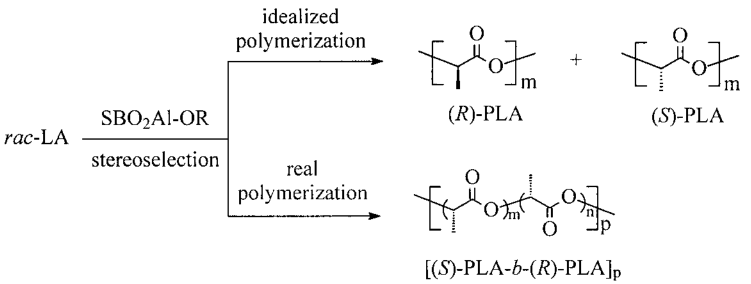
More substantial progress in the area of stereocontrolled polymerization of heterocyclic monomers has recently been achieved for LA polymerization. Stereochemical microstructure of PLA macromolecules formed in the ROP of LA can be controlled by the monomer composition in the feed [proportion of (*R*,*R*)-, (*S*,*S*)-, and (*R*,*S*)-LA stereoisomers] and/or by the stereochemical preference of the initiating/catalytic system. Moreover, the polymerization process should be devoid of racemization and intermolecular transestrification (equation 3c). Elimination of these side reactions is particularly efficient with a single-site, enatioselective and/or enantioelective covalent alkoxides bearing bulky Schiff’s base ligands of the general structure $SBO_2Al\text{-}OR$.



$SBO_2Al\text{-}OR$

(*R*) and/or (*S*)

This method originally developed by Spassky[37,39,40] was then followed by Baker,[41] Coates,[42,43] Feijen[44], Nomura,[45] and in our laboratory.[46] In polymerization of *rac*-LA mediated either with achiral [R’ = $-(CH_2)_m-$] or chiral, racemic [R’: (*R*,*S*)-(1,1’-binaphtyl-2,2’)-diyl] catalyst $SBO_2Al\text{-}OR$ the multiblock stereocopolymers [(*S*)-PLA-*b*-(*R*)-PLA]$_p$ were prepared due to a chain-end control or an enantiomorphic site control of the monomer addition, respectively (Scheme 8). Because segmental exchange via transesterification was excluded (bulky bidendate ligand around the active site), the

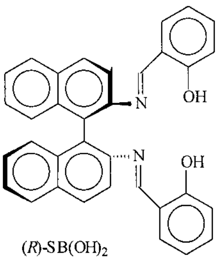


(8)

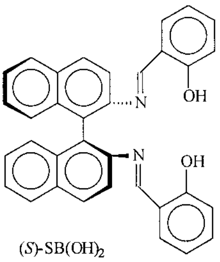
multiblock structure was attributed to the exchange of the growing chains between active centers of various configurations.[43]

The independent kinetic measurements, carried out for the (S)-SBO2Al-OiPr/(S,S)-LA and (S)-SBO2Al-OiPr/(R,R)-LA systems, exhibited a 28:1 preference for the polymerization of (S,S)-LA over (R,R)-LA (i.e., stereoelection coefficient kR(R,R)/kR(S,S) = 28).

New opportunities were provided by the $SB(OH)_2/Al(O^iPr)_3$/*rac*-LA polymerization system employing a combination of stereoelection with (*S*)- and (*R*)-ligands exchange at the Al-alkoxide active centers [see (*R*)-$SB(OH)_2$ and (*S*)-$SB(OH)_2$ structures below].[46]



(*R*)-$SB(OH)_2$



(*S*)-$SB(OH)_2$

Two step polymerization of *rac*-LA was initiated by a (*S*)-$SB(OH)_2/Al(O^iPr)_3$ system and mediated in the second step by (*R*)-$SB(OH)_2$ added to the reacting mixture. The stereoelectivity was close to that determined for the process with an additional synthetic step of isolation and purification of the $SBO_2Al\text{-}O^iPr$ alkoxide. The resultant poly(*rac*-LA) has a gradient stereocopolymer structure and exhibits enhanced thermal stability due to the stereocomplex formation with a melting temperature (T_m) equal to 210 °C. This is the highest T_m reported till now for PLA prepared directly from *rac*-LA.

Acknowledgement

This work was supported by the Polish Ministry of Science and Information Technology (grant no. K065/T09/2003 realized in the years 2003-2006).

[1] *"Biopolymers"*, Vol. 3a, *"Polyesters I. Biological Systems and Biotechnological Production"*; Vol. 3b, *"Polyesters II. Properties and Chemical Synthesis"*; Vol 4, *" Polyesters III. Application and Commercial Products"*, Y. Doi, A. Steinbuechel, Eds., Wiley-VCH, Weinheim 2002.
[2] F. S. Dainton, K. J. Ivin, *Q. Rev. Chem. Soc.* **1958**, *12*, 61.
[3] H. Sawada, *"Thermodynamics of Polymerization"*, Marcel Dekker, Inc., New York 1976.
[4] A. Duda, S. Penczek, in: *"Biopolymers"*, Vol. 3b, *"Polyesters II. Properties and Chemical Synthesis"*, Y. Doi, A. Steinbuechel, Eds., Wiley-VCH, Weinheim 2002, p.371.
[5] A. Kowalski, A. Duda, S. Penczek, *Macromolecules* **2000**, *33*, 689.
[6] A. Kowalski, A. Duda, S. Penczek, *Macromolecules* **2000**, *33*, 7359.
[7] S. Penczek, A. Duda, S. Slomkowski, *Makromol. Chem. Macromol. Symp.* **1992**, *54/55*, 31.
[8] J. Baran, A. Duda, R. Szymanski, S. Penczek, *Macromol. Symp.* **1997**, *123*, 93.
[9] S. Penczek, A. Duda, R. Szymanski, *Macromol. Symp.* **1998**, *132*, 441.
[10] A. Kowalski, J. Libiszowski, A. Duda, S. Penczek, *Macromolecules* **2000**, *33*, 1964.
[11] A. A. Evstropov, B. V. Lebedev, T. G. Kulagina, Ye. B. Lyudvig, B. G. Belen'kaya, *Vysokomol. Soed. Ser. A* **1979**, *21*, 2038.
[12] A. Duda, S. Penczek, *Macromolecules* **1990**, *23*, 1636.
[13] J. Libiszowski, A. Kowalski, R. Szymanski, A. Duda, J.-M. Raquez, P. Degee, P. Dubois, *Macromolecules* **2004**, *37*, 52.
[14] B. V. Lebedev, T. G. Kulagina, Ye. B. Lyudvig, T. H. Ovchinnikova, *Vysokomol. Soed. Ser. A* **1982**, *24*, 1490.
[15] S. Sosnowski, S. Slomkowski, S. Penczek, L. Reibel, *Makromol.Chem.* **1983**, *184*, 2159.
[16] K. Shinno, M. Miyamoto, Y. Kimura, Y. Hirai, H. Yoshitome, *Macromolecules* **1997**, *30*, 6438.
[17] J. Mosnacek, A. Duda, J. Libiszowski, S. Penczek, submitted to *Macromolecules.*
[18] G. Montaudo, M. S. Montaudo, C. Puglisi, F. Samperi, N. Spasky, A. LeBorgne, M. Wisniewski, *Macromolecules* **1996**, *29*, 6461.
[19] K. Ito, Y. Hashizuka, Y. Yamashita, *Macromolecules* **1977**, *10*, 821.
[20] H. Jacobson, W. H. Stockmayer, *J. Chem. Phys.* **1950**, *18*, 1600.
[21] S. Penczek, A. Duda, R. Szymanski, T. Biela, *Macromol. Symp.* **2000**, *153*, 1.
[22] P. Kurcok, P. Dubois, R. Jerome, *Polym. Internat.* **1996**, *41*, 479.
[23] A. Kowalski, A. Duda, S. Penczek, *Macromolecules* **1998**, *31*, 2114.
[24] J.-M. Raquez, *"Controlled Synthesis of Biodegradable (Co)polyesters by Ring-Opening Polymerization of 1,4-Dioxan-2-one"*, Ph. D. Thesis, University of Mons-Hainaut, Mons (Belgium) 2003, p. 91.
[25] A. Hofman, S. Slomkowski, S. Penczek, *Makromol. Chem.* **1984**, *185*, 91; **1987**, *188*, 2027
[26] A. Duda, A. Kowalski, S. Penczek, H. Uyama, Sh. Kobayashi, *Macromolecules* **2002**, *35*, 4266.
[27] W. M. Stevels, M. J. K. Ankone, P. J. Dijkstra, J. Feijen, *Macromolecules* **1996**, *29*, 6132.
[28] K. L. Singfild, J. K. Hobby, A. Kelner, *J. Cryst. Growth* **1998**, *183*, 683.
[29] A. Duda, *J. Polym. Sci., Part A: Polym. Chem.* **1992**, *30*, 21.
[30] K. Teranishi, N. Iida, T. Araki, S. Yamashita, H. Tani, *Macromolecules* **1974**, *7*, 421.
[31] R. A. Gross, Y. Zhang, G. Konrad, R. W. Lenz, *Macromolecules* **1988**, *21*, 2657.
[32] P. J. Hocking, R. H. Marchessault, *Polym. Bull.* **1993**, *30*, 163.
[33] J. E. Kemnitzer, S. P. McCarthy, R. A. Gross, *Macromolecules* **1993**, *26*, 6143.
[34] H. R. Kricheldorf, S. R. Lee, N. Scharnagl, *Macromolecules* **1994**, *27*, 3139.
[35] K. A. M. Thakur, R. T. Kean, E. S. Hall, J. J. Kolstad, T. A. Lindgren, M. A. Doscotch, J. I. Siepmann, E. J. Munson, *Macromolecules* **1997**, *30*, 2422.
[36] A. LeBorne, N. Spassky, *Polymer* **1989**, *30*, 2312.
[37] A. LeBorne, V. Vincens, M. Joulglard, N. Spassky, *Makromol. Chem. Macromol. Symp.* **1993**, *73*, 37.
[38] T. Satoh, B. M. Novak, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **2000**, *41(1)*, 112.
[39] N. Spassky, M. Wisniewski, Ch. Pluta, A. LeBorgne, *Macromol. Chem. Phys.* **1996**, *197*, 2627.
[40] M. Wisniewski, A. LeBorgne, N. Spassky, *Macromol. Chem. Phys.* **1997**, *198*, 1227.
[41] Ch. P. Radano, G. L. Baker, M. R. Smith III, *J. Am. Chem. Soc.* **2000**, *122*, 1552.
[42] T. M. Ovitt, G. W. Coates, *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 4686.

[43] T. M. Ovitt, G. W. Coates, *J. Am. Chem. Soc.* **2002**, *124*, 1316.
[44] Z. Zhong, P. J. Dijkstra, J. Feijen, *J. Am. Chem. Soc.* **2003**, *125*, 11291.
[45] N. Nomura, R. Ishi, M. Akakura, K. Aoi, *J. Am. Chem. Soc.* **2002**, *124*, 5938.
[46] K. Majerska, A. Duda, *J. Am. Chem. Soc.* **2004**, *126*, 1026.