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Amines as (co)initiators of cyclic esters' polymerization*)

Summary — A review reports on application of amines as (co)initiators in the ring-opening polymerization of aliphatic cyclic esters. First, the use of tertiary amines (R_3N) as initiators of the controlled polymerization of highly strained, four-membered β-lactone (β-propiolactone, PL) is described [equation (1)]. Then attempts at the high temperature polymerizations of the medium strained, six- and seven-membered δ- and ε-lactones initiated with primary amines (RNH_2) or α-amino acids are briefly discussed. Finally, it is shown in more detail that the best results have been obtained recently in the processes catalyzed additionally with tin(II) octoate [$Sn(Oct)_2$]. Mechanisms of these polymerizations are also discussed. Results of the kinetic studies [equation (9) and (10)] as well as ^1H NMR, MALDI TOF mass spectrometry, and size exclusion chromatography (SEC) measurements, carried out in the authors' laboratory, indicate that polymerizations of ε-caprolactone (CL) or L,L-lactide (LA) initiated with $RNH_2/Sn(Oct)_2$ fulfill living process criteria and therefore allow to fully control the syntheses of the corresponding polymers. The selected syntheses applications, such as preparation of the copolymers *N*-carboxyanhydrides of α-aminoacids and LA [equation (7)] or star-shaped polymers based on polyamino dendrimers [formula (I) and (II)] are also described.

Key words: ε-caprolactone, L,L-lactide, β-lactones, α-amino acids, amines, tin(II) octoate, ring-opening polymerization, aliphatic polyesters, star-shaped polymers.

The most prominent synthetic aliphatic polyesters, namely poly(L-lactide) (PLA) and poly(ε-caprolactone) (PCL) are usually prepared by ring-opening polymerization (ROP) of the corresponding cyclic monomers: L,L-lactide (LA) and ε-caprolactone (CL). This method provides sufficient polymerization control, giving polymers of the required molecular weights and fitted with the desired end-groups. For the third important aliphatic polyester — poly(β-butyrolactone) — methods of the controlled ring-opening polymerization are not available yet. It is mostly prepared by means of a bacterial synthesis. The resulting polymers find a wide application range: from specialty biomedical polymers to high-tonnage commodity thermoplastics [1].

Concerning synthesis of PCL and PLA there is a variety of compounds initiating polymerization of the corresponding cyclic ester monomers. These initiators encompass: alkaline and multivalent metal alkoxides and carboxylates [2—8], metal free carbenes [9] or enzymes [10, 11]. The best control of cyclic esters polymerization has eventually been reached with multivalent metal alkoxides and carboxylates as (co)initiators. This is described in a series of papers coming from our laboratory (see refs. [12-21] and literature cited therein).

More recently, it has been reported that in tin(II) 2-ethyl hexanoate {tin octoate [$Sn(Oct)_2$]} initiated polymerization of cyclic esters primary amines can serve as effective coinitiators [22—24]. Also polymerization of CL initiated by natural amino acids at elevated temperature has been reported [25]. These observations open new possibilities, *e.g.* in the synthesis of polypeptide-poly(aliphatic ester) block copolymers or star-shaped copolymers on the basis of polyamino dendrimers.

Various practically important properties of poly(aliphatic ester)s such as solution or melt viscosity, degradation rate or mechanical and thermal parameters can be adjusted by the macromolecular architecture (topology). Particularly interesting properties are provided by the branched or star-shaped polymers, which can be prepared with the multifunctional initiators/chain transfer

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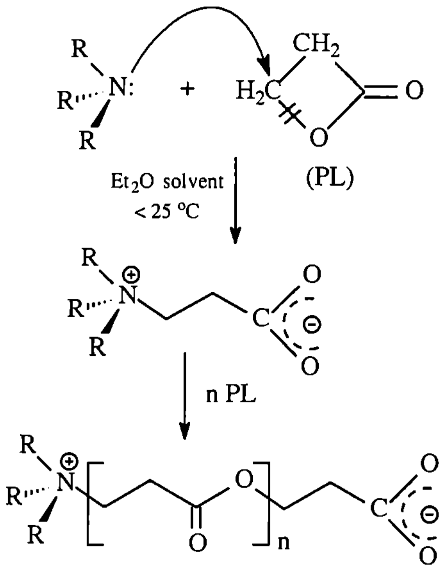
agents. In the cyclic esters polymerization the polyols were most often used for this purpose (see *e.g.* refs. [26-31]). However, availability of the soluble polyols enabling control of molecular weights of the prepared star-shaped polyesters is rather limited. This was one of the reasons that we decided to check a possibility of using for a similar purpose another class of multifunctional reagents — polyamine dendrimers fitted with terminal amino groups able to coinitiate [in the presence of $Sn(Oct)_2$] polymerization of cyclic esters [32].

The present paper summarizes briefly application of amines as (co)initiators of cyclic esters polymerization.

DIRECT INITIATION OF CYCLIC ESTERS POLYMERIZATION WITH AMINES

Early studies of ROP of highly strained β-lactones revealed that a tertiary amine (R_3N) reacting with a monomer at ambient temperature gives in the initiation step [equation (1a)] the corresponding betaine [33—35], *e.g.*:

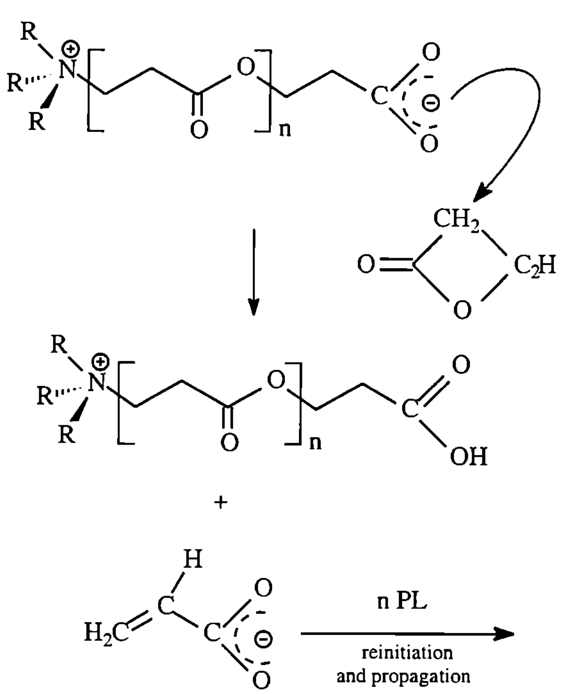


(1a)

(1b)

(PPL)

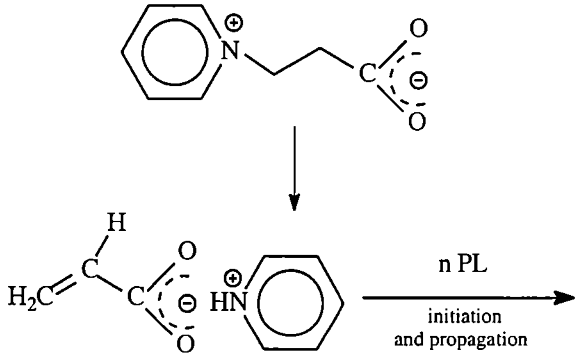
Then, initiation is followed by propagation [equation (1b)] in which carboxylate anion, playing a role of active species, attacks β-carbon atom in the lactone ring with alkyl-oxygen bond scission and reformation of the carboxylate anion. End-group analysis, *e.g.* by means of ^1H NMR, confirmed the zwitterionic structure of the growing macromolecules [36, 37]. Number-average molecular weights (M_n) of the resultant polyesters did not exceed 10^4. Further, more systematic studies of anionic polymerization of β-lactones have shown that independently on a structure of the initiator used propagation proceeds eventually on the carboxylate species [4—7]. However, propagation in the tertiary amine initiated polymerization can be accompanied by a proton abstraction side reaction leading to chain transfer [(equation (2)] [38]:



(2)

On the other hand, α,α'-disubstituted β-lactones are devoided of this side reaction and were claimed to polymerize in agreement with a living polymerization scheme [3]; although anionic polymerization of non-substituted β-propiolactone fulfills also, in the properly chosen conditions, living process criteria [39].

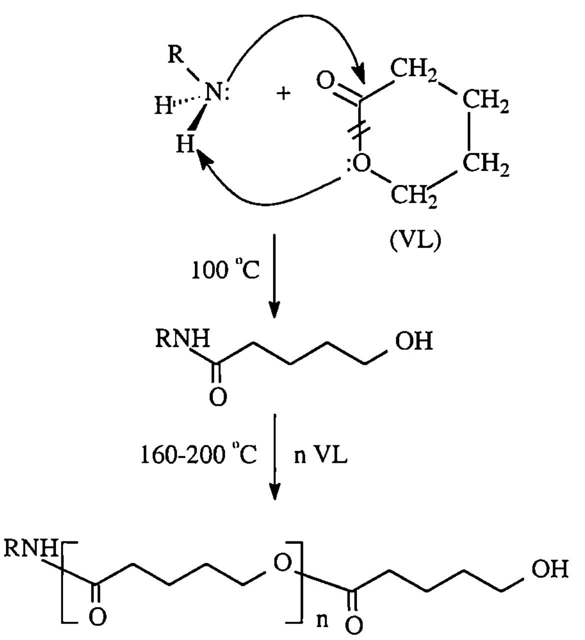
^{1}HNMR studies of the pyridine initiated ROP revealed possibility of another side reaction — Hofmann degradation followed by chain transfer to monomer [equation (3)] [40]:



(3)

Thus, the initial hopes related to a possibility of the controlled polymerization of β-lactones have failed. Only when crown ethers or cryptands, complexing alkali metal counterions, were applied in the carboxylate initiators, high molecular weight poly(β-propiolactone) (PPL) with controlled end groups and $M_n \approx 10^5$ was successfully prepared [4—7, 39, 41].

Larger ring, medium strained lactones, such as δ-valerolactone (VL) or ε-caprolactone (CL) do not undergo ring-opening reaction with tertiary amines. However, direct reaction of primary amines (RNH_2) is quite

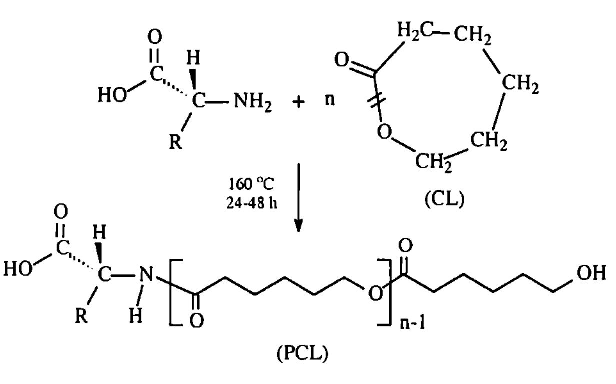

(4a)

(4b)

facile at elevated temperature (>100 °C) and yields the corresponding α,ω-hydroxyamide quantitatively [equation (4a)]. Further propagation proceeds on the resulting hydroxide groups as active species, but non-catalyzed polymerization requires higher temperature reaching 200 °C [equation (4b)] [42, 43].

The exclusive acyl-oxygen bond scission in this kind of polymerization is typical also for other anionic or covalent (of pseudoanionic character) polymerizations of six- or higher-membered ring lactones, contrary to the four-membered ones in which rather alkyl-oxygen bond scission dominates [4—8].

More recently, ROP of CL initiated with natural amino acids (*e.g.*: L-alanine, phenyl alanine or leucine) has been reported [equation (5)]. Namely, polymerization carried out at 160 °C gave poly(ε-caprolactone) with M_n up to $2.3 \cdot 10^4$ bearing amino acid residue and hydroxyl group as chain-ends [25].


(5)

R = CH_3, $PhCH_3$, $CH_2CH(CH_3)_2$

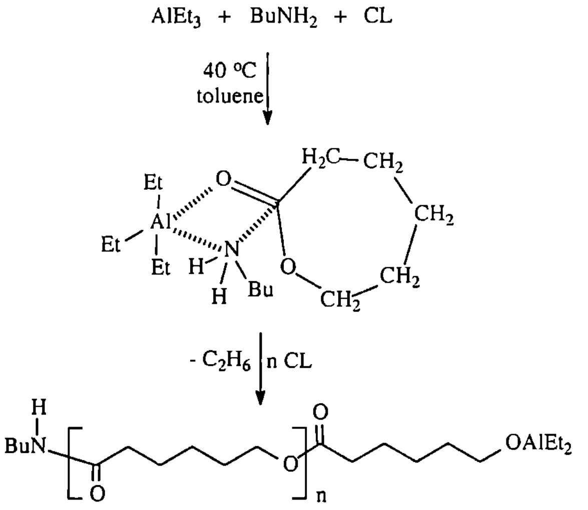
Polymerization degree was controlled by the monomer and amino acid concentrations ratio in the feed as confirmed by the ^1H NMR and size exclusion chromatography (SEC) measurements of the isolated polymers (PCL).

CATALYZED POLYMERIZATION OF CYCLIC ESTERS INITIATED WITH AMINES

As it has been described in the preceding section amines are able to initiate controlled polymerization of medium-strained cyclic esters, but in order to obtain reasonable polymerization time and quantitative yield temperature above 150 °C is required. Moreover, the reported molecular weights were limited and never exceeded $\overline{M}_n = 3 \cdot 10^4$. We show below that applications of coinitiator/catalyst (amine) systems with coinintiators such as triethylaluminum ($AlEt_3$) or tin(II) octoate [$Sn(Oct)_2$] allow to decrease polymerization temperature, increase molecular weights of the resulting polyesters, and govern perfect control (M_n, end groups) of the polymerization due to the living process conditions.

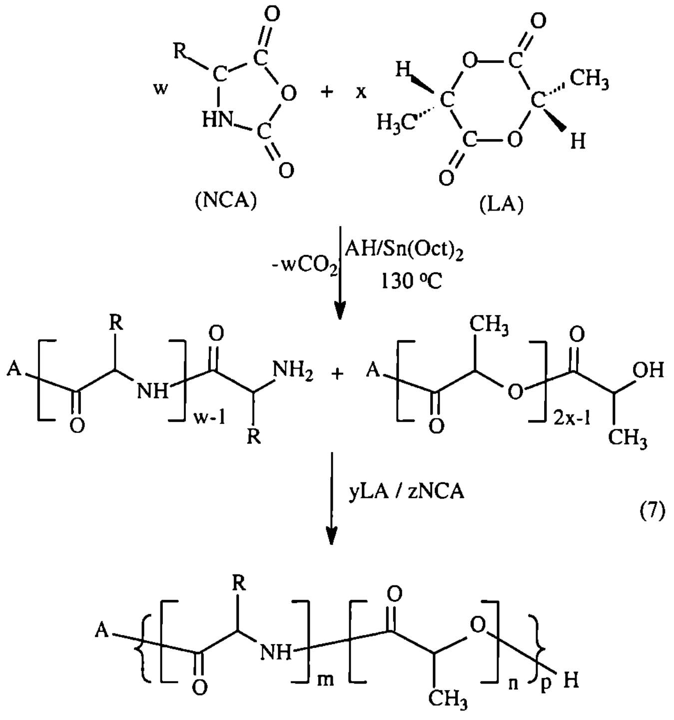
In one of the first attempts of the catalyzed, amine initiated polymerization of CL the $AlEt_3$/butylamine ($BuNH_2$) system was applied.

IR and ^1H NMR spectra analysis of the isolated PCL has supported a coordination-insertion polymerization mechanism with the selective rupture of the acyl-oxygen of CL monomer [equation (6)]. Polymerization proceeded in a controlled way at ambient temperature in a manner typical for dialkylaluminum monoalkoxide active species [44]. However, application of this approach looks to be limited to a synthesis of telechelic CL oligomers ($M_n \leq 10^4$) because of the relatively low polymerization rate.


(6)

Catalysis with $Sn(Oct)_2$ enabled synthesis of the random and block copolymers of *N*-carboxyanhydrides of α-aminoacids (NCA) and L,L-lactide (LA), containing peptide bonds in the main chain [equation (7)].

Derivatives containing free carboxylic acids in side chains were prepared by debenzylation (H_2/Pd/charcoal) of their protected precursors [45].



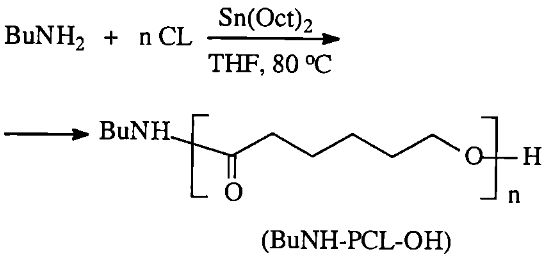
(7)

AH = R'OH or R'NH$_2$, where R' — any alkyl radical,
R = PhCH$_2$OC(O)CH$_2$CH$_2$ or PhCH$_2$

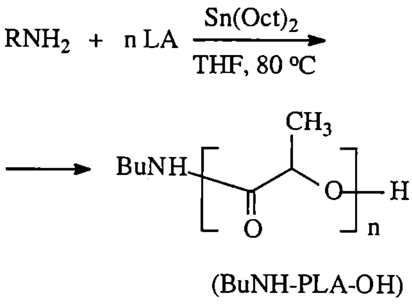
The best results have been achieved for phenylalanine derivative, containing chemically stable pendant group, for which M_n was controlled by the comonomers to initiator (AH) initial concentrations ratio. M_n was the linear function of comonomers conversion pointing out to the living polymerization mechanism; low dispersity indexes (M_w/M_n = 1.10) of the copolymer supported the latter conclusion. On the other hand, higher conversions (≈90 %) for the copolymers showing moderate molecular weights ($M_n < 10^4$) required relatively long reaction time (72 h) at 130 °C [45].

In the alternative approach of LA/NCA block copolymer synthesis, polymerization of LA was initiated with t-BuOC(O)NHCH$_2$CH$_2$OH/ZnEt$_2$ (2:1) mixture; the resulting BuOC(O)NHCH$_2$CH$_2$O-PLA-OH was deprotected with trifluoroacetic acid giving amino-terminated PLA (H$_2$N-CH$_2$CH$_2$O-PLA-OH) used eventually as the macroinitiator of NCA polymerization [46].

More recently, we have decided to study the mechanism of CL and LA polymerizations initiated with Sn(Oct)$_2$/BuNH$_2$ system [32]. MALDI TOF and ^{1}H NMR spectra of the reacting mixtures showed exclusive presence of signals corresponding to C$_4$H$_9$NH-[C(O)(CH$_2$)$_5$O]$_n$-H and C$_4$H$_9$NH-[C(O)CH(CH$_3$)O]$_n$-H chains. Moreover, it has been shown that molecular weights of the polyesters are controlled by monomers and BuNH$_2$ coinitiator concentrations in the feed, *i.e.* that every molecule of BuNH$_2$ initiates the growth of exactly one polyester chain. Thus, the starting amine is transformed into the amido tail end-group and polymerizations of CL and LA proceed according to the following net equations:



(8a)



(8b)

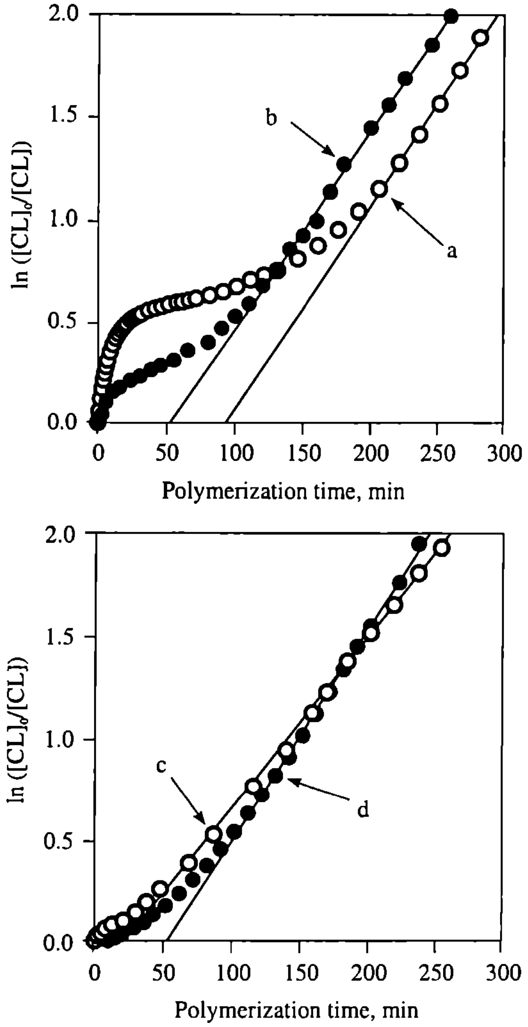
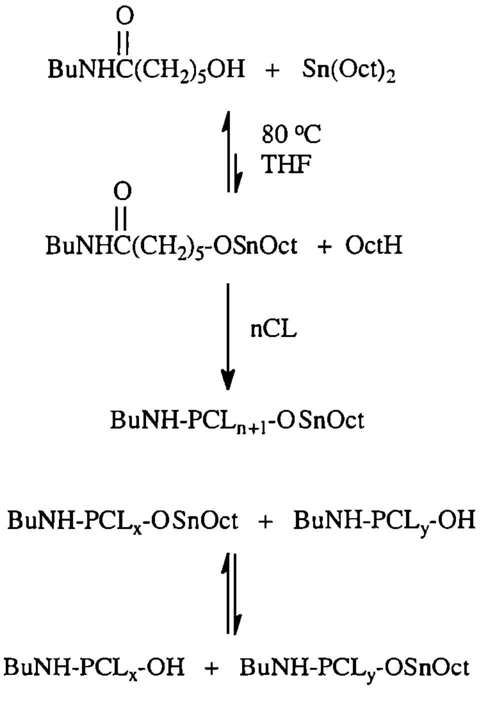


Fig. 1. First-order kinetic dependencies for CL polymerization initiated with Sn(Oct)$_2$/primary amine mixture. Conditions: $[CL]_0$ = 2 mol L^{-1}, $[Sn(Oct)_2]_0$ = 0.05 mol L^{-1}, $[NH_2]_0$ (in mol L^{-1}) = 0.40 (a), 0.18 (b), 0.05 (c, d); amine: C$_4$H$_9$NH$_2$ (a—c), DAB-Am-32 (d); THF solvent, 80 °C [32] [DAB-Am-32 — polyamine dendrimer, see table 1 and structure (II)]

After determining the structures of the polyester chains formed in CL or LA/$Sn(Oct)_2$/$BuNH_2$ system we studied the kinetics of these processes. The results obtained are presented above in the semilogarithmic coordinates on the example of CL polymerization. In the plots obtained for CL monomer (Fig. 1) three, kinetically distinguishable polymerization steps are clearly seen. The first one corresponds to the maximum rate (r_p = $-d[CL]/[CL]dt = \{\ln([CL]_0/[CL])\}/\Delta t$) of CL monomer consumption. Concentration of monomer reacted in this step is approximately proportional to the initial concentration of $BuNH_2$ ($[BuNH_2]_0$). On the basis of the latter observation we assumed that the polymerization starts from a direct reaction between CL and $BuNH_2$ [equation (8a), n = 1].

Thus, after the first step is completed, the initial mixture $Sn(Oct)_2/BuNH_2$ is converted into $Sn(Oct)_2/BuNHC(O)(CH_2)_5OH$ mixture and in principle is equivalent to the already studied by us $Sn(Oct)_2/ROH$ [where ROH = $BuNHC(O)(CH_2)_5OH$] system in which carboxylate-alkoxide ligands exchange reaction takes place [equation (9a)] [47, 48]. The resulting tin(II)-alkoxide species initiate polymerization and then propagation proceeds [equation (9b)]. Finally, the chain-transfer reaction provides $BuNH\text{-}[C(O)(CH_2)_5O]_n\text{-}H$ chains [equation (9c)].



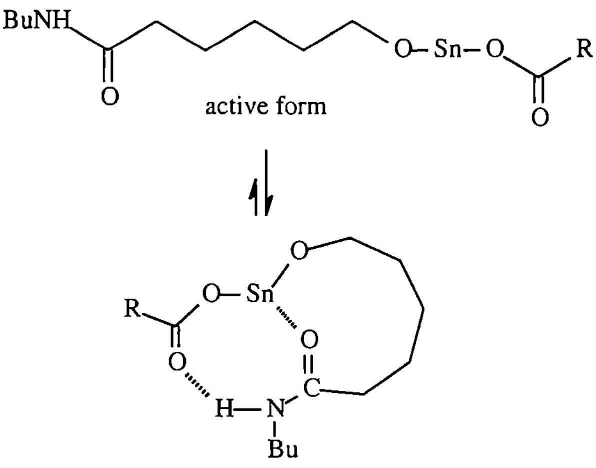
$$\mathrm{BuNH\overset{\overset{O}{\|}}{C}(CH_2)_5OH + Sn(Oct)_2} \xrightleftharpoons[\text{THF}]{80\,^{\circ}\text{C}} \mathrm{BuNH\overset{\overset{O}{\|}}{C}(CH_2)_5\text{-}OSnOct + OctH} \quad (9a)$$

$$\mathrm{BuNH\overset{\overset{O}{\|}}{C}(CH_2)_5\text{-}OSnOct} \xrightarrow{n\mathrm{CL}} \mathrm{BuNH\text{-}PCL_{n+1}\text{-}OSnOct} \quad (9b)$$

$$\mathrm{BuNH\text{-}PCL_x\text{-}OSnOct + BuNH\text{-}PCL_y\text{-}OH} \rightleftharpoons \mathrm{BuNH\text{-}PCL_x\text{-}OH + BuNH\text{-}PCL_y\text{-}OSnOct} \quad (9c)$$

However, after the relatively fast initial period the polymerization slows down and the higher is $[BuNH_2]_0$ the observed retardation effect is more pronounced (Fig. 1, curves a, b, and c). We tentatively ascribe this kinetic effect to formation of the amide/tin alkoxide cyclic complex, as depicted in equation (10).

Tin(II) eagerly assumes tricoordinate pyramidal structure employing its empty *p*- or *d*-orbitals [49, 50].



(10)

dormant species

$R = CH(C_2H_5)C_4H_9$

Presumably, tin(II)-alkoxide bond in the intramolecularly coordinated species, comparing with the non-coordinated ones, is more hindered and thus much less susceptible towards coordination with the forthcoming monomer. The „key-lock" structure of the dormant species was proposed by us on the basis of *ab initio* and DFT molecular orbital calculations carried out using 8-Opteron PC cluster and Gaussian 03 program.

This kind of coordination is also, at least potentially, possible *via* intermolecular reaction. Since $[Sn(Oct)_2]_0$ is relatively low, and equilibrium in equation (9a) is shifted to $Sn(Oct)_2$ side, probability of the bimolecular coordination is substantially lower then the unimolecular one, enhanced by the anchimeric assistance effect.

For oligomeric and then polymeric α-amido-ω-hydroxyl $\{BuNH[C(O)(CH_2)_5O]_n\text{-}SnOct\}$ chains the active-dormant species equilibrium becomes more shifted to the linear, active species side with increasing polymerization degree and the retardation effect becomes less important. Therefore, the polymerization accelerates and eventually its rate (r_p) becomes constant (third step). Thus, in principle, we should expect the final r_p's identical with those obtained for CL/$Sn(Oct)_2$/BuOH system [47] under the otherwise identical conditions. Actually, r_p's determined in the present paper are up to four times lower then expected. This result suggests that intermolecular complexation cannot be completely neglected.

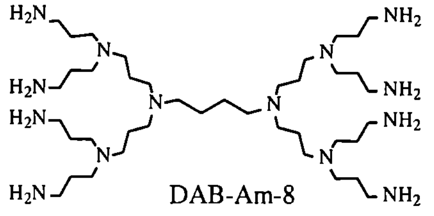
SYNTHESIS OF STAR-SHAPED POLYESTERS WITH POLYAMINE DENDRIMERS AS COINITIATORS

Kinetic data reported in Fig. 1 (curve d, filled points) show that the DAB-Am-32 polyamine dendrimer is able to coinitiate CL polymerization, giving r_p's similar to those determined for $BuNH_2$. This result strongly suggests that all NH_2 groups in DAB-Am-32 take part in the polymer chain growth, giving eventually the regular, star-shaped polyester. The latter conclusion was sup-

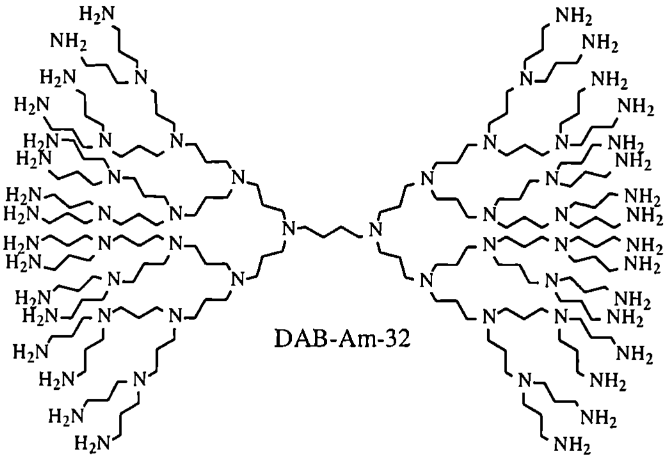
T a b l e 1. Comparison of M_n values of star-shaped PCL determined by SEC-MALLS, osmometry, and ^{1}H NMR[a] [32]

Dendrimer	$([M]_0 - [M]_{eq})/[DAB]_0$	M_n[b] (calcd)	M_n (osm.)	M_n (NMR)	M_n[e] (SEC)	M_w/M_n[f] (SEC)
DAB-Am-8	58.9	7500	6900[c]	7500	—	1.74
DAB-Am-8	858	98 700	79 600[d]	79 000	114 000	2.71
DAB-Am-32	2607	301 100	230 200[d]	287 500	373 000	2.27

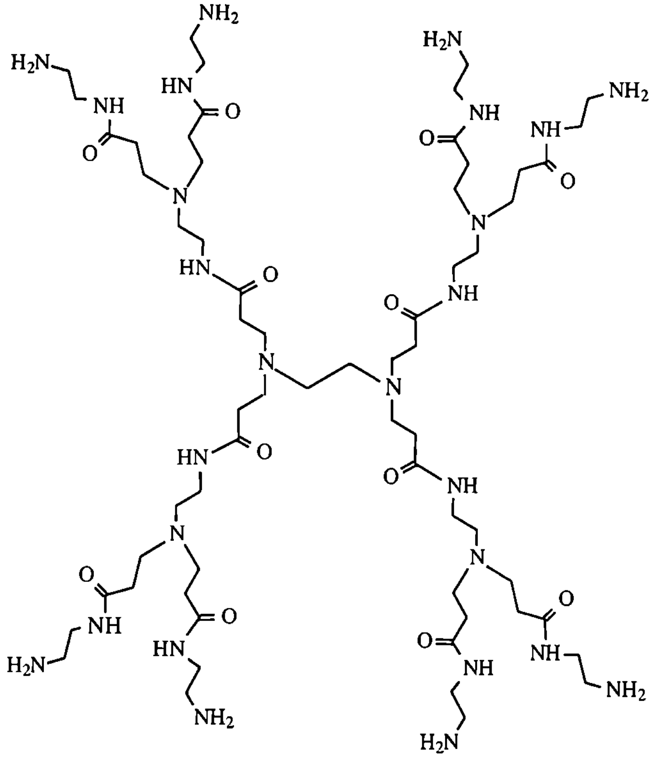
[a] $[LA]_0 = 1.5$ mol L^{-1}, $[CL]_0 = 2.0$ mol L^{-1}, $[Sn(Oct)_2]_0 = 2 \cdot 10^{-3}$ mol L^{-1}, THF solvent, 80 °C, [b] calculated according to equation (12), [c] Vapour-Pressure Osmometry, [d] High-Speed Membrane Osmometry, [e] Laser Light Scattering detector, [f] Refractive Index detector; calibration with polystyrene standards.



(I)



(II)



(PAMAM $G_{1.0}$)

(III)

ported by the molecular weight characteristics of the polyesters, prepared on DAB-Am-8 and DAB-Am-32 cores [see (I) and (II)], collected in Table 1.

Although molecular weights distributions were relatively broad (cf. M_w/M_n column) and there was also a certain scatter of the experimental M_n values determined from SEC, osmometric, and ^{1}H NMR measurements, these values were in a good agreement, within the expected experimental error, with the theoretically predicted molecular weights [M_n(calculated), equation (12)].

The net reaction scheme of a synthesis of the star-shaped polyester based on the polyamino dendrimer reads:

$$R(NH_2)_x + nx\,CL \rightarrow R[NH\text{–}PCL_n\text{–}OH]_x \qquad (11)$$

Assuming that back-biting side reactions are excluded, the expected molecular weights [M_n(calculated)] can be calculated from the simple expressions, usually applicable for living polymerization mechanism:

$$M_n(\text{calculated}) = M_{CL}\,[CL]_0/[DAB]_0 + M_{DAB} \qquad (12)$$

where: M_{CL} *denotes molecular weight of CL (114.14),* M_{DAB} *that of DAB-Am-8 or DAB-Am-32 (773 or 3514, respectively).*

Similar results have been obtained by us also for LA polymerizations coinitiated with DAB dendrimers [32] and in other laboratory with poly(amido amine) dendrimer (PAMAM $G_{1.0}$) [see structure (III)] [24].

CONCLUSIONS

The present literature minireview shows that amines were applied as (co)initiators in polymerization of aliphatic cyclic esters only rarely. The initial hopes related to tertiary amines as initiators of the controlled polymerization of highly strained, four-membered β-lactones have failed because of chain transfer to monomer side reactions. More promising were attempts of the high temperature polymerizations of the medium strained, six- and seven-membered δ- and ε-lactones initiated with primary amines or α-amino acids. The best results, however, have been obtained recently in polymerizations catalyzed additionally with tin(II) octoate $Sn(Oct)_2$. Polymerizations of ε-caprolactone or L,L-lactide initiated with primary amine/$Sn(Oct)_2$ system show features characteristic for living process and therefore allow to carry the fully controlled syntheses of the corresponding polymers. Using this approach there were prepared random and block copolymers of *N*-carboxyanhydrides (NCA) and L,L-lactide (LA) containing peptide bonds in the main chain as well as star-shaped polymers based on the polyamine dendrimers.

Following our previous papers on the mechanism of CL and LA polymerization initiated by $Sn(Oct)_2$ in presence of hydroxyl group containing compounds [H_2O, alcohols or hydroxy-carboxylic acids (ROH)] we have shown that, in principle, CL or LA/$Sn(Oct)_2$/primary amine (RNH_2) system does not differ mechanistically from CL or LA/$Sn(Oct)_2$/ROH system. ^1H NMR, MALDI-TOF mass spectrometric and kinetic studies revealed that in the first step of polymerization initiated with $Sn(Oct)_2/RNH_2$ mixtures formation of α-amido-ω-amidoalcohol [RNH-m-OH (R'OH)] (where m denotes the unimeric unit derived from CL or LA) proceeds. Then, the further steps of polymerization follow with R'OH as coinitiator. Thus, eventually $Sn(Oct)_2/RNH_2$ initiated polymerization proceeds by simple monomer insertion into ...-Sn-OR" bond, reversibly formed in the reaction ...-SnOct + R"OH ≡ ...-Sn-OR" + OctH, where R"OH is either the low molar mass coinitiator (R'OH) or a macromolecule fitted with hydroxyl end-group ([RNH-$(m)_n$-OH]. These interconversions take place throughout the whole polymerization process. $Sn(Oct)_2$ itself does not play an active, direct role in the polymerization.

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REFERENCES

1. „Biopolymers", (a) Vol. 3a: „Polyesters I — Biological Systems and Biotechnological Production"; (b) Vol. 3b: „Polyesters II — Properties and Chemical Synthesis"; (c) Vol. 4: „Polyesters III — Applications and Commercial Products" (eds. Steinbüchel, A., Doi, Y.), Wiley-VCH, Weinheim 2002.
2. Lundberg R. D., Cox E. F.: „Lactones" in „Ring-Opening Polymerization" (eds. Frish K. C., Reegen S. L.), Marcel Dekker, New York, London 1969, p. 247.
3. Johns D. B., Lenz R. W., Luecke A.: „Lactones", in „Ring-Opening Polymerization" (eds. Ivin K. J., Saegusa T.), Elsevier Applied Science Publishers, London, New York 1984, Vol. 1, p. 461.
4. Jerome R., Teyssie Ph.: „Anionic Ring-Opening Polymerization: Lactones" in „Comprehensive Polymer Science", Vol. 3: „Chain Polymerization", Part I, (eds. Allen G. et al.), Pergamon Press, Oxford 1989, p. 501.
5. Loefgren A., Albertson A.-Ch., Dubois P., Jerome R.: *J. Macromol. Sci.-Rev. Macromol. Chem. Phys.* 1995, **C35**, 379.
6. Mecerreyes D., Jerome R., Dubois P.: *Adv. Polym. Sci.* 1998, **147**, 1.
7. Slomkowski S., Duda A.: „Anionic Ring-Opening Polymerization" in „Ring-Opening Polymerization: Mechanism, Catalysis, Structure, Utility", (ed. Brunelle D. J.), Hanser Publishers, Munich, Vienna, New York, Barcelona 1993, p. 87.
8. Duda A., Penczek S.: „Mechanisms of Polyaliphatic Ester Formation" in „Biopolymers", Vol. 3b: „Polyesters II — Properties and Chemical Synthesis", (eds. Steinbüchel, A., Doi, Y.), Wiley-VCH, Weinheim 2002, p. 371.
9. Connor, E. F., Nyce G. W., Myers M., Moeck A., Hedrick J. L: *J. Am. Chem. Soc.* 2002, **124**, 914.
10. Kobayashi, S.: *J. Polym. Sci. Part A: Polym. Chem.* 1999, **37**, 3041.
11. Kobayashi S., Uyama H., Kimura S.: *Chem. Rev.* 2001, **101**, 3793.
12. Duda A.: *Polimery* 2004, **49**, 469.
13. Duda A., Penczek S.: *Polimery* 2003, **48**, 16.
14. Duda A.: *Polimery* 2002, **47**, 469.
15. Duda A., Kowalski A., Libiszowski J.: *Polimery* 2000, **45**, 465.
16. Duda A.: *Polimery* 1998, **43**, 135.
17. Duda A.: *Polimery* 1995, **40**, 393.
18. Duda A.: *Polimery* 1994, **39**, 403.
19. Duda A.: *Polimery* 1992, **37**, 293.
20. Duda A.: *J. Polym. Sci., Part A: Polym. Chem.* 1992, **30**, 21.
21. Duda A., Penczek S.: *Polimery* 1989, **34**, 429.
22. Kowalski A., Duda A., Penczek S.: *Macromolecules* 2000, **33**, 7359.
23. Rypacek F.: *5th International Workshop on Biodegradable Plastics and Polymers*, Stockholm, Sweden, June 9—13, 1998.
24. Cai Q., Zhao Y., Bei J., Xi F., Wang S.: *Biomacromolecules* 2003, **4**, 828.
25. Liu J., Liu L.: *Macromolecules* 2004, **37**, 2674.
26. Spinu M., Jackson C., Keating M. Y., Gardner K. H.: *J. Macromol. Sci. -Pure Appl. Chem.* 1996, **A33**, 1497.
27. Lee S. -H., Kim S. H., Han Y. K., Kim Y. H.: *J. Polym. Sci., Part A: Polym. Chem.* 2001, **39**, 973.
28. Zhao Y. L., Cai Q., Jiang J., Shuai X. T., Bei J. Z., Chen C. F., Xi F.: *Polymer* 2002, **43**, 5819.
29. Sanda F., Sanada H., Shibasaki Y., Endo T.: *Macromolecules* 2002, **35**, 680.
30. Ydens Y., Degee Ph., Dubois Ph., Libiszowski J., Duda A., Penczek S.: *Macromol. Chem. Phys.* 2003, **204**, 171.

31. Biela T., Duda A., Rode K., Pasch H.: *Polymer* 2003, **44**, 1851.
32. Kowalski A., Libiszowski J., Biela T., Cypryk M., Duda A., Penczek S.: *Macromolecules* 2005, sent to the Editorial Office.
33. Gresham T. L., Jansen J. E., Shaver F. W.: *J. Am. Chem. Soc.* 1948, **70**, 998.
34. *French Patent* 1, 231, 163 (1960).
35. Thiebaut R., Fisher N., Entienne Y., Coste J.: *Ind. Plast. Mod.* 1962, **14**, 13.
36. Jaacs V., Mathes N.: *Makromol. Chem.* 1970, **131**, 295.
37. Mathes N., Jaacs V.: *Makromol. Chem.* 1971, **142**, 209.
38. Kagiya T., Sano T., Fukui K.: *Kogyo Kagaku Zasshi* 1964, **67**, 951; *ibid.* 1965, **68**, 1144.
39. Slomkowski S., Penczek S.: *Macromolecules* 1976, **9**, 367; ibid. 1980, **13**, 229.
40. Yamashita Y., Ito K., Nakakita F. *Makromol. Chem.* 1969, **127**, 179.
41. Slomkowski S.: *Polymer* 1986, **27**, 71.
42. Young D. M., Hostettler F., Shriver L. C., McLaughlin R. W.: *Polym. Prepr. (Am. Chem. Soc. Division of Paint Plastics, and Printing Ink Chemistry)* 1956, **16(3)**, 108.
43. Saotome K., Kodaira Y.: *Makromol. Chem.* 1965, **82**, 41.
44. Dubois P., Degee P., Jerome R., Teyssie P.: *Macromolecules* 1992, **25**, 2614.
45. Rypacek F., Stefko I., Machova L., Kubies D., Brus J.: *Polym. Prepr. (Am. Chem. Soc. Div. Polym. Chem.)* 2002, **39(2)**, 126.
46. Caillol S., Lecommandoux S., Mingotaud A. -F., Schappacher M., Soum A., Bryson M., Meyrueix R.: *Macromolecules* 2003, **36**, 1118.
47. Kowalski A., Duda A., Penczek S.: *Macromol. Rapid Commun.* 1998, **19**, 567.
48. Kowalski A., Duda A., Penczek S.: *Macromolecules* 2000, **33**, 689.
49. Donaldson J. D., Jelen A.: *J. Chem. Soc. A* **1968**, 1448.
50. Birchal T., Faggiani R., Lock C. J. L., Manivannan V.: *J. Chem. Soc., Dalton. Trans.* **1987**, 16759.