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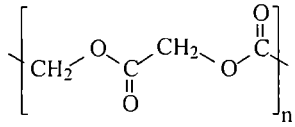
Synthesis of aliphatic polyesters of various architectures by the controlled ring-opening polymerization of cyclic esters

Summary — A review covering 80 references presents recent studies on the controlled synthesis of poly(aliphatic ester)s (PAE's), mostly including poly(ε-caprolactone) and poly(L-lactide). In the introduction, general features and practical applications of PAE's, the latter resulting mostly from ability of these polymers to (bio)degradation, are briefly discussed; polymerization methods leading to PAE's are also presented. Then, the ring-opening polymerization of ε-caprolactone (CL) and L,L-dilactide (LA), including thermodynamic and kinetic polymerizability of CL and LA is described. Finally, recently elaborated methods of synthesis, of poly(ε-caprolactone)s and poly(L-dilactide)s of various architectures, such as linear homopolymers, and star-shaped polymers are presented in a more detail.

Key words: poly(aliphatic ester), (bio)degradation, ε-caprolactone, L,L-dilactide, ring-opening polymerization, covalent (pseudoanionic) polymerization, star-shaped polymer.

Poly(aliphatic ester)s (PAE's) could be discriminated from other classes of synthetic polymers by their ability to "spontaneous" degradation to H_2O and CO_2 in the natural environment and by their biocompatibility. Besides, PAE's exhibit useful mechanical and thermal properties [1—8]. Representative examples of these polymers include: poly(glycolide) [PGL — (I)], poly(lactide) [PLA — (II)], poly(ε-caprolactone) [PCL — (III)], poly(β-butyrolactone) [PBL — (IV)] or poly(butylenesuccinate) [PBS — (V)].



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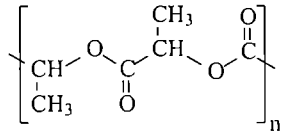

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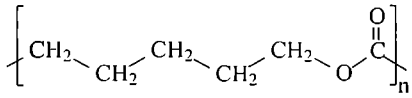

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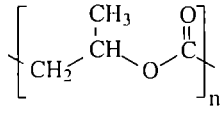

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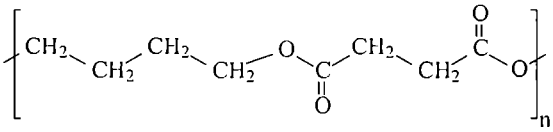

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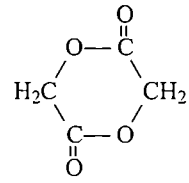
PAE's found special, mostly biomedical applications, such as bioresorbable surgical sutures, slow-release drug delivery systems, fracture bone fixation devices or scaffolds for tissue repair and regeneration [1, 4, 9—18]. Some of these polymers are being considered as environmentally friendly commodity materials and are based on the substrates available from the renewable resources (*e.g.*: Biogreen®, Biopol®, Bionolle®, Lacea®, NatureWorks®). Their applications include the food packaging, hygienic products, agricultural mulch films and bugs, agrochemicals, fishery materials or non-woven fabrics [4, 19—24].

PGL, PLA, and PCL are usually prepared by controlled, ring-opening polymerization (ROP) of the cyclic monomers: glycolide [GL — (VI)], dilactides [LA — (VII)] and ε-caprolactone [CL — (VIII)], respectively [25—32]. For PBL methods of the controlled synthesis, *via* β-butyrolactone [BL — (IX)] polymerization, are not yet available and the commercial polymer comes from the bacterial synthesis [2—4].



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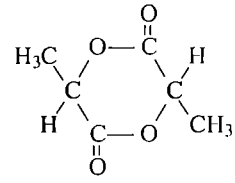

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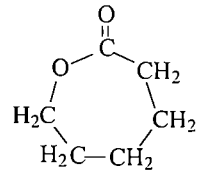

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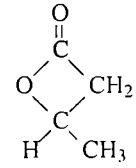


(IX)

The other process which also leads to the aliphatic polyesters is based on the polycondensation of aliphatic diols with aliphatic dicarboxylic acids (eq. 1a) or with dicarboxylic acid chlorides (eq. 1b) and on the polycondensations of aliphatic α,ω-hydroxycarboxylic acids (eq. 1c):

$$n\,HO{-}R^1{-}OH + n\,HO(O)C{-}R^2{-}C(O)OH \longrightarrow HO{-}[R^1C(O)OR^2C(O)O]_n{-}H + (2n-1)\,H_2O\uparrow \quad (1a)$$

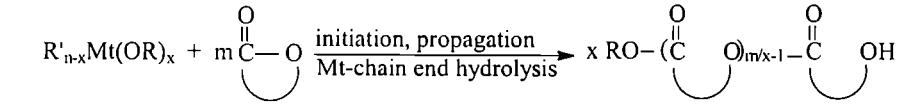
$$(n+1)\,HO{-}R^1{-}OH + n\,Cl(O)C{-}R^2{-}C(O)Cl \longrightarrow HO{-}[R^1C(O)OR^2C(O)O]_n{-}R^1{-}OH + 2n\,HCl\uparrow \quad (1b)$$

$$n\,HO{-}R{-}C(O)OH \longrightarrow HO{-}[RC(O)O]_n{-}H + (n-1)\,H_2O\uparrow \quad (1c)$$

where: *R, R^1, and R^2 denote alkylene groups* [33—40].

Several aliphatic polyesters prepared by polycondensation, like PBS-type polymers (*e.g.* Bionolle®), are considered as a large-scale production rivals of PCL or PLA. This synthetic route is also used in the alternative method of PLA industrial production (*e.g.* Lacea®) [2—4, 41, 42]. Moreover, polycondensation is still the major technological method of production of the aliphatic-aromatic polyesters, such as poly(alkylene terephthalate)s [43].

The early studies of polycondensation carried out by Carothers [33—36] revealed formation, apart from the expected high molar mass linear polymers, also low molar mass cyclic side products. Some of these, for example CL, were then isolated, purified, and used by Carothers [36] as monomers in the ROP, providing linear aliphatic polyesters. Eventually, polymerization of cyclic esters



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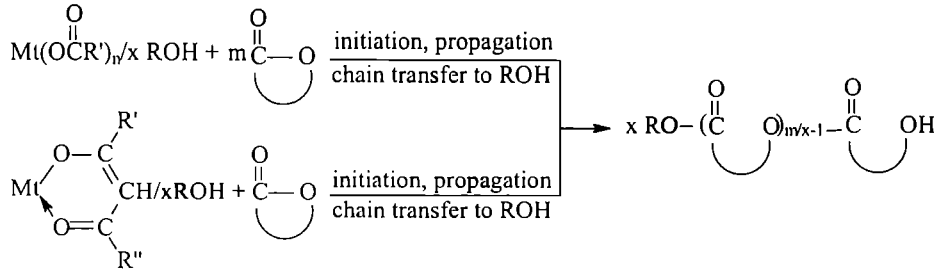

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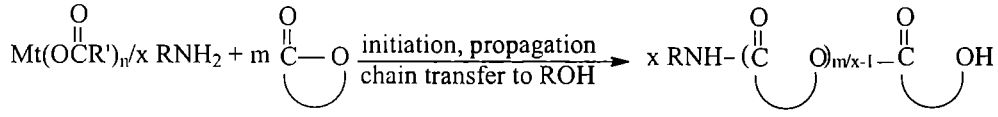


(3)

has become the preferred preparation route for the well-defined high molar mass aliphatic polyesters and became also an efficient tool in studies of the mechanism of ROP. This is because in many polymerization systems involving cyclic esters termination and chain transfer could be excluded [30—32]. More recently, ROP has been also extended to the enzyme-catalyzed processes [44, 45].

The present paper reviews methods of the controlled synthesis of PCL and PLA of various architectures and their characterization, which were elaborated in our laboratory.

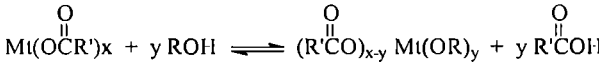
GENERAL FEATURES OF RING-OPENING POLYMERIZATION OF CYCLIC ESTERS

Polymerization of cyclic esters, including ε-caprolactone (CL) or lactides (LA), was initiated with a large number of cationic, anionic, and covalent compounds. However, only covalent (pseudoanionic) initiators provided sufficient molar mass and end-groups control in the resulting polyesters [25—32]. The latter issue was reviewed several times by us [30—32, 46—51].

Typically, pseudoanionic initiators applied in the polymerization of cyclic esters involve multivalent metals [*e.g.*: Zn, Sn(II), Al, La, Y, Sn(IV), Ti] and can be divided into the three subclasses: alkoxides (eq. 2a), carboxylates, and 3-oxa-1-enolates (eq. 2b).

Carboxylates [*e.g.* tin(II) 2-ethylhexanoate] and oxaenolates (*e.g.* aluminum acetylacetonate) are not able to initiate the polymerization *per se* and require presence of a cointiator — a compound bearing hydroxyl group (ROH):H_2O, an alcohol or hydroxycarboxylic acid. Possibility of coinitiation with primary amines, such as alkylamines [52], polyaminoacids [53], and polypropyleneimine dendrimers (Astramols^{TM}) [54] has also been explored (eq. 3).

However, as we have shown in a series of recently published papers [52, 55—59], independently on the initiating system applied the actual initiator and then the active species assume the metal alkoxide structure. The latter species are formed, for example, in the carboxylate-alkoxide ligands exchange reaction:



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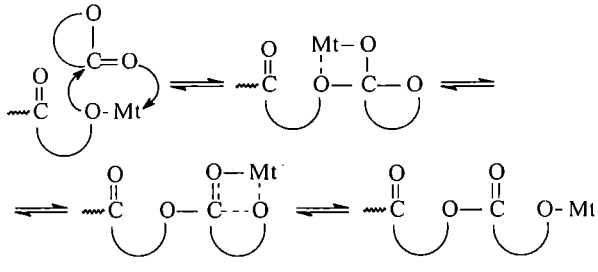
It is generally accepted, on the basis of the indirect proofs, such as solvent effects or kinetics of polymerization [60, 61], that polyester chain growth on the multivalent metal alkoxides proceeds *via* four-center coordination-insertion mechanism:



(5)

Thus, ions are not formed at any stage of the path from substrates to products in this mechanism and a monomer addition formally proceeds by a nucleophilic attack of the alkoxide growing species on the carbonyl carbon atom with acyl-oxygen bond scission in the monomer molecule.

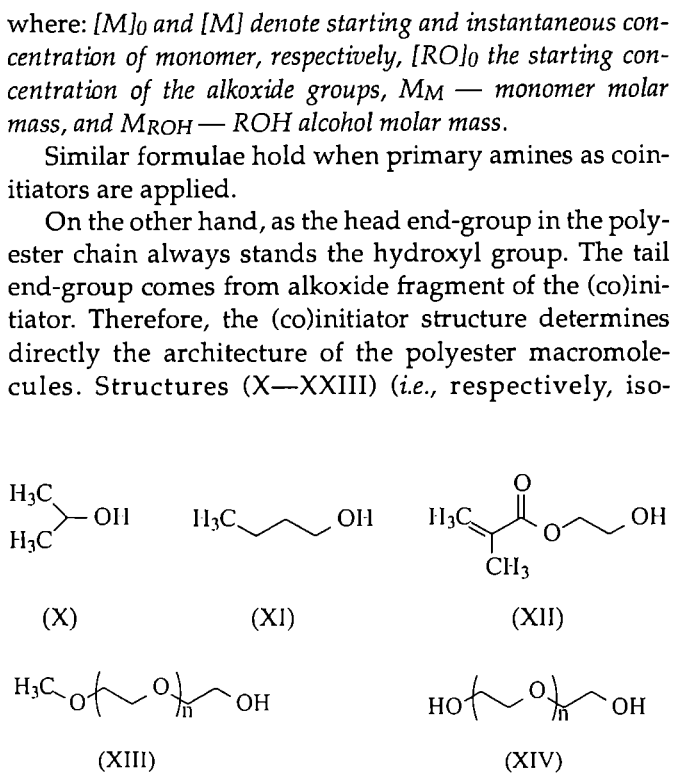
The number average molar masses (M_n) of the resulting (linear) polyesters can be predetermined by the ratio of concentrations of the consumed cyclic ester monomer and of the alkoxide group [from $R_{n-x}Mt(OR)_x$ initiator or from ROH coinitiator]:

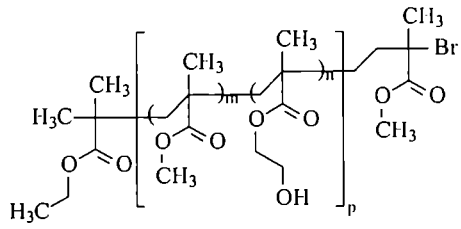
$$M_n = M_M \frac{([M]_0 - [M])}{[RO]_0} + M_{ROH} \qquad (6)$$

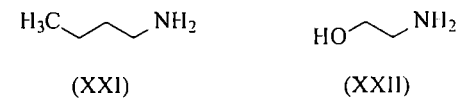
where: *$[M]_0$ and $[M]$ denote starting and instantaneous concentration of monomer, respectively, $[RO]_0$ the starting concentration of the alkoxide groups, M_M — monomer molar mass, and M_{ROH} — ROH alcohol molar mass.*

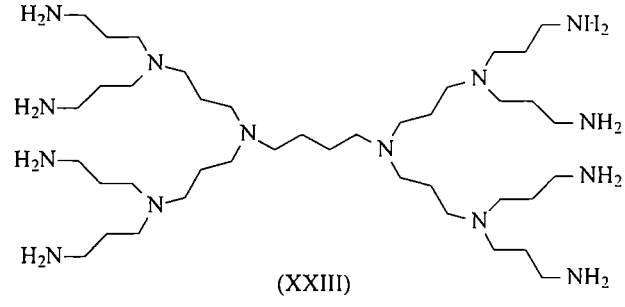
Similar formulae hold when primary amines as coinitiators are applied.

On the other hand, as the head end-group in the polyester chain always stands the hydroxyl group. The tail end-group comes from alkoxide fragment of the (co)initiator. Therefore, the (co)initiator structure determines directly the architecture of the polyester macromolecules. Structures (X—XXIII) (*i.e.*, respectively, isopropanol (*i*-PrOH), *n*-butanol (BuOH), 2-hydroxylethylmethacrylate (HEMA), methyl ether of poly(ethylene glycol) (MEPEG), poly(ethylene glycol) (PEG), α,ω-dihydroxy-polybutadiene (DHPBD), trimethylolpropane (TMP), di(trimethylolpropane) (DTMP), dipentaerithritol (DPE), poly(3-ethyl-3-hydroxymethyloxetane) (PEHMO), poly(methylmethacrylate-*co*-2-hydroxyethylmethacrylate) (PMH), *n*-butylamine ($BuNH_2$), 2-ethanolamine (NH_2EtOH), polypropyleneimine octaamine dendrimer, Generation 2.0 (Astramol™, DAB-Am-8) are examples of (co)initiators [alcohols (X—XIII), polyols (XIV—XX), amines (XXI, XXII), polyamines (XXIII)] applied by us in preparing PCL and PLA of various architectures.









POLYMERIZABILITY OF ε-CAPROLACTONE AND L,L-DILACTIDE

Thermodynamic polymerizability

Driving force of polymerization of a majority of cyclic esters comes from the negative enthalpy change (ΔH_p^0) related to the ring-strain release, prevailing the entropy decrease, during the polymerization process. Only polymerization of a larger ring, non-strained monomers (macrolides) can be entropically driven [31, 32].

Table 1. Standard thermodynamic parameters for CL and LA (298 K)

Monomer	ΔH_p^0, kJ·mol^{-1}	ΔS_p^0, J·mol^{-1}·K	$[M]_{eq}$, mol·L^{-1}	Ref.
CL[a)]	-28.8	-53.9	$6 \cdot 10^{-2}$	63
LA[b)]	-22.9	-25.0	$1 \cdot 10^{-2}$	64

[a)] Standard states: monomer — neat liquid, polymer — condensed.
[b)] Standard states: monomer, polymer — 1.0 mol·L^{-1} solution in dioxane-1,4.

CL and LA belong to the medium strained cyclic esters (see the pertinent ΔH_p^0 values, Table 1) and exhibit relatively low equilibrium concentrations ($[M]_{eq}$) allowing these monomers to be polymerized almost quantitatively. $[M]_{eq}$ given in Table 1 for CL was calculated from the standard enthalpy (ΔH_p^0) and entropy (ΔS_p^0) of polymerization according to the equation:

$$[M]_{eq} = \exp(\Delta H_p^0/RT - \Delta S_p^0 / R) \quad (7)$$

where: *T is the absolute temperature and R the gas constant [62].* According to our experience, in solution polymerization of CL, carried typically at room temperature or below, the CL monomer is consumed "completely" — size exclusion chromatography (SEC) and ^1H NMR readings gave $[M]_{eq} = 0$. The discrepancy between calculated and measured $[M]_{eq}$ is related to the method of ΔH_p^0 and ΔS_p^0 determination, based on heats of combustion and of heat capacities for liquid monomer and partially crystalline polymer [63].

$[M]_{eq}$ for LA was measured by us directly in the polymerization mixtures by means of SEC [64]. In contrast to CL polymerization of LA requires higher temperatures at which $[M]_{eq}$ becomes relatively high. Thus, for a temperature range from 80 to 133°C $[LA]_{eq}$ changes from 0.058 to 0.151 mol·L^{-1}. This means that almost 2 mol% of LA is left at equilibrium during its homopolymerization at 133°C ([LA] in bulk is equal to 8.7 mol·L^{-1}). More recently, it has been shown that solid state polymerization accompanied by crystallization of the resulting PLA considerably decreases the unreacted LA monomer content [65].

Kinetic polymerizability

The highest polymerization rates of cyclic esters provide ionic (ion-pairs or "free" ions) alkoxide active species (Table 2) but at the same time they are the least selective ones leading, for example in CL polymerization, to the extensive formation of the low molar mass macrocycles [46, 47, 49]. Preliminary studies of anionic LA polymerization initiated with $(CH_3)_3SiO^-K^+$ carried out in our laboratory revealed both kinetic and material chain termination resulting in only partial LA consumption (*e.g.*: 70 mol% at $[LA]_0 = 1$ mol·L^{-1}, $[(CH_3)_3SiO^-K^+]_0 = 1$ mol·L^{-1}, THF, 20°C) [66].

Table 2. Rate constants of propagation in anionic and pseudoanionic polymerization of CL and LA

Monomer	Active species	Solvent, temp., °C	k_p L·mol^{-1}·s^{-1}	Ref.
CL	...-C(O)$(CH_2)_5O^-$ ("free" ions)	THF, 20	330	67
CL	...-C(O)$(CH_2)_5O^-$, K^+ (ion-pairs)	THF, 20	4.65	68
CL	...-(O)$(CH_2)_5$O-$AlEt_2$	THF, 25	$3.9\cdot10^{-2}$	69
CL	[...-C(O)$(CH_2)_5O]_3Al$	THF, 20	0.5	70, 71
LA	[...-C(O)CH(CH_3)O]$_3$Al	THF, 20	$7.5\cdot10^{-5}$	71
LA	[...-C(O)CH(CH_3)O]$_3$Al	THF, 80	$8.2\cdot10^{-3}$	71
CL	[...-C(O)$(CH_2)_5O]_2Sn$	THF, 80	$7.8\cdot10^{-2}$	32
LA	[...-C(O)CH$(CH_3)O]_2$Sn	THF, 80	0.5	57
LA	[...-C(O)CH$(CH_3)O]_2$Sn	THF, 20	$4\cdot10^{-3}$	57
CL	[...-C(O)$(CH_2)_5O]_2SnBu_2$	THF, 80	$4\cdot10^{-1}$	32
LA	[...-C(O)CH$(CH_3)O]_2SnBu_2$	THF, 80	$1.5\cdot10^{-2}$	57
CL	[...-C(O)$(CH_2)_5O]_3Y$	CH_2Cl_2, 21	0.21	72—75
LA	[...-C(O)CH$(CH_3)O]_3Y$	CH_2Cl_2, 21	$7.3\cdot10^{-2}$	72—75

Covalent active species [*e.g.* alkoxides of Al, Sn(II), Sn(IV) or Y] although much less reactive than the ionic ones (see also Table 2) lead to a fully controlled polymerization in which undesired side reactions, such as proton abstraction or macrocyclization (*via* backbiting) were practically eliminated [46—50].

Polymerization of CL on the *tris*-aluminium alkoxide active species proceeds much faster than that of LA (k_p = 0.5 *vs.* $7.5\cdot10^{-5}$ L·mol^{-1}·s^{-1} under the otherwise identical conditions), in agreement with the expected difference of reactivities for the primary (CL) and secondary (LA) alkoxide active species. In the case of *bis*-tin(II) alkoxides the opposite behavior is observed — LA propagates faster than CL does ($k_p = 0.5$ *vs.* $7.8\cdot10^{-2}$ L·mol^{-1}·s^{-1}). Plausible explanation of this difference, although still not known, may involve more subtle elements of the aggregation and/or coordination phenomena. Both for the aluminum and tin derivatives the alkyl substituents at the metal atom decrease polymerization rate because of their positive induction effect. 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.

Inspection into the kinetic data in Table 2 reveals also the following reactivity order of active species in LA polymerization: [...-C(O)CH$(CH_3)O]_3Y$ > [...-C(O)CH$(CH_3)O]_2$Sn > [...-C(O)CH$(CH_3)O]_3$Al pointing to the importance of the alkoxide oxygen-metal bond polarization, which decreases in the same direction. Thus, the highest rates of LA polymerization at room temperature reported till now were found for yttrium and other rare earth alkoxides, studied by Feijen *et al.* [72] and Spassky *et al.* [73—75]. However, synthetic applications of these relatively reactive alkoxides are still limited because they are prone to undergo side reactions.

SYNTHESIS OF LINEAR, STAR-SHAPED, AND COMB--LIKE POLY(ε-CAPROLACTONE) AND POLY(L-LACTIDE)

Kinetic data discussed in the preceding section suggest that aluminum alkoxides are probably the best suited initiators for the controlled synthesis of PCL. Indeed, Figure 1 shows that in the dialkylaluminium alkoxide (R_2AlOR')/CL polymerization system molar mass (M_n) of the resulting PCL can be predicted on the basis of

feed composition in a wide range of M_n: from 10^3 up to at least $\approx 5 \cdot 10^5$.

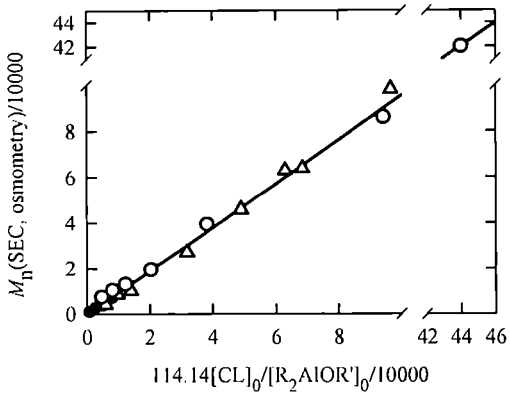


Fig. 1. Polymerization of CL initiated with dialkylaluminium alkoxides (R_2AlOR'). Dependence of molar mass (M_n) of PCL measured by osmometry and/or by SEC (the latter based on PCL standards) on M_n calculated from the feed composition; $M_n(calcd) = 114.14([CL]_0/[R_2AlOR']_0$. Conditions of polymerization: $[CL]_0 = 2.0$ mol·L^{-1}, THF solvent, 25°C; initiators: (○) i-Bu_2AlOMe, (Δ) Et_2AlOEt, (●) $Et_2AlOCH_2CH{=}CH_2$ [66, 76].

Analysis of the ^{1}H NMR spectra of the reaction mixtures and of the isolated polymers indicated that the polymerization proceeds according to the following equations [76, 77]:

$$R_2AlOR' + n\ CL \xrightarrow{\text{initiation, propagation}} R'O-(cl)_n-AlR_2 \quad (8a)$$

$$R'O-(cl)_n-AlR_2 \xrightarrow[\text{- aluminium derivatives}]{HCl_{aq}\ (e.g.)} R'O-(cl)_n-H \quad (8b)$$

where: cl = C(O)(CH$_2$)$_5$O.

Initiation with the more reactive Al(O*i*-Pr)$_3$, gave the similar polymerization control, providing that the trimeric form of this initiator was used [70].

Aluminum alkoxides found limited applications in the PLA synthesis mostly because of the low reactivity of the secondary aluminum alkoxide active species, even at the elevated temperatures (see the pertinent values of k_p in Table 2). Better results have been obtained with the tin(II) alkoxide initiators applied recently in our laboratory [57].

Figure 2 illustrates dependence of the predicted and measured molar masses of PLA obtained in polymerization of LA initiated with Sn(OBu)$_2$:

$$Sn(OBu)_2 + n\ LA \xrightarrow[\text{propagation}]{\text{initiation,}} BuO-(la)_p-Sn-(la)_q-OBu \quad (9a)$$

$$BuO-(la)_p-Sn-(la)_q-OBu \xrightarrow[-\ SnCl_{2\ aq}]{HCl_{aq}} BuO-(la)_n-H \quad (9b)$$

where: la = C(O)CH(CH$_3$)O.

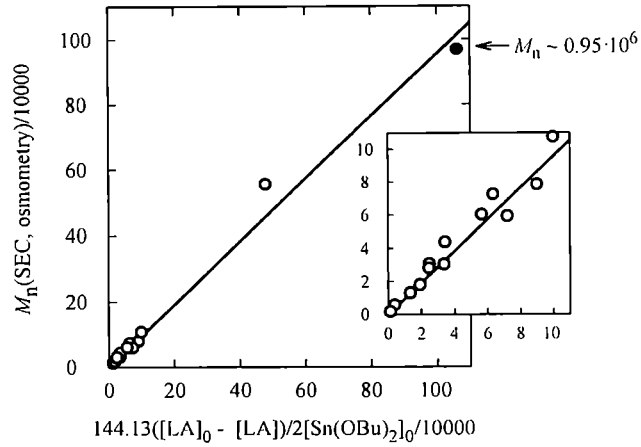


Fig. 2. Polymerization of LA initiated with Sn(OBu)$_2$. Dependence of M_n of PLA measured by osmometry and SEC on M_n calculated from the feed composition; $M_n(calcd) = 144.13([LA]_0 - [LA])/2[Sn(OBu)_2]_0$. Conditions of polymerization: (○) $[LA]_0$ from 1.0 to 3.0 mol·L^{-1}, THF solvent, 80°C; (●) polymerization in bulk, 120°C [57].

To the best to our knowledge, this is the first example of such a precise molar mass control in LA polymerization reaching the values of M_n practically equal 10^6. Structure of the "living" BuO-(la)$_p$-Sn-(la)$_q$-OBu and deactivated BuO-(la)$_n$-H macromolecules was confirmed by means of the ^{1}H NMR and MALDI-ToF spectra analysis [57].

In the industrial synthesis of PLA and in other practical applications, however, almost exclusively tin(II) 2-ethylhexanoate [tin octoate, (Sn(Oct)$_2$] as initiator is used [2—4, 6, 7, 19, 21, 24]. This is mostly due to its commercial availability and higher chemical stability in comparison with the alkoxides. As it was mentioned already in the introduction carboxylates, such as Sn(Oct)$_2$, are able to start the polyester chain growth only in the presence of a coinitiator bearing the hydroxyl or primary amino group. For example, in the LA/Sn(Oct)$_2$/BuOH reaction mixture polymerization proceeds according to the following equations [52]:

$$Sn(Oct)_2 + BuOH \rightleftharpoons OctSnOBu + OctH \quad (10a)$$

$$OctSn-OBu + BuOH \rightleftharpoons Sn(OBu)_2 + OctH \quad (10b)$$

$$...-SnOBu + n\ LA \xrightarrow{\text{initiation, propagation}} ...-Sn-(la)_n-OBu \quad (10c)$$

$$...-Sn-(la)_p-OBu + H-(la)_q-OBu \xrightleftharpoons{\text{fast chain transfer}} \quad (10d)$$

$$\rightleftharpoons H-(la)_p-OBu + ...-Sn-(la)_q-OBu$$

where: Oct = O(O)CH(C$_2$H$_5$)C$_4$H$_9$.

Practically, when [BuOH]$_0$ >> [Sn(Oct)$_2$]$_0$, the net equation reads:

$$BuOH + n\ LA \xrightarrow{Sn(Oct)_2} BuO-(la)_n-H \quad (11)$$

Similarly, in the case of the $BuNH_2$ coinitiated polymerization:

$$BuNH_2 + n\,LA \xrightarrow{Sn(Oct)_2} BuNH-(la)_n-H \qquad (12)$$

The number average degree of polymerization of the polyester formed in the cyclic ester/$Sn(Oct)_2$/coinitiator systems is fixed by the $([M]_0 - [M])/[coinitiator]_0$ ratio due to the fast exchange reactions of the chain transfer to (macro)alcohol (*e.g.* eq. 10d). MALDI ToF mass spectra presented in Figure 3 show that in the resulting PLA chain-ends coming from the intentionally introduced coinitiator (BuOH or $BuNH_2$ in a given example) are exclusively present.

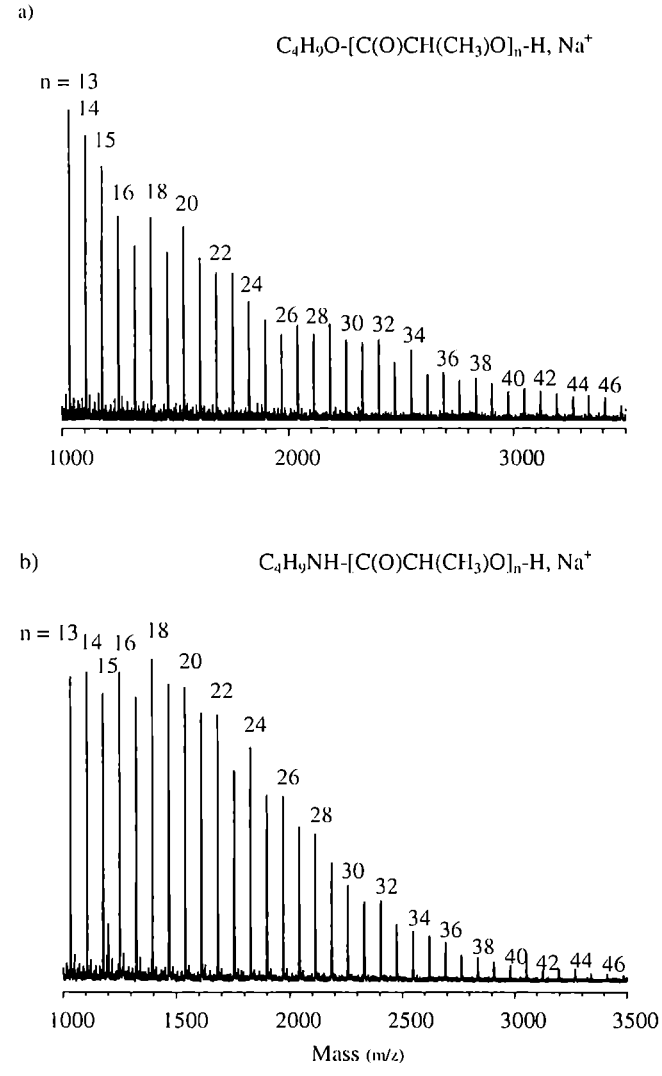


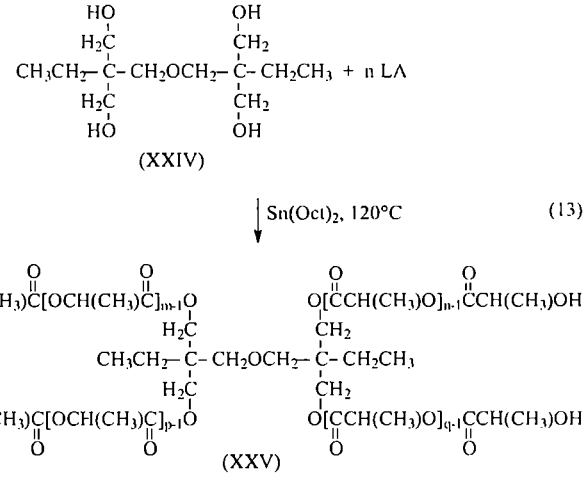
Fig. 3. MALDI-ToF mass spectra (1000—3500 m/z range) of: (a) LA/Sn(Oct)2/BuOH [66] and (b) LA/Sn(Oct)2/BuNH2 [52] reacting mixtures. Conditions of polymerization: $[LA]_0$ = 1.0 mol·L^{-1}, $[Sn(Oct)_2]_0$ = 0.05 mol·L^{-1}, $[BuOH]_0$ = 0.10 mol·L^{-1}, $[BuNH_2]_0$ = 0.12 mol·L^{-1}; THF solvent, 80°C.

The initiation system employing $Sn(Oct)_2$ is particularly useful in preparation of aliphatic polyesters involved in more complex architectures. In Table 3 are collected polymerization conditions and molar mass data, for some of the block and graft copolymers, and star-shaped polymers prepared more recently in our laboratory based on the coinitiators having polyol or polyamine structures [54, 78—80]. All entries in Table 3 exhibit satisfactory agreement between the planned (calculated) and measured molar masses.

It is worth to note that the values of M_n reported in Table 3 were obtained by means of osmometry giving the actual values without respect of the macromolecular architecture.

Another problem related to the application of the multifunctional derivatives as coinitiators is the actual number of alcohol or amino functions starting growth of the polyester chain. This can be solved with combined ^{1}H NMR/Liquid Chromatotography at the Critical Conditions (LC-CC) analysis as it is shown below on the example of a series of polymerization of LA in which mono-, di-, tri-, tetra-, and hexaols were used as initiators [78].

Indeed, agreement of the assumed and resulting molar masses does not necessary mean that all hydroxyl groups in a given polyol have been reacted with $Sn(Oct)_2$ and started growth of the PLA chain. On the other hand, comparison the ^{1}H NMR spectra of DTMP tetraol (XXIV) and star-shaped DTMP-(PLA-OH)$_4$ (XXV), carried out



by us in ref. [78] revealed quantitative transformation of all ...-CH_2-OH hydroxyl functions into the ...-C(O)CH(CH_3)-OH end-groups of the PLA chains (eq. 13).

Moreover, M_n determined from a ratio of the relative intensities of signals corresponding to the main chain and the end-group protons was equal to $8.2 \cdot 10^3$, what is in a good agreement with the value measured by osmometry (Table 3, entry 4). Similar analysis of the ^{1}H NMR spectra, carried out by us for PLA's prepared with DEG, TMP, DPE, and PEHMO, confirmed their two-, three-, six-, and thirteen-arms structure [78].

Table 3. Feed compositions of the polymerization mixtures and molar masses (M_n) of the resulting linear and star-shaped polylactides [54, 78—80]

Entry	Initiating system	$[I]_0$ [f], mol·L^{-1}	M	$[M]_0$, mol·L^{-1}	α [g]	M_n(calcd) [h]	M_n(osm) [i]
1.	$Sn(OBu)_2$ [a]	$1.93 \cdot 10^{-3}$	LA	2.29	0.10	8625	8970
2.	$Sn(Oct)_2$/DEG [b]	$1.56 \cdot 10^{-1}$				7800	9000
3.	$Sn(Oct)_2$/TMP [b]	$1.65 \cdot 10^{-1}$				7400	7800
4.	$Sn(Oct)_2$/DTMP [b]	$1.8 \cdot 10^{-1}$				6900	8800
5.	$Sn(Oct)_2$/DPE [b]	$1.68 \cdot 10^{-1}$				7400	11 300
6.	$Sn(Oct)_2$/PEHMO [b] [c]	$2 \cdot 10^{-1}$	LA	8.4	≈0.99	7420	8300
7.	$Sn(Oct)_2$/DHPBD [a] [d]	$1.61 \cdot 10^{-2}$	CL	2.0	≈1.0	19 330	21 000
8.	$Sn(Oct)_2$/DHPBD [a] [d]	$9.65 \cdot 10^{-3}$	LA	1.0	0.94	19 210	20 900
9.	$Sn(Oct)_2$/PMH [a] [e]	$4.62 \cdot 10^{-3}$	CL	2.0	≈1.0	62 600	61 800
10.	$Sn(Oct)_2$/PMH [a] [e]	$6.3 \cdot 10^{-3}$	LA	1.0	0.94	34 700	34 300
11.	$Sn(Oct)_2$/DAB-Am-8 [a]	$2.33 \cdot 10^{-3}$	CL	2.0	≈1.0	98 700	79 600
12.	$Sn(Oct)_2$/DAB-Am-8 [a]	$1.36 \cdot 10^{-3}$	LA	1.0	0.94	100 000	87 200

[a] THF solvent, 80°C, $[Sn(Oct)_2]_0 = 0.05$ mol·L^{-1}.
[b] Bulk polymerization, 120°C, $[Sn(Oct)_2]_0 = 0.08$ mol·L^{-1}.
[c] $M_n = 1420$. [d] $M_n = 5170$. [e] $M_n = 13200$.
[f] $[I]_0$ stands for starting concentrations of: OBu groups in $Sn(OBu)_2$, polyols, and polyamines.
[g] $\alpha = ([M]_0 - [M])/[M]_0$, as determined from SEC traces.
[h] M_n(calcd) = $M_M \alpha [M]_0/[(co)initiator]_0 + M_I$ (where: M_M and M_I stand for molar masses of monomer and (co)initiator, respectively).
[i] Measured by vapor pressure ($M_n < 3.5 \cdot 10^4$) or membrane ($M_n > 3.5 \cdot 10^4$) osmometry.

Figure 4 shows a series of HPLC traces recorded for R-(PLA-OH)$_x$ bearing 1, 2, 3, 4, and 6 arms and with M_n close to 10^4 (linear Bu-PLA-OH and HO-PLA-DEG-PLA-OH can formally be considered as star-shaped PLA's with 1 or 2 PLA-OH arms). Measurements were carried out at 50°C using critical composition of a mobile phase, established for the linear PLA (*i.e.* dioxane-1,4/*n*-hexane mixture containing 56.25 vol.% of dioxane). As it is clearly seen in Figure 4 elution volumes increase with the number of PLA-OH arms in R-(PLA-OH)$_x$. Such behavior could be explained assuming that strength of the macromolecule — column packing attractive forces increases with the increasing number of PLA arms fitted with the hydroxyl end-groups, which are mostly responsible for these interactions.

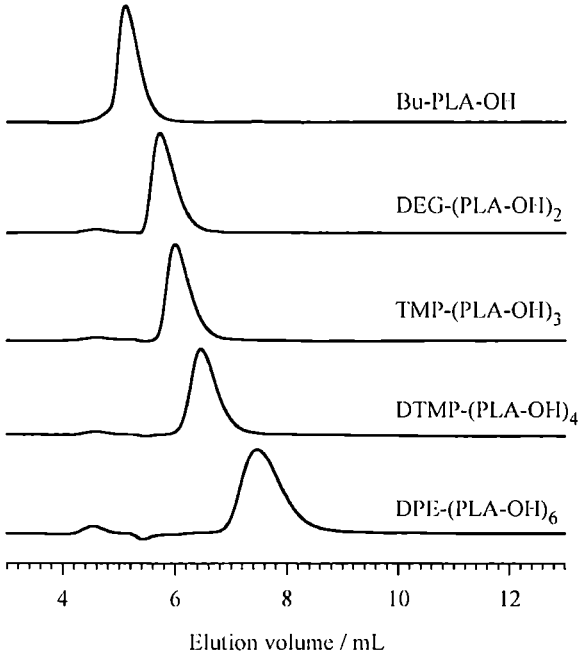


Fig. 4. LC-CC traces of star-shaped poly(L-lactide)s [R-(PLA-OH)$_x$] fitted with various number of PLA arms. Mobile phase — dioxane-1,4/n-hexane mixture containing 56.25 vol.% of dioxane; 50°C [78].

CONCLUSION

Various practically important properties of poly(aliphatic ester)s as a material, for example their degradation rate or thermal and mechanical resistance, can be adjusted by their macromolecular architecture. Results discussed in the present review show that recently macromolecular engineering offered methods for the precise synthesis of poly(aliphatic ester)s having both the predetermined molar masses and the assumed structures. Ring-opening polymerization (ROP) of cyclic aliphatic esters has appeared as a method of choice. Molar mass control reaches at least the level of $M_n \approx 10^6$. Coinitiators/chain transfer agents (polyols, primary polyamines), giving rise of various, sometimes sophisticated, macromolecular structures of the resulting polyesters became available commercially. Also progress in the controlled radical polymerization and in the ring-opening polymerization of the functional monomers gives new diversified possibilities of synthesis of the non-conventional polyols or polyamines.

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