Progress in Polymerization of Cyclic Esters: Mechanisms and Synthetic Applications

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Summary: Recent advances in the controlled ring-opening polymerization of aliphatic cyclic esters are briefly reviewed. Particular attention is paid to the high molecular weight linear, branched, and star-shaped poly(lactide)s and poly(ε-caprolactone) synthesis. It is concluded that despite the plethora of initiating and/or catalytic systems applied for this purpose the best results so far were achieved with Al- and Sn(II) derivatives. Analytical methods employed for aliphatic polyesters of various architectures characterization, including SEC-MALLS, LC-CC, and fluorescence spectroscopy, are also discussed.

Keywords: aliphatic polyesters; controlled polymerization; ε-caprolactone; lactides; star polymers

Introduction

Poly(L-lactide) (PLA) and poly(ε-caprolactone) (PCL), are usually prepared by a ring-opening polymerization (ROP) of the corresponding cyclic monomer: L,L-lactide (LA) and ε-caprolactone (CL). This method provides sufficient polymerization control, giving polymers of the expected molar masses and fitted with the desired end-groups.[1–6] There is also known process providing high molar mass PLA by a direct polycondensation.[7] For the third important aliphatic polyester – poly(β-butyrolactone) (PBL) methods of the controlled ring-opening polymerization of the β-butyrolactone monomer are still developed (see e.g. ref.[8]), but the commercially available PBL is prepared by means of a bacterial synthesis.[9] More recently, it has been shown that a direct CO/propylene oxide copolymerization paves a new way for PBL synthesis.[10]

The ROP of CL and LA can be initiated and/or catalyzed by a large variety of compounds encompassing: alkaline and multivalent metal aliphatic alkoxides (or alkylalkoxides) ($M(OR)_m$) and aryloxides ($M(OAr)_x$), carboxylates ($M(O_2CR')_x$), acetylacetonates ($M(acac)_x$),[1–6] protonic acids,[11–13] carbenes (>C:)[14,15] or enzymes (lipases)[16,17] (Scheme 1).

In some of these initiating systems, except the metal alkoxides, presence of a coinitiator, such as H_2O, aliphatic alcohol (ROH) or primary amine (RNH_2), is required to start the polyester chain growth. Systematic mechanistic and kinetic studies, carried out in our laboratory, have revealed that independently of the initiating system (e.g.: ML_y, ML_y/ROH, ML_y/RNH_2, where L = aliphatic alkoxide, aromatic alkoxide, carboxylate or acetylacetonate ligand) ROP of cyclic esters proceeds with participation of the metal-alkoxide bond as an active species in the monomer insertion process. A dynamic exchange of ligands at the metal atom:

$$ML_y + ROH \rightleftharpoons RO\text{–}ML_{y-1} + LH \quad (1\ (a))$$

$$ML_y + RNH_2 \rightleftharpoons RNH\text{–}ML_{y-1} + LH \quad (1\ (b))$$

provides the actual initiating and then propagating species.[18–24]

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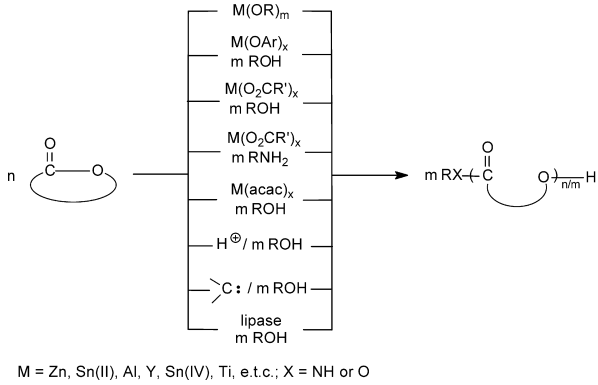


Scheme 1.
Ring-opening polymerization of aliphatic cyclic esters.

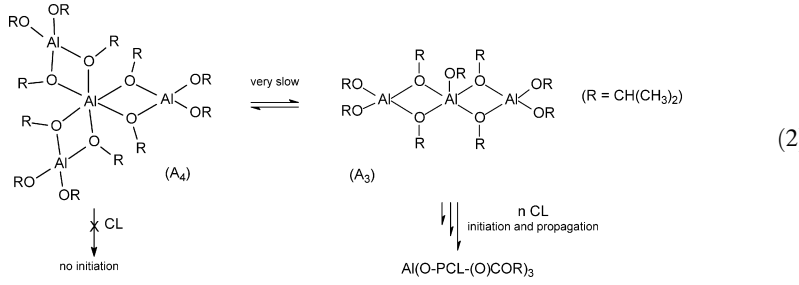
The present paper briefly reviews methods of the controlled synthesis and characterization of PCL and PLA of various architectures elaborated in our laboratory.

Controlled Synthesis of Linear Polyesters

Several initiating and catalytic systems was applied in the linear PCL and PLA synthesis.[1–6] Sometimes the aim of using a new system is not clear; there is no improvement when compared with the existing systems and their only virtue is that nobody was using the same ones. Better studied catalysts, based on Zn, Sn(II), or Al give polymerizations devoid of termination and with strongly depressed transesterification. On the other hand, there is a search of the metal-free catalysts,[11–17] like carbenes or enzymes for the expected application in the biomedical field. However, with the latter catalysts possibilities of molar mass and architecture control are still rather limited. Thus, in the present paper we confine ourselves to discussion of the Al and Sn(II) compounds belonging to the most convenient and versatile initiators of CL and LA polymerizations and investigated in our laboratory.[18–33]

First, we used dialkylaluminum alkoxides (R'_2AlOR) in both synthetic and mechanistic studies. A number of well defined macromolecules with well controlled size and the end-groups was prepared with these initiators.[25–29] As it is seen in Figure 1 (a), we were able to control molar masses of PCL from $M_n \approx 10^3$ up to the values approaching 5×10^5.

After understanding a difference between aluminum *tris*-isopropoxide trimer ($\{Al(O^iPr)_3\}_3$ (A_3)) and tetramer ($\{Al(O^iPr)_3\}_4$ (A_4)) reactivities (cf. Equation (2)), the isolated A_3 has become the most versatile one for the controlled polymerization of cyclic esters, particularly of CL. It provides fast and quantitative initiation, moderately fast propagation ($k_p = 0.6\ L \cdot mol^{-1} \cdot s^{-1}$ comparing to 0.039 $L \cdot mol^{-1} \cdot s^{-1}$ for Et_2AlOEt; 25 °C, THF) and relatively good selectivity (with regard to transesterification).[2,30–33]



(2)

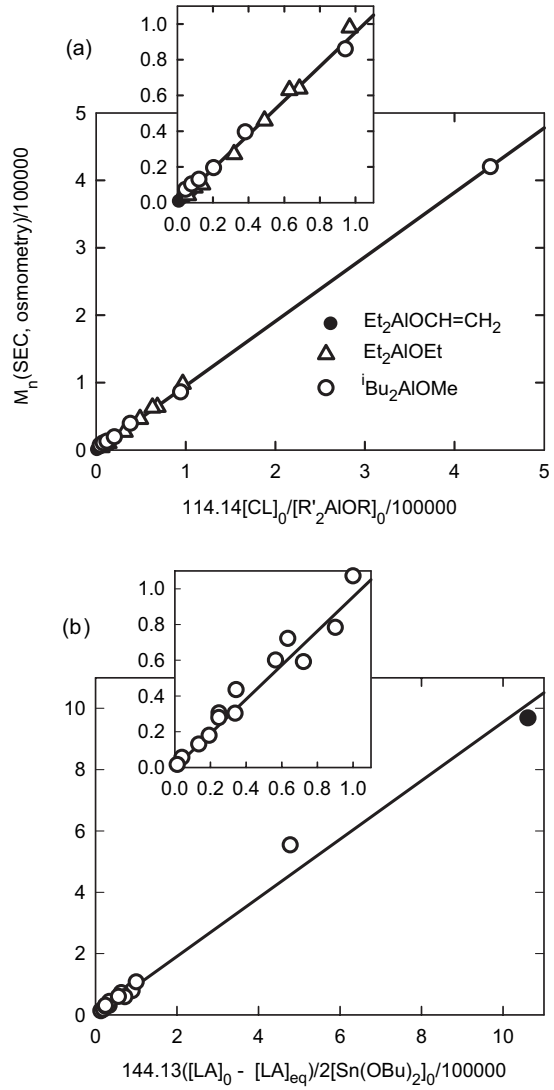


Figure 1.
Dependencies of the measured molar masses versus the calculated values on the basis of the feed composition. Polymerization of: (a) CL initiated with R′$_2$AlOR, THF, 25 °C;[26,35] (b) LA initiated with Sn(OBu)$_2$, (□) THF, 80 °C, (□) bulk, 120 °C.[21]

Thus, Al(O^{i}Pr)$_3$ in the form of A_3 looks to be ideally suited for the synthesis of aliphatic polyesters, since apart from a good selectivity it provides, in contrast to tin octoate (cf. below), a direct control of polymerization degree of the resulting polyester, by simply adjusting the $([LA]_0 - [LA]_{eq})/3[Al(O^iPr)_3]_0$ ratio. On the other hand, it looks that there is an upper limit of M_n ($\approx 3 \times 10^5$) of PLA and PCL which can be obtained with Al(O^{i}Pr)$_3$,[31,34] whereas with Sn(OBu)$_2$-$M_n \approx 10^6$ has been reached (see Figure 1 (b)).[21] Reasons of such a limitation are not yet well-understood.

Tin octoate [Sn(O(O)CCH(C_2H_5)C_4H_9)$_2$, tin(II) 2-ethylhexanoate, denoted further as Sn(Oct)$_2$] is probably the most often used

(co)initiating compound in the polymerization of cyclic esters.[1–6] This is mostly due to its commercial availability, physical state (liquid), and higher chemical stability in comparison with the alkoxides. $Sn(Oct)_2$ is not an initiator as such and starts the polyester chain growth only when reacted with coinitiator bearing hydroxyl or primary amino group (Equations 1, L = O(O)CCH(C_2H_5)C_4H_9).[18–24] Resulting in this reaction –SnOR or –SnNHR groups initiate polymerization; –SnNHR group is also converted into the –Sn$O(CH_2)_5$C(O)NHR or –SnOCH(CH_3)C(O)OCH(CH_3)C(O)NHR alkoxide species after the first monomer insertion (CL or LA, respectively). Thus, eventually the tin(II) alkoxide species carry the kinetic chain like any other metal alkoxide. The number average degree of polymerization (DP_n) of the polyester formed in the cyclic ester (M)/$Sn(Oct)_2$/coinitiator systems is given by the $([M]_0 - [M])/[\text{coinitiator}]_0$ ratio due to the initiation and fast exchange reactions: the chain transfer to water, alcohol, amine and then to the resulting macroalcohol.

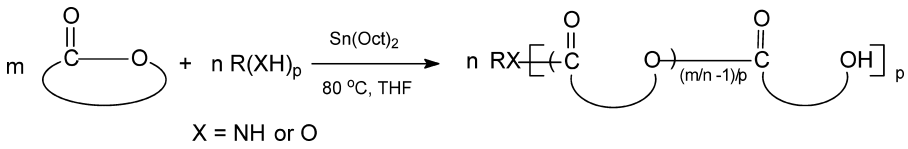
In the case of polymerization carried out with ''pure'' $Sn(Oct)_2$ the polyester chain growth is coinitiated with impurities, adventitiously present in $Sn(Oct)_2$ and in monomer. Using the standard high vacuum technique and $Sn(Oct)_2$ of 99.0 mol-% purity we were able to obtain both PCL and PLA in M_n range from 1.2×10^5 to $\approx 9 \times 10^5$ depending on the monomer and $Sn(Oct)_2$ concentrations in the feed.[18,20,22,35] Thus, $M_n \approx 10^6$ looks to be a limit of M_n of the aliphatic polyesters prepared by the ring opening polymerization, and is related to the impurities concentration level. Similar threshold value ($M_v \approx 9 \times 10^5$) has been already reported by Pennings et al.[36] some time ago.

More recently, a concept of *single-site* initiators, bearing bulky bidendate phenoxide or imidate ligands, has thoroughly been explored,[5,37–41] among others, in order to avoid the mechanistic complexity resulting from the aggregation-deaggregation exchange reactions, in which *multiple-site* alkoxides are usually engaged.[28–31] These exchange processes were studied for the relatively high total concentrations of active sites, close to room temperature. If we take into account that the actual polymerization process is conducted at concentration of active species as low as 10^{-3}–10^{-4} $\text{mol} \cdot \text{L}^{-1}$ and at elevated temperatures (> 100 °C), then the ''multiple-site'' species are becoming to behave as the ''single-site'' at these conditions. The single-site initiators explored until now do not show any particular advantage over the multiple-site ones with regard to the molar mass or end-group control. On the other hand, some of these derivatives were successfully applied in a stereocontrolled polymerization of racemic and meso lactide (see e.g. our paper[23] and references cited therein). An important result has been obtained recently with an initiator studied in our laboratory. When $\{Al(O^iPr)_3\}_3$ was reacted with the bidendate Schiff's base, (*S*)-(+)-2,2′-[1,1′-binaphtyl-2,2′-diylbis(nitrylomethilidyne)]diphenol, then the bulky ligand around the Al atom practically eliminated transesterification from LA homo- and copolymerization. Similar phenomenon was also reported for CL polymerization, when dendrons have been put around Al atom.[42] These both results are in agreement with our earlier observations showing that increase of the bulkiness of ligands located at the Al-alkoxide species leads to the depression of transesterification.[43]

Controlled Synthesis of Star-shaped Polyesters

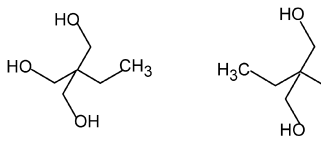
Star-shaped polymers, bearing strictly defined number of linear arms provide useful models for studies of the branched macromolecular structures. In a dynamically growing area of biocompatible and biodegradable polymers, synthesis and characterization of star-shaped aliphatic polyesters are particularly advanced.[44–54] Perhaps, the most commonly used method for the synthesis of star-shaped polymers is based on the ''core first'' approach in which a multifunctional reagent (a core) plays a role of coinitiator and/or transfer agent. Particularly useful for this purpose is initiating system employing $Sn(Oct)_2$. A structure of polyol or polyamine, used as

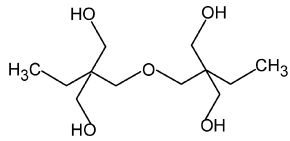
a core, directly determines the architecture of the polyester macromolecules. Structures shown below give examples of cores applied by us for synthesis of the branched and star-shaped PCL's and PLA's.[24,55–59]

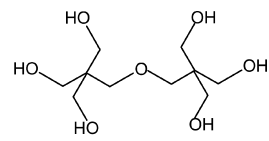


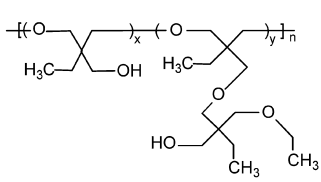
(3)

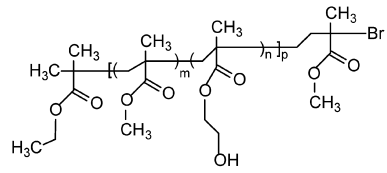
Typical molar mass characteristics of the star-shaped PCL's and PLA's, prepared firmed quantitative transformation of the core hydroxyl or amino groups into the polyester arms end-groups:[24,56,58,59]

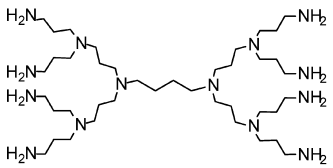

(TMP)

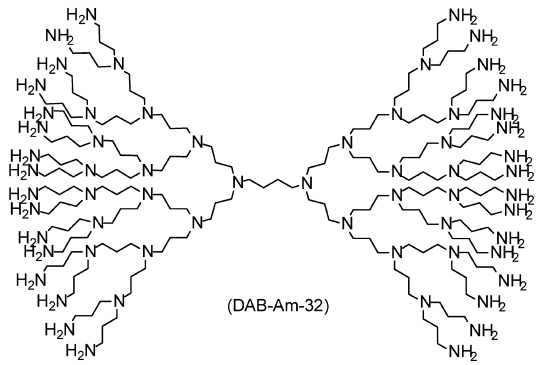

(DTMP)


(DPE)


(PEHMO)


(P(MMA-*co*-HEMA))


(DAB-Am-8)


(DAB-Am-32)

M_n's of the resulting polyesters, for all of the monomer/core/$Sn(Oct)_2$ polymerizing systems studied by us, were controlled by the ratio of concentration of the consumed monomer and that of the coinitiator/transfer agent in the feed, similarly as in the synthesis of linear polyesters. Moreover, for all branched and star-shaped polymers bearing linear arms short enough ($DP_n \leq 100$) the ^{1}H NMR analysis consistent with DAB-Am-8 and DAB-Am-32 cores, are shown in Table 1.

Although there is a certain scatter of the experimental M_n's determined from SEC, osmometry, and ^{1}H NMR these values are in a good agreement, within the usual experimental error, with the theoretically predicted molar masses (M_n(calcd)). Dispersities (M_w/M_n) are typically well below 1.10 and point to a narrow molar mass

Table 1.
Comparison of molar masses of the star-shaped PCLs and PLAs determined by SEC-MALLS, osmometry, and ^{1}H NMR[a)].[24]

Dendrimer Monomer	$([M]_o - [M]_{eq})/[DAB]_o$	M_n[b)] (calcd)	M_n[c)] (osm.)	M_n (NMR)	M_n[d)] (SEC)	M_w/M_n[d)] (SEC)
DAB-Am-8 CL	858	98700	79600	79000	114000	1.04
DAB-Am-32 (L,L)-LA	2075	302600	253600	285000	376900	1.02
DAB-Am-32 CL	2607	301100	230200	287500	373000	1.05
DAB-Am-32 (D,D)-LA	2051	299100	208100	291000	356400	1.03

a) $[LA]_o = 1.5$ mol L^{-1}, $[CL]_o = 2.0$ mol L^{-1}, $[Sn(Oct)_2]_o = 2 \times 10^{-3}$ mol L^{-1}, THF solvent, 80 °C.
b) $M_n(calcd) = M_M ([M]_o - [M]_{eq})/[DAB]_o + M_{DAB}$.
c) High-speed membrane osmometry.
d) Multiangle laser light scattering (MALLS) detector.

distribution resulting from the living character of the involved polymerization process. It has to be reminded, however, that linear arms of a given $(M_w/M_n)_{arm}$ located at a core lead to star macromolecules having lower $(M_w/M_n)_{star}$, in comparison with $(M_w/M_n)_{arm}$, as it stems from Equation (4),

$$(M_w/M_n)_{star} = 1 + \frac{(M_w/M_n)_{arm} - 1}{x} \cdot \frac{(M_{n(star)} - M_{core})^2}{(M_{n(star)})^2} \quad (4)$$

where x denotes the number of arms in one macromolecule.[60] Moreover, kinetic data reported in ref. 24 show that DAB-Am-32 polyamine dendrimer and $BuNH_2$ coinitiate CL polymerization, giving similar polymerization rates when calculated per one NH_2 (1.7×10^{-4} vs. 1.4×10^{-4} s^{-1}, respectively), under the otherwise identical conditions: $[LA]_0 = 1.0$ mol · L^{-1}, $[Sn(Oct)_2]_0 = [NH_2]_0 = 0.05$ mol · L^{-1}, THF, 80 °C. This result strongly suggests that all NH_2 groups in DAB-Am-32 take part in the polymer chain growth, resulting eventually in the regular, 32-arm star-shaped polyester architecture.

Another proof, based on the Stockmayer-Zimm theory,[61,62] showing that indeed the n-functional core provides the n-arm star-shaped polyester comes from a comparison of the conformation plots obtained for the PLA's prepared by means of BuOH and DPE coinitiated polymerizations (Figure 2).

Equations shown below, relating the branching ratios ($g_M = RMS_{branched}/RMS_{linear}$) with the number of arms (f):

$$g_M = 6f/[(f+1)(f+2)] \quad (5)$$

$$g_M = (9f-3)/[(f+1)(2f+1)] \quad (6)$$

have been proposed for stars having arms with arbitrary chosen molar mass dispersities: $M_w/M_n = 2$ or 1.5 (Equations (5) or (6), respectively).[62] The example illustrated in Figure 2 gives $g_M = 0.63$ and then $f = 6.2$ or 5.1 being not far from the value assumed for the six-functional initiator ($f = 6$).

As shown above, simple SEC analysis with MALLS detector can be used for a direct determination of the number of arms in the star-shaped polymers. This method, although fast and convenient, can only be employed for analysis of polymers of the uniform architecture and of high enough

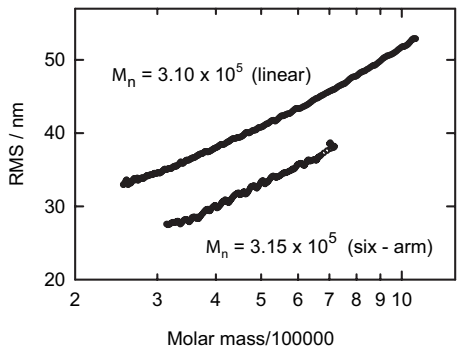
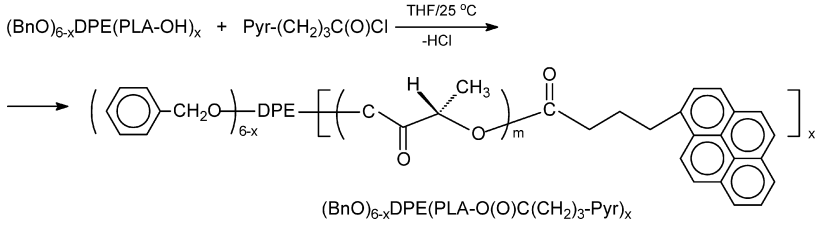


Figure 2.
Conformation plots [the Root Mean Square (RMS) radius versus the molar mass] for linear and star-shaped six-arm PLA's (both of $M_n \approx 3 \times 10^5$) obtained from SEC-MALLS measurements. Polymerization conditions: $[LA]_0 = 2.0$ mol · L^{-1}, $[Sn(Oct)_2]_0 = 10^{-3}$ mol · L^{-1}, THF, 80 °C; BuOH (linear PLA) and DPE (six-arm PLA) employed as coinitiators.[35]

molar masses (radius of gyration should be higher than 10 nm because of the MALLS detector limit). This is because polymers with different architectures usually have different hydrodynamic volumes for a given molar mass. On the contrary, Liquid Chromatography at the Critical Conditions (LC-CC) behavior is very sensitive to the macromolecular architecture and to the presence and concentration of functional groups attached to the macromolecules.[55,56,59,63–65] Figure 3 shows an example of the LC-CC analysis of the equimass mixture of a series of PLA's [$(BnO)_{6-x}$DDPE(PLA-OH)$_x$, $x = 1$–6)] bearing from 1 to 6 linear PLA arms linked to the corresponding cores.[59]

As expected the elution volumes increased monotonically with the increasing number of PLA-OH arms in one macromolecule and were independent on the given PLA molar mass due to the critical conditions and the separation conditions were good enough to discriminate macromolecules of various architectures in their mixture.

Thus prepared and characterized PLA's were quantitatively functionalized by us with pyrenyl end-groups:[58]



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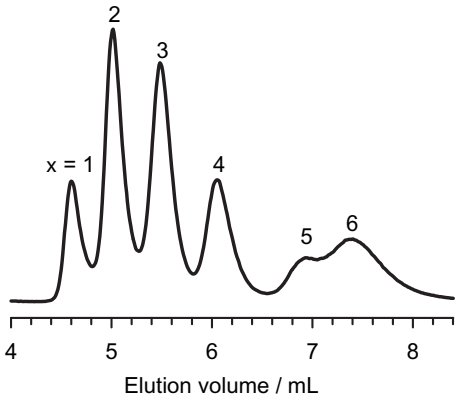

Figure 3.
LC-CC trace of equimass mixture of star-shaped PLA's [$(BnO)_{6-x}$DPE(PLA-OH)$_x$, $x = 1-6$] of $M_n \approx 1.25 \times \times 10^4$.[59]

Then, internal dynamics and mobility of the PLA chains in THF solution at 25 °C, with regard to the number of PLA arms in one $(Bn)_{6-x}$DPE(PLA-O(O)C$(CH_2)_3$-Pyr)$_x$ macromolecule and the individual arm DP_n, was followed by fluorescence spectroscopy. Analysis of both, static and time-resolved spectra of the star-shaped PLA's revealed dynamic segmental motion resulting in end-to-end cyclization, accompanied by an excimer formation. Probability and rate of the latter reaction increased with increasing number of arms and with decreasing their DP_n. Moreover, time-resolved measurements revealed that for macromolecules containing few (i.e. 2 or 3) arms the pyrene moieties are located in the interior of the star-shaped PLA's, whereas in the instance of the higher number of arms (4–6) they are located at the periphery of the star-shaped PLA's. Thus, increasing the number of arms leads to their stretching away from the center of the star-shaped macromolecule.

Conclusions

Properties of aliphatic polyesters, for example their degradation rate or thermal and mechanical resistance, can be adjusted by macromolecular architecture. Results discussed in the present paper show that macromolecular engineering offers efficient methods for the precise synthesis of aliphatic polyesters with predetermined

molar masses and of the assumed architecture. These methods employ, among others, the ring-opening polymerization of cyclic aliphatic esters as a powerful synthetic tool. Molar mass control reaches the level of $M_n \approx 10^6$. Coinitiators/chain transfer agents (polyols, primary polyamines), giving rise of various macromolecular structures of the resulting polyesters, became available commercially.

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