

STEREOCHEMICAL ASPECTS OF THE CONTROLLED
RING-OPENING POLYMERIZATION OF CHIRAL CYCLIC ESTERS

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Abstract :

The stereochemical aspects of controlled polymerization of lactide and β -butyrolactone are discussed. The physicochemical and thermal properties of these polymers are shown to be depending on the stereochemical structure of the macromolecular chain. Different types of processes involving change of enantiomeric composition in the course of the polymerization reaction are examined in function of different initiators used. The formation of stereocomplexes from stereocopolymers of various enantiomeric compositions is reported.

INTRODUCTION

Aliphatic polyesters are interesting materials for applications in biomedical, pharmacological and packaging applications (Ref. 1-4).

Synthetic polyhydroxyacids such as polylactides (PLA) and polyhydroxybutyrates (PHB) are polymers bearing asymmetric carbon atoms in the main chain. Their physicochemical and degradation properties may strongly depend on their stereochemical structure and it is possible to adjust the physical and mechanical characteristics by adjusting the balance of configurational units in the stereocopolymers (Ref. 5-8). The most efficient method of synthesis of high molecular weight polyhydroxyacids is the ring-opening polymerization of the corresponding cyclic esters, i.e., lactide (LA) and β -butyrolactone (BL). The chemical synthesis of polymers with defined and controlled characteristics (structure, molecular weight) requires suitable initiators leading to a living type process. The livingness of systems in ring-opening polymerization of cyclic esters was recently discussed in terms of selectivity, defined as the ratio of rate constant of propagation reaction to the rate constant of the competing side reaction which is mainly transesterification reaction (Ref. 9).

In this paper we want to discuss in the case of LA and BL monomers both of the aspects of controlled polymerizations : those related to the livingness of the systems and those dealing with stereochemical arrangements of the macromolecular chain. In addition some

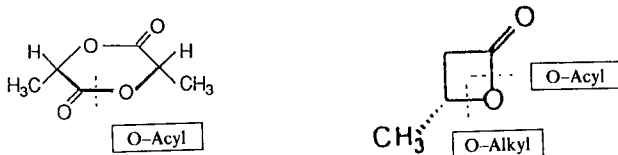
results on the synthesis of block copolymers and the formation of stereocomplexes between stereocopolymers of various enantiomeric compositions will be given. The presentation includes results taken from the literature and from our recent investigations mostly unpublished.

DISCUSSION AND RESULTS

Various kinds of initiators (anionic, cationic, coordination-insertion) may be used for the polymerization of lactides and lactones (Ref. 10-11). Aluminium alkoxide initiators ($Al(OR)_3$, R_2AlOR') were particularly studied since they lead to living type polymerization with lactides and ϵ -caprolactone (Ref. 9,10,12,13). For BL, porphinato type aluminium initiators (Ref. 14) exhibit living type behaviour. All these initiators have a relatively low reactivity. Recently it was reported that rare-earth alkoxides show a very high reactivity in the polymerization of lactones and lactides (Ref. 15-20). For some of them a living type behaviour was observed. High rates of polymerization were also observed in the case of anionic initiators, e.g., $tBuOK$, CH_3CO_2K , CH_3OK with addition of crown-ethers, but some side reactions were identified (Ref. 21-23).

Ring-opening reaction

The ring-opening reaction in the polymerization of lactones and lactides may occur through O-acyl or O-alkyl cleavage. In the case of O-acyl cleavage, the reaction proceeds with retention of configuration of the asymmetric carbon atom, while in the case of O-alkyl ring-opening an inversion of the asymmetric center occurs and the recurring polymer unit has an opposite configuration of that of initial monomer. In the case of lactide polymerization, almost all of the initiators open the cycle through O-acyl bound with retention of configuration. Partial racemization was reported when using some anionic initiators (Ref. 21). The situation is somewhat different in the case of BL : depending on the initiator used, O-acyl or O-alkyl cleavage is observed and this must be taken into account when the synthesis of a particular polyenantiomer is desired.



The initiators opening BL through O-acyl bound include $\text{Al}(\text{OiPr})_3$, $\text{R}_2\text{AlOR}'$, alumoxanes, Schiff's bases Al alkoxides, $\text{R}_3\text{SnOR}'$, distannoxanes, $\text{Zn}[\text{OAl}(\text{OR})_2]_2$, $\text{ZnEt}_2/\text{H}_2\text{O}$, $\text{ZnEt}_2/\text{diol}$, yttrium alkoxides, while O-alkyl cleavage is observed for CH_3ONa , CH_3OK , tBuOK , TPPAICl , SALCENAICl , $\text{AlEt}_3/\text{H}_2\text{O}$.

Preparation of stereocopolymers

The polymerization of mixtures of stereoisomers can proceed with no change or with a change of the initial enantiomeric composition during the reaction.

Polymerizations with no change in enantiomeric composition

In this process the enantiomeric composition of the polymer is identical to that of the starting or the reacting monomer at any stage of the reaction, i.e., at any conversion.

Three types of structural arrangements in the polymer chain are possible :

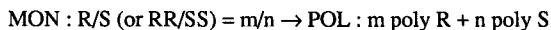
- a) a random distribution of R,S (or RR and SS for lactide) configurational units :



The examination of triads (or higher n-ads) relations indicates that these distributions obey a Bernoullian statistics (Ref.24). A linear relation is found between optical purities of starting monomers and resulting polymers.

Typical examples of such behaviour are for example, polymerizations of lactide with Sn octoate (Ref.25), and Zn powder (Ref.5). For BL random distributions were found for polymerizations initiated with $\text{ZnEt}_2/\text{H}_2\text{O}$ (Ref. 6-7).

- b) an isotactic arrangement leading to a mixture of enantiomeric -RRRRRR- or -SSSSSS- type chains. In that case the process is called "stereoselective" or "enantiosymmetric" :



Only partial stereoselectivity was observed in few polymerizations, for example in the case of β -BL polymerized with $\text{AlEt}_3/\text{H}_2\text{O}$ initiator systems of different compositions (Ref.26,27)

- c) a syndiotactic arrangement of the type -RSRSRS-. Poly (β -butyrolactone)s with highly enriched alternate structures were recently prepared using some alumoxanes (Ref.28), stannoxane (Ref.7) and various alkyl tin alkoxide initiators (Ref. 29-30). Tin octoate according to very recent results presents also some syndiotactic stereospecificity in polymerization of lactides (Ref. 31).

Polymerizations with change of enantiomeric composition

Two types of mechanisms can be distinguished depending on the achiral or chiral nature of the initiator.

1) GROWING CHAIN MECHANISM

In the previously studied cases when monomers with unbalanced enantiomeric compositions were polymerized in the presence of achiral initiators ($\text{Al}(\text{O}i\text{Pr})_3$, $\text{ZnEt}_2/\text{H}_2\text{O}$, Sn octoate,...) no variation of optical purity (o.p.) of the unreacted monomer was noticed, i.e., no preferential consumption of one of the enantiomers occurred.

In our recent studies we have used for the polymerization of lactides aluminium Schiff's base alkoxide initiators. The achiral initiator derived from the simplest Schiff's base bearing the ethylene diamine moiety SALENAlOCH_3 was found to be efficient for the polymerization of (D,L)-lactide in solution and a living type behaviour was observed up to 70% of conversion (Ref.13). At higher conversions the molecular weight distribution (MWD) broadens and transesterification reactions occur. Very recently the polymerization of lactide with various enantiomeric compositions using SALENAlOCH_3 initiator was performed (Ref.32). The examination of the optical properties of the prepared stereocopolymers revealed that their optical rotatory powers were higher than expected from optical purity of starting monomer feeds (Fig.1).

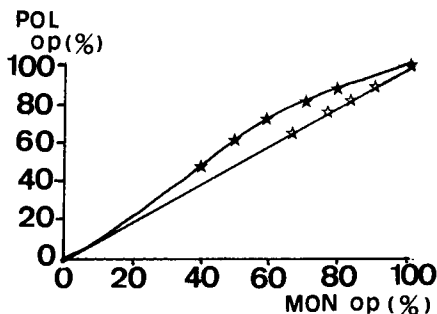


Fig. 1. Optical purities (o.p.) of prepared poly lactides vs reacting monomers.
 Initiators: ★ SALENAlOCH_3 (Ref. 32) ☆ Sn octoate (Ref 25)
 (—) theoretical line for statistical enantiomeric distribution.

The microstructure of enantiomerically enriched stereocopolymers was examined by ^{13}C NMR at high field. From the experimental values of the proportions of tetrads observed on the methine carbon atom and hexads observed on the carbonyl carbon atom, it appears clearly that the microstructure of stereocopolymers obeys a first order Markovian distribution of units with a reactivity ratio (rates of homo/cross propagation) equal to 2.8. This means that these stereocopolymers contain long isotactic sequences of D- and L-type units. Such type of Markovian distribution is known to fit with a growing chain mechanism (Ref.24). The properties of these

lactide stereocopolymers are unusual, since whatever their enantiomeric composition all the prepared polymers are crystalline (Fig. 2). The temperature of fusion decreases from 178°C (o.p.=100%) to 112°C (o.p.=40%). For stereocopolymers of lower optical purity including the racemic one, melting points around 150°C are observed.

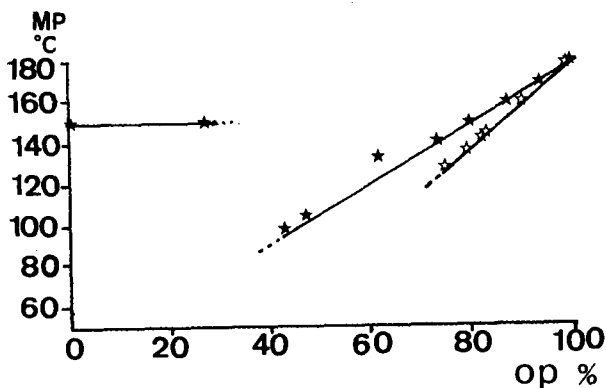


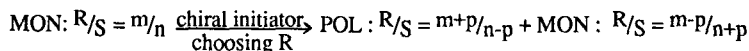
Fig. 2. Melting points of lactide stereocopolymers obtained with different initiator systems : ★ SALENAlOCH₃ (Ref 32) ☆ Sn octoate (Ref. 25)

Their origin is due to the formation of stereocomplexes as substantiated by examination of X-ray diffraction profiles. Thus the stereocomplexation may occur between chains containing relatively short enantiomeric blocks.

2) CHIRAL CATALYSIS

The second mechanism involving a change in enantiomeric composition during the reaction and requiring the presence of a chiral initiator is called "stereoelective", "enantioasymmetric" and very recently the terminology "asymmetric enantiomer-differentiating" was proposed. The ideal definition of such a process is : "A polymerization in which starting from a mixture of enantiomeric monomer molecules, only one type of enantiomer is polymerized".

This means that in the case of an exclusive choice of R-enantiomer for example, at half-reaction a pure R-type polymer is obtained and the remaining unreacted monomer is pure (S)-enantiomer. Usually the stereoelective process is not as perfect and the reaction can be expressed in the following way :



Stereoselective polymerizations were extensively studied in the case of substituted oxiranes, thiranes and much less with β -lactones and other heterocycles (Ref.33-35). The first case of stereoselective polymerization of (D,L)-lactide was reported by us in 1996 with a chiral aluminium alkoxide initiator SALBinaphAlOCH₃ derived from a chiral Schiff's base bearing binaphthyl moiety (Ref. 36). A rather high stereoselectivity was observed. A polymer with 88% enantiomeric enrichment in D units was obtained at 19% of conversion. The polymerization reaction shows a living type character and narrow MWD ($\overline{M}_w / \overline{M}_n = 1.10-1.30$) were obtained up to very high conversions, which indicates that transesterification reactions do not occur significantly with this sterically hindered initiator. Some results of this polymerization are reported in Table 1.

Tab. 1 Stereoselective polymerization of (D,L)-LA and (R,S)-BL using (R)SALBinaphAlOCH₃ as initiator system

MON	[M]/[I]	Temp (°C)	time (h)	Conv (%)	\overline{M}_n 10^{-3}	MWD	o.p. (%)		r
	in moles						Mon	Pol	
(D,L)-LA (a)	75	70	5	19	4.8	1.05	20	88	20
	75	70	22	62.5	5.7	1.05	95	65	
	75	70	111	90	11.5	1.1	100	13	
(R,S)-BL (b)	188	20	24	62	11.6	1.07	22		1.3
	484	20	96	84	33.6	1.10	30		

(a) in toluene solution (b) in bulk

All the obtained polymers were dextrorotatory, i.e., with predominant D-units. The stereoselectivity $r = k_D/k_L$, which is the ratio of rate constants of consumption of the two enantiomers was calculated on the basis of a first-order relation and found to be close to 20, which means that the optical purity of unreacted monomer at half reaction is around 80%. It is the highest stereoselectivity reported in asymmetric ring-opening polymerization of cyclic esters and the first example of such a high resolution in homogeneous conditions with a living type behaviour. The thermal properties prepared polylactides show again interesting features : the polymer at 19% of conversion exhibits a sharp melting peak at 145°C, a value expected for a stereocopolymer of optical purity close to 80%, while the polymer of low optical purity obtained at 90% of conversion

shows a melting point at 185°C, which indicates the formation of a stereocomplex, as substantiated by examination of X-ray diffraction pattern profiles (Ref.36).

The same SALBinaphAlOCH₃ initiator was used for the stereoselective polymerization of racemic β-BL. As seen from results given in Table 1, the stereoselectivity observed ($r=1.3$) is fifteen times lower than that observed for (D,L)-lactide. The polymerization appears to have a living type behaviour since narrow MWD is found at high conversion. The magnitude of the choice (stereoselectivity) depends on the nature of guest-host association between the two partners (monomer-initiator) and is not easily predictable. We have tried to polymerize (R,S)-BL with various chiral initiators, but never the stereoselectivity exceeded 2.0 (Table 2). None of these initiators, with the exception of ZnEt₂/(R)-DMBD, a heterogeneous type initiator (Ref.37), which is partly isospecific, lead to crystalline polymers.

Tab.2 Stereoselective polymerization of (R,S)-BL in bulk using different initiators

Initiator	[M]/[I]	Temp (°C)	time (h)		\overline{DP}_n (d)	MWD (d)	Mon o.p (%) (e)	r (f)
(R)- SALBinaphAlOCH ₃ (a)	188	20	24	62	138	1.07	15	1.3
	484	20	96	84	400	1.10	46	
(R) SALBinaph AlCH ₃ (tetra Cl) (a) (b)	260	20	24	55	150	1.10	2.5	1.1
(R) SALBinaph AlCl (a)	52	70	3	35	23 (g)		13	2.0
	52	70	7	55			23	
(R,R)-SALCENAICI (a)	20	60	4	85	12	1.1	16	1.2
AlEt ₃ /(R)-DMBD (c)	20	20	432	13			0.1	<1.1
ZnEt ₂ /(R)-DMBD (c)	20	20	2.75	53	238 (h)	2.5 (h)	15	1.6
	20	20	5.5	84			46	

(a) Chiral moiety in the Schiff's base : Binaph=(R)-1,1-binaphthyl-2,2'diamine ; CEN=(1R,2R)-1,2-cyclohexanediamine

(b) using dichlorosalicylaldehyde (c) DMBD = 3,3-dimethyl-1,2-butanediol

(d) SEC in THF versus polystyrene standards (e) optical purity of unreacted monomer

(f) stereoselectivity ratio ($r = k_R/k_S$) (g) by ¹H NMR (h) fraction insoluble in MeOH

Stereocomplexes

In the previous chapter on stereocopolymers the formation of stereocomplexes was observed in the course of the polymerization of stereoisomeric mixtures of lactides with Schiff's base aluminium initiators. At the same time no formation of stereocomplexes

were detected in the polymerization of BL with the same initiators. We have observed for the first time the formation of stereocomplexes during polymerization reactions in stereoselective (Ref.38) and stereoelective (Ref.39) polymerizations of racemic *t*-butylthiirane with zinc initiators. The presence of two enantiomeric polymeric chains of opposite configuration is required in order to obtain the formation of stereocomplexes. However the mixing of two enantiomeric polymer chains does not lead in all cases to stereocomplexes. Two types of behaviour must be distinguished.

In the first case the racemic material obtained from the mixture of two polyenantiomers exhibits the same physical properties, e.g., melting point, solubility and has the same crystalline structure as the parent homopolymers. Examples of this class of polymers are : poly(methyloxirane), poly(methylthiirane), poly(hydroxybutyrate) and some other polymers (Ref.40). Tadokoro has explained this behaviour by the presence in the racemic polymer of equal amounts of polyenantiomeric crystallites. Therefore the optically active and the racemic polymer have the same crystalline structure and the same physical properties.

In the second case the properties of the racemic blend are very different of that of parent homopolymers. For example, a raise of 50°C is observed in the melting point for the stereocomplex and the crystalline structure of the latter is different of that of the polyenantiomer. According to Tadokoro (Ref.41) the optical compensation in the material takes place in the crystalline unit cell forming a so-called racemic crystallite.

As already mentioned stereocomplexes were obtained during polymerization reactions in the case of poly(*t*-butylthiirane) (Ref.38,42) and poly(*t*-butyloxirane) (Ref.43). For some other polymers the stereocomplexes were obtained by mixing both of the polyenantiomers which requires the chemical synthesis of both homopolymers by an independent way.

Stereocomplexes from blends were reported for a series of substituted poly (β -propiolactone)s (Ref.44,45) and more recently for polylactides (Ref.46,47). Differential scanning calorimetric, structural, morphological studies were reported in great detail in a series of papers by Tsuji, Ikada et al (Ref.48,49). The corresponding polylactides were synthesized by polymerization of D- and L-lactides using Sn octoate as initiator system. Later, Brochu, Prud'homme et al (Ref.50) prepared L- and D-homopolymers with aluminium isopropoxide as initiator and obtained stereocomplexes from blends.

In both cases the melting points of prepared polyenantiomers were close to 180°C and those of stereocomplexes around 230-235°C (Ref.25,50). We have prepared stereocomplexes from stereocopolymers synthesized using SALENAIOCH₃ as initiator system. The nascent stereocomplex prepared from blends of pure poly L- and poly D-lactides exhibited a melting point of 247°C, somewhat higher than the previous ones. More interesting were the results obtained from blending of stereocopolymers with different optical purities. It is known that PLA'S prepared using Sn octoate or Al(OiPr)₃

as initiators lost their crystallizability when their optical purity became smaller than 76%. For PLA's prepared with Sn octoate the limit value of o.p. for stereocomplex formation is 83% with a melting point around 180°C (Ref.25,49) In the case of polylactides prepared with Al(OiPr)₃ initiator system, the stereocomplex obtained from a polymer blend of 100L/80D exhibited a melting point of 195°C (at the maximum peak) (Ref.50) As previously discussed the stereocopolymers prepared from SALENAIOCH₃ initiator are crystalline whatever their optical purity. We have prepared stereocomplexes by precipitation of mixed L- and D-enriched stereocopolymers dichloromethane solutions into methanol.

Two general types of blends were studied. The first type of blends was obtained from stereocopolymers having the same optical purity, i.e., PLAX + PDAX, where X is the optical purity of the starting monomer mixture. The second type of blends was prepared from stereocopolymers having different optical purities, i.e., PLAX + PDAY. X and Y were varied from 100 to 26%. The main results are presented in Table 3. All of the blends were found to form stereocomplexes and exhibited high melting points. The melting point for products of the same optical purity are much higher than those reported for polymers obtained with Sn octoate and Al(OiPr)₃ initiators.

Tab 3. Temperatures of fusion of different lactide stereocomplexes prepared from different L- and D-stereocopolymers obtained with SALENAIOCH₃ initiator.

Polymers	LA 100 174°C	LA 87 157°C	LA 73 138°C	LA 43 104°C	LA 26 149°C
DA 100 174°C	247 (224)	225 (215)	210 (203)	198 (180)	187 (177)
DA 87 158°C	225 (207)	213 (205)	203 (194)	193 (180)	180 (177)
DA 73 144°C	213 (202)	205 (198)	198 (187)	187 (177)	179 (144)
DA 46 122°C	197 (183)	n.p	188 (182)	176 (176)	166

Nomenclature : LAX and DAX = polymers prepared from a lactide monomer mixture enriched in L- or D enantiomer respectively with an optical purity of X%.

The temperature of fusion is taken at the end of the melting points. Numbers in parentheses correspond to a second scan.

n.p. = not prepared, but probably very similar to DA87/LA43 stereocomplex.

It is clear that these enhanced thermal properties are again the consequence of the presence of long enantiomeric sequences in these polymers (for DA 40 or LA 40 the

average length is 15 D or L units, that is 30 repeating units of the same configuration). From these results it is possible to estimate the presence of sequences containing 50 repeating units of the same configuration in the macromolecular chains of the stereocomplex obtained in the course of stereoelective polymerization of (D,L)-lactide with SALBinaphAlOCH₃ initiator system ($T_m = 187^\circ\text{C}$) (Ref.32).

Another original route of synthesis of stereocomplexes was described in the group of Feijen (Ref.51). It consists in preparation of stereoblock copolymers by sequential ring-opening polymerization of D- and L-lactides with Al(OiPr)₃ initiator. The block copolymer shows a melting temperature of 205°C , which is lower than those found for stereocomplexes obtained from pure L- and D-chains, but is still much higher than that found for a pure polyenantiomer. The inter or intramolecular nature of the formed stereocomplex is not yet established.

The same group have also investigated the properties of triblock lactide copolymers prepared with a central polyethylene glycol (PEG 6000) sequence. Triblocks with L- or D-lactide sequences of at least 60 lactyl units show crystallinity of the PLA phase ($T_m \sim 160^\circ\text{C}$). The blends of triblocks with lactides of opposite configuration showed an increased melting point of the PLA phase ($T_m \sim 205\text{-}220^\circ\text{C}$) (Ref.52).

More recently the same authors reported on the thermal properties of diblock copolymers of ϵ -caprolactone and lactide enantiomers of opposite configuration. The polymers were prepared by sequential polymerization of ϵ -caprolactone and D- or L-lactide using Y5 ($\mu\text{-O}$)(OiPr)₁₃ as initiator system. At least 40 lactyl units are necessary to obtain the crystallization of enantiomeric lactide sequences ($T_m \sim 145\text{-}150^\circ\text{C}$). The melting points of blends of enantiomeric block copolymers is increased up to $200\text{-}210^\circ\text{C}$ (Ref.53). Stereocomplexes formation in the case of ϵ -caprolactone-lactide copolymers were also reported by Murdoch and Loomis (Ref.47). We have very recently prepared diblock ϵ -caprolactone D- or L-lactide copolymers using Y(OCH₂CH₂OiPr)₃ initiator system in dichloromethane solution at room temperature. These blocks contained around 120 ϵ -CL units and 115 lactyl units with an average MWD = 1.3-1.4. The individual block copolymers exhibit melting points of 55°C for ϵ -CL -sequences and around 163°C for the lactyl sequence. The blend of the two enantiomeric block copolymers produced a stereocomplex material with two melting temperatures : $T_{m1} = 57^\circ\text{C}$ (ϵ -CL -sequences), $T_{m2} = 229^\circ\text{C}$ for the lactide stereocomplex sequence.

Finally another method of in situ preparation of lactide stereocomplex was recently reported by Spinu et al (Ref.54). This procedure combines polymerization with stereocomplexation by heating in the presence of Sn octoate catalyst L-LA monomer and preformed PDLA polymer. The stereocomplex is formed in situ as the polymerization proceeds. The DSC thermogram exhibits a peak at 220°C characteristic of the stereocomplex and a minor peak at 169°C corresponding to some residual PDLA

homopolymer. It can be mentioned that recently, on the basis of molecular simulation, a model of stereocomplex crystal growth was proposed (Ref.55).

CONCLUSIONS

The controlled living type polymerization of β -butyrolactone and lactide may be realized with a series of metal alkoxide initiators, those derived from rare-earth metals being the most reactive. The polymerization reaction of enantiomerically enriched monomers proceeds with most of the initiators with no change of the enantiomeric composition during the reaction leading to statistical type stereocopolymers.

Complex aluminium alkoxide initiators derived from Schiff's bases lead on the contrary to block stereocopolymers obeying to a Markovian type distribution which are crystalline whatever the enantiomeric composition. These polymers exhibit enhanced thermal properties. Chiral initiators induce an asymmetric polymerization. A rather high stereoelectivity was observed in the case of lactide. Stereocomplexes were formed at high conversions. Lactide stereocomplexes were also prepared from blends of block stereocopolymers of various enantiomeric composition and from block copolymers, e.g., ϵ -caprolactone-*b*-lactide.

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