



The Ring-Opening Polymerization–Polycondensation (ROPPOC) Approach to Cyclic Polymers

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A new concept called ring-opening polymerization–polycondensation (ROPPOC) is presented and discussed. This synthetic strategy is based on the intermediate formation of chains having two end groups that can react with each other. The ROPPOC syntheses are subdivided into three groups according to the nature of the chain ends: two ionic end groups, one ionic and one covalent chain end, and a combination of two reactive covalent end groups may be involved, depending on the catalyst. The usefulness for the preparation of cyclic polymers is discussed with a review of numerous previously published examples. These examples concern the following classes of cyclic polymers: polypeptides, polyamides, and polyesters, including polycarbonates and cyclic polysiloxanes. It is demonstrated that the results of certain ROPPOC syntheses are in contradiction to the Jacobson–Stockmayer theory. Finally, the usefulness of ROPPOCs for the detection of polydisperse catenanes is discussed.

stable end groups as demonstrated for the anionic polymerization of cyclosiloxanes (Scheme 1A) or the proton catalyzed polymerization of oxiranes presented in Scheme 1B. Stable end group means that these end groups do not react with each other under the reaction conditions used for the ROP under investigation. When a polymer chain possesses two end groups that can react with each other, as it is true for any normal polycondensation, the polymer can either react with another chain with the result of chain extension or it can cyclize by intramolecular condensation. According to the “Ruggli–Ziegler dilution principle” decreasing concentration of the reactive species favors cyclization over chain growth. The phosgenation of bisphenol-A outlined in Scheme 2 is a typical example for the formation of large cycles by

end-to-end cyclization involving a highly electrophilic acid chloride end group.^[1,2]

An analogous scenario results in a ROPPOC process, where the catalyst generates chains having a nucleophilic and an electrophilic end group which can react with each other. A typical example is presented in Scheme 3 for the tributyltin chloride catalyzed ROP of L-lactide with formation of cyclic polylactides.^[3] In this case the highly electrophilic acid chloride group is formed temporarily as reaction intermediate. Hence the characteristic difference between a normal ROP and ROPPOC consists in the fact that in the latter case two end groups are generated which can react with each other. The characteristic difference between a normal polycondensation and ROPPOC approach consist in the higher cyclization tendency of the latter. In the case of a normal POC all reactive bifunctional species are present in their maximum possible concentration at any time. Yet, in a ROPPOC process not all ring-opening polymerizations start at the same time. Hence, the actual the temporary concentration may be several orders of magnitude lower than in the case of normal POC with the consequence of a higher cyclization/chain growth ratio.


For a proper understanding of both, normal POC and ROPPOC syntheses it is important to differentiate between irreversible and reversible polymerizations. In this regard there is no difference between both systems. In the irreversible case, they cannot react with the polymer backbone and cycles are exclusively formed by end-to-end cyclization. In the reversible case, cyclic oligomers are formed by the so-called backbiting attack of one end group (usually the nucleophilic one) onto the polymer chain. The reversibility of this reaction establishes a ring–chain,

1. Introduction

Ring-opening polymerization–polycondensation (ROPPOC) is an abbreviation for a polymerization process, which combines ring-opening polymerization (ROP) with simultaneous polycondensation (POC). The characteristic and preparative useful consequence of this approach is the formation of cyclic polymers which may contain cycles with high molar mass meaning masses above 100 000 g mol⁻¹. For a proper understanding of the fundamentals of a ROPPOC approach, it is useful to look at normal ROP's. Normal ROP's yield linear chains having two

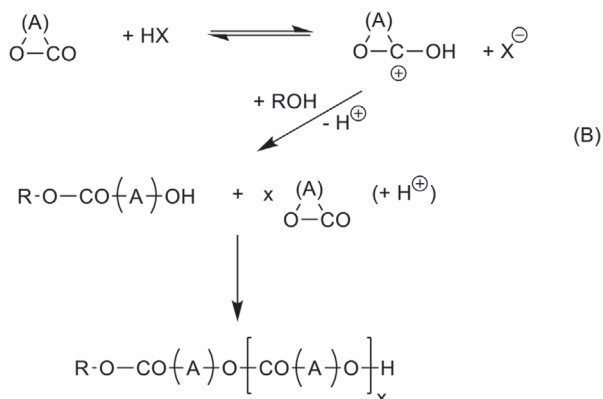
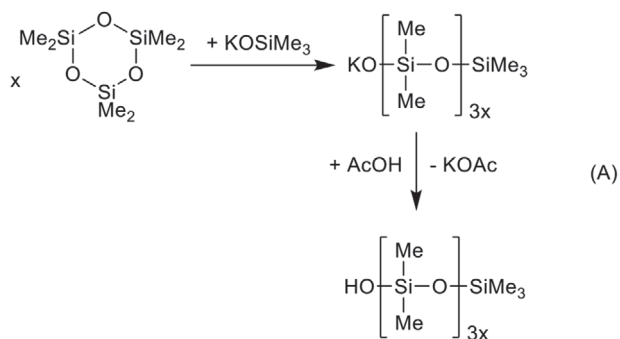
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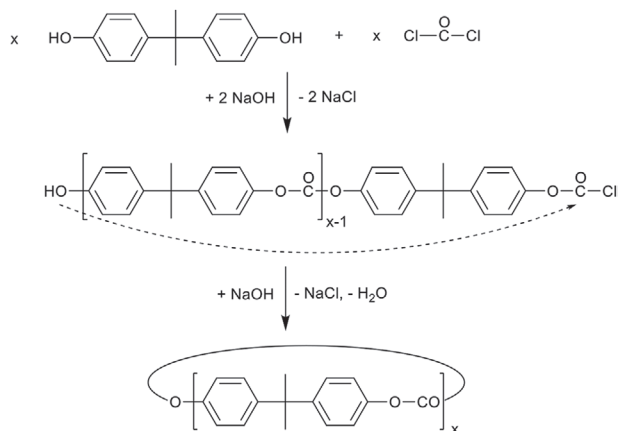
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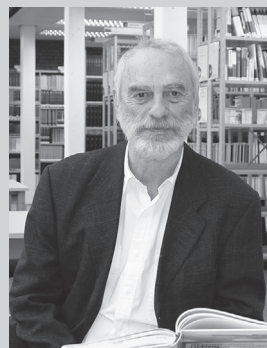


Scheme 1. Simplified formulation of a ROP with A) activated chain end or B) activated monomer.

ring–ring, and chain–chain equilibrium which involves as many ring-opening growing steps as degradation steps. Hence, any reversible polycondensation such as the syntheses of nylons or poly(ethylene terephthalate) in the melt is to a large extent a ROP, an aspect which is usually not mentioned in textbooks. Lactide is the rare case of a monomer which allows for the realization of both, reversible and irreversible ROPPOCs and also allows for their differentiation by MALDI-TOF mass spectrometry as demonstrated for the imidazole catalyzed ROPPOC synthesis of cyclic



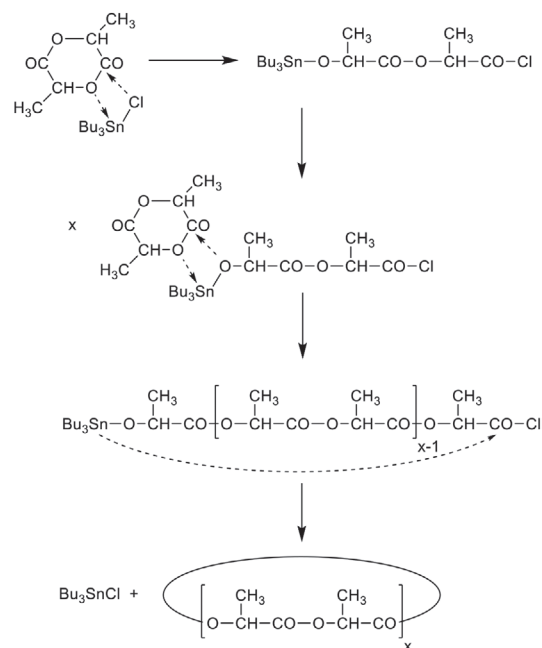
Scheme 2. Simplified formulation of a classical irreversible polycondensation with end-to-end cyclization.



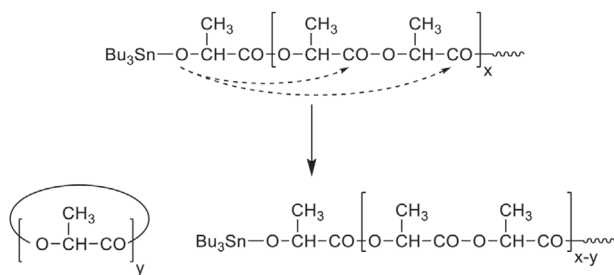
Hans R. Kricheldorf obtained his Ph.D. (1969) and habilitation (1975) from the Albert-Ludwigs University of Freiburg im Breisgau. He was appointed as an assistant professor in 1980 and was a full professor at the University of Hamburg from 1982 until his retirement in 2008. His research is mainly focused on polycondensation and ring-opening polymerization. He has authored several books on polymer chemistry and the role that errors and fallacies might play in the progress of science.



Steffen M. Weidner studied chemistry at Humboldt University in Berlin and received his Ph.D. (1996) from the Technical University of Berlin. He works at the Federal Institute for Materials Research and Testing (BAM). His research is driven from a regulatory perspective with strong ties to academia and industry. He is interested in developing suitable hyphenated chromatography approaches for reducing the complexity of mass spectrometry of synthetic polymers.



Scheme 3. Simplified scheme of a ROPPOC synthesis of cyclic poly(lactides) by means of tributyltin chloride (or other alkyltin chlorides).



Scheme 4. Formation of even- and odd-numbered cycles by (reversible) backbiting cyclization.

polylactides.^[4] An irreversible ROPPOC will yield even-numbered cycles as outlined in Scheme 3, whereas the existence of “backbiting” reactions results in equal quantities of even- and odd-numbered cycles (**Scheme 4**). In most cases of irreversible polymerization, the irreversibility is a priori evident from the chemical stability of the polymer backbone, for example when cyclic poly-peptides are synthesized at low temperatures (Section 2.1).

The following text is subdivided into three sections according to the nature of the end groups:

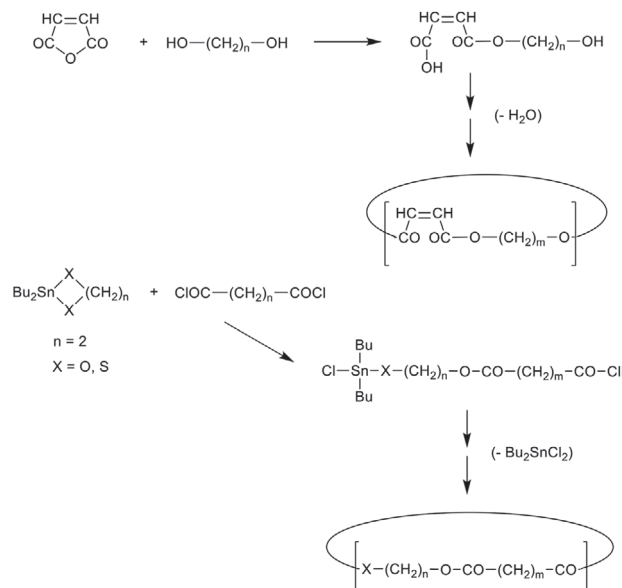
1. ROPPOC involving two ionic chain ends, so-called zwitterionic polymerization (ZIP).
2. ROPPOC involving one ionic and one covalent end group.
3. ROPPOC based on two covalent end groups.

The inclusion of zwitterionic polymerizations into the ROPPOC systems deserves a short discussion of the question how a ROPPOC synthesis of cyclic polymers can be distinguished from a ring-expansion polymerization (REP). Laurent and Grayson have included ZIPs into the group of REPs without discussing the justification for this measure, and more recently Wu et al. have uttered the same opinion.^[5,6] For the following reasons the authors of this article do not agree with this view. For the definition of REP two alternative consistent versions may be formulated.

- I. The growing species are permanently closed cycles, so that beginning with the monomers up to the final polymers all species in the reaction mixture are cycles.
- II. REP is a formal label for all polymerizations that involve transformation of cyclic monomers into cyclic polymers regardless of reaction mechanism and structure of intermediate reaction products.

According to definition I, a ZIP may only be considered as REP when the zwitterionic chains form cycles permanently closed by a contact ion pair with the consequence that a growing step proceeds as concerted rearrangement of monomer and ionic groups without opening of the ring. This requirement is difficult to prove and has not been proven for the experiments published so far. Furthermore, two research groups reported results which clearly indicate that the reaction mixtures contained open-chain zwitterions with fully solvated end groups (Sections 2.2 and 2.3). Therefore, the ZIPs reported so far are classified by the authors as ROPPOC and not as REP. A borderline case is discussed in Section 2.3 concerning the ZIP of β -lactones.

According to definition II, all ROPPOC syntheses discussed below must be included into the definition of REP. Furthermore, all polycondensations and polyadditions of cyclic monomers,



Scheme 5. Examples of ring-opening polycondensations.

such as phthalic anhydride, maleic anhydride and various heterocyclic monomers must be considered as REP. Two examples were outlined in **Scheme 5**, but more examples were discussed in a recent book chapter.^[7] The reason why all polycondensations and polyadditions of cyclic monomers performed in the melt or in solution must be classified as REP according to definition II is the modern theory of step-growth polymerizations. According to Gordon et al.^[8] and Stepto and coworkers^[9,10] cyclization competes with chain growth at any stage of a step-growth polymerization and at 100% conversion all reaction products are cycles. This theory was originally elaborated and experimentally proven for kinetically controlled step-growth polymerizations (SGPs); its consequences for reversible polycondensations are discussed in Section 5.^[2] However, the authors consider such a broadening of the definition of REP to be more confusing than helpful and there are also theoretical arguments that suggest classifying ROPPOCs as a special class of polymerizations.

A useful and important aspect for a classification of polymerizations is the definition of conversion (p). For chain growth polymerizations, conversion is defined by the consumption of monomers according to Equation (1). This equation is also valid for all ROPs and for all REPs according to definition I

$$p = \frac{(N_{m0} - N_{mt})}{N_{m0}} \quad (1)$$

with N_{m0} and N_{mt} = number of monomers at the beginning of the polymerization and at time t .

For SGPs, the conversion is defined by the consumption of functional groups according to Equation (2)

$$p = \frac{N_{f0} - N_{ft}}{N_{f0}} \quad (2)$$

with N_{f0} and N_{ft} = number of functional groups at the beginning of a polycondensation and at time t .

For ROPPOCs at least two definitions are needed to describe the most important aspects of the polymerization process. Equation (1) still holds for ROP alone, but does, of course not monitor the progress of the end-to-end cyclization which is based on the consumption of end groups. However, Equation (2) is not useful for this purpose, because in the case of a ROPPOC N_{f0} is zero and N_{ft} begins with zero passes through a maximum and ends with zero. In contrast, N_{f0} represents in a normal polycondensation the maximum number of functional groups and N_{ft} steadily decreases with time. However, a variant of Equation (2), namely Equation (3), meets all requirements.

$$p = \frac{N_{f1} - N_{f2}}{N_{f2}} \quad (3)$$

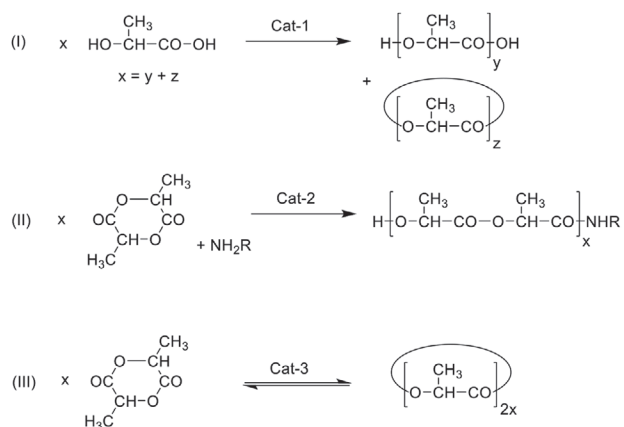
with $N_{f1} > 0$: number of functional groups formed after partial reaction of the catalyst with monomers at an arbitrary time t_1 ; N_{f2} : number of functional groups at any time after t_1 .

This short discussion of p illustrates that ROPPOCs do neither fit in with true REPs nor with classical polycondensations and thus, deserve to be classified as new special type of polymerizations. For the proper understanding of ROPPOCs, it is also useful to consider that ROPPOCs are a group of polymerizations which cover the area between the following three limiting cases (which are all outside the definition of ROPPOC):

- I. Polycondensations of linear monomers, which depending on the conversion, yield mixtures of linear and cyclic species in various ratios (Section 5).
- II. ROPs yielding linear chains, which possess one sort of stable end groups, so that condensation reactions involving both sorts of end groups cannot occur.
- III. Ring–ring equilibration reactions in the absence of ring–chain equilibration.

Scheme 6 (in combination with **Scheme 7**) illustrate these three limiting cases on the basis of lactic acid, because all three cases outlined in these schemes have experimentally been realized.

Finally, it should be mentioned, that a first review on zwitterionic polymerizations has been published about 10 years ago, but without mentioning the acronym ROPPOC.^[11] Furthermore, it should be mentioned that zwitterionic polymerizations

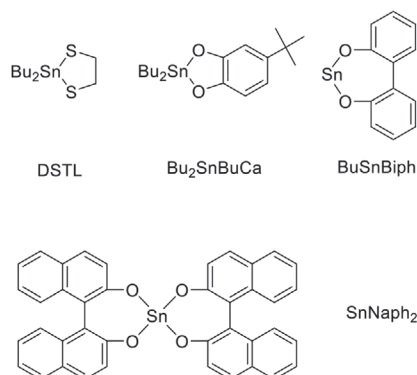


Scheme 6. Three cases of polymerizations yielding polylactides which are outside the definition of ROPPOC.

Cat-1: protic acids e.g. $\text{H}_3\text{C}-\text{C}_6\text{H}_4-\text{SO}_3\text{H}$ possibly in combination with transesterification catalysts such as Bu_2SnO or $\text{Sn(II) 2-ethylhexanoate (SnOct}_2)$

Cat-2: transesterification catalysts such as SnOct_2 or Bu_2SnO

Cat-3: cyclic tin catalysts such as DSTL, Bu_2SnBuCa , SnBiph or SnNaph_2



Scheme 7. Catalysts enabling ring–ring equilibration of lactide (see (III) in Scheme 6).

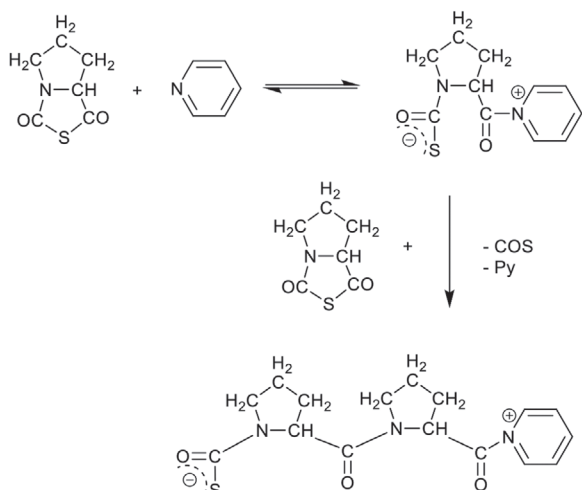
proceeding by charge-cancellation polyaddition and/or do not yield cyclics either because of stable end groups or because of intensive side reactions are not discussed in this review.^[12]

2. ROPPOCs Based on Two Ionic End Groups (Zwitterionic Polymerizations)

2.1. Zwitterionic Polymerizations of Amino Acid-*N*-Carboxyanhydrides

α -Amino acid *N*-carboxyanhydrides (NCAs) were the first class of monomers where ZIPs were observed. In 1951, Wieland formulated a heterolytic cleavage of the NCA ring by the nucleophilic attack of a tertiary amine onto CO-5.^[13] However, he did neither present any experimental data nor did he outline a polymerization mechanism. Almost at the same time the research group of Wessely studied oligomerizations and polymerizations of *N*-substituted α -NCAs catalyzed by pyridine.^[14] Cyclic dimers, that is, *N,N'*-disubstituted 2,5-dioxopiperazines, were isolated, and their yields increased with increasing bulkiness of the *N*-substituent. Formation of higher oligomers was assumed because amino and carboxylic end group characteristic for linear polypeptoids were not detectable. Direct mass spectrometric evidence for the formation of cyclic oligomers and polymers was not feasible at that time. Those authors purposely avoided any mechanistic discussion, but from what is known today, it becomes obvious, that their reaction products were the result of zwitterionic polymerizations.

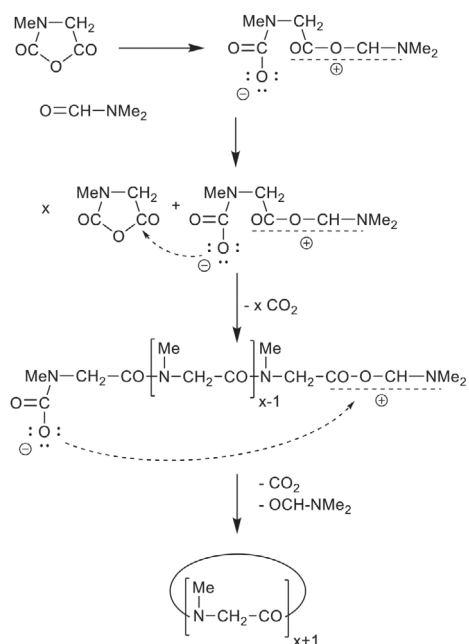
In 1974, Kricheldorf studied tert-amine catalyzed polymerization of L- and D,L-proline-*N*-thiocarboxyanhydrides (ProNTAs).^[15] When pyridine was used as catalyst the cyclic dimer was isolated and a ZIP mechanism was formulated for the first time to explain this result (**Scheme 8**). Analogous studies were performed 2 years later with Sar-NCA and Sar-NTA.^[16] Again a zwitterionic mechanism was formulated to explain why



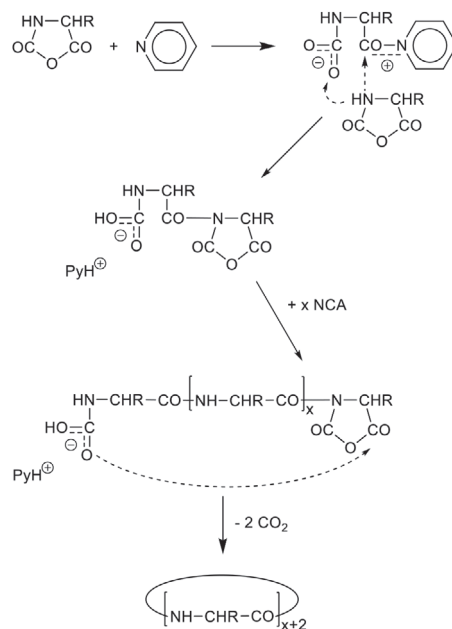
Scheme 8. Zwitterionic polymerization mechanism formulated in ref. [15] to explain the formation of cyclic dimers.

pyridine is a considerably better catalyst than more basic tertiary amines, when *N*-substituted NCAs or NTAs were used as monomers.

In 2005, it was reported that cyclic oligopeptides were formed as byproducts in primary amine-initiated polymerizations of Phe-NCA, when the solution of the NCA in dimethylformamide (DMF) was stored for a few minutes at 20–22 °C prior to addition of the primary amine.^[17] A systematic study revealed that polar nucleophilic solvents, such as DMF, *N*-methyl pyrrolidone, dimethyl sulfoxide or tetramethyl urea, indeed catalyzed the formation of cyclic polypeptides that were identified by MALDI-TOF mass spectrometry up to degrees of polymerization (DPs) around 50.^[18] In the case of *N*-substituted NCAs it is obvious, that a zwitterionic mechanism is the only



Scheme 9. Zwitterionic polymerization of Sar-NCA catalyzed by dimethylformamide.

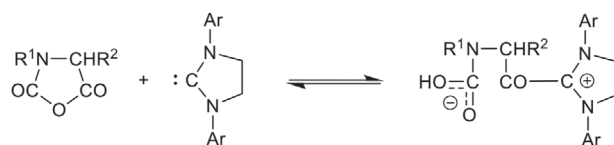


Scheme 10. Pyridine-catalyzed ROPPOC of α -amino acid NCAs proceeding via one covalent electrophilic end group.

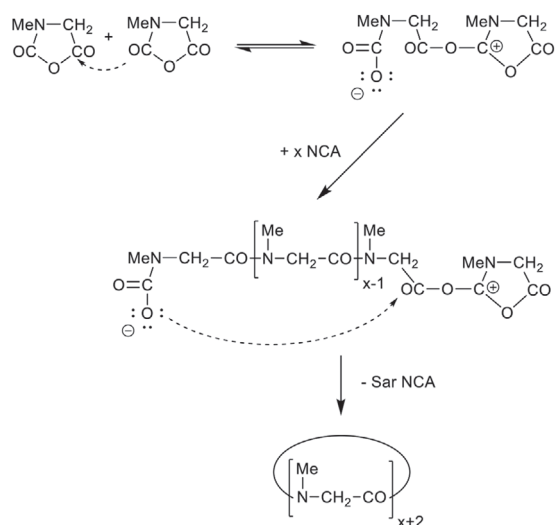
reasonable explanation for the formation of cyclic polypept(o)ides (**Scheme 9**). However, with *N*-unsubstituted NCAs the initial formation of a zwitterionic monomer may be followed by rapid migration of the *N*-proton, so that the following ROPPOC process proceeds via two covalent end groups (**Scheme 10**). Therefore, the tertiary amine-catalyzed polymerization of *N*-unsubstituted NCAs is discussed in Section 4.

Zwitterionic polymerizations of *N*-substituted NCAs catalyzed by a *N*-heterocyclic carbene were described by Guo et al. in much detail (**Scheme 11**).^[19] Such carbenes are much stronger nucleophiles than pyridine or other tert-amines. However, they are also considerably more basic, so that polymerizations of chiral NCAs run a high risk of racemization. Formation of cyclic polypeptides was also observed in thermal polymerizations of NCAs when these monomers are heated for several hours above their melting points.^[20] A self-initiated zwitterionic polymerization (**Scheme 12**) was forwarded as most likely explanation of these results. As already mentioned above in connection with Pro-NTA, polymerizable sulfur analogs of α -NCAs exist as well as NCAs and NTAs of β -amino acids (**Scheme 13**).^[21] Pyridine-catalyzed polymerizations were reported, but all these studies were performed at a time when modern mass spectrometric methods were not available, so that the identification of cyclic polypeptides or polyamides was not feasible.^[22–24]

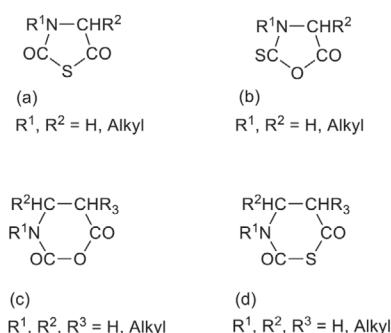
The results presented above and in the following sections of this paper might suggest that ZIPs are an effective approach to



Scheme 11. Reversible formation of a zwitterion from an *N*-heterocyclic carbene.

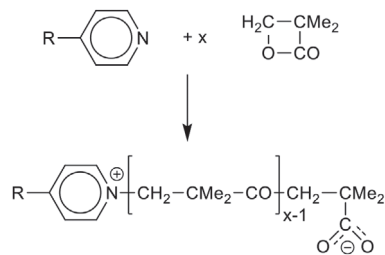


Scheme 12. Self-catalyzed thermal zwitterionic polymerization of Sarcosine-NCA.

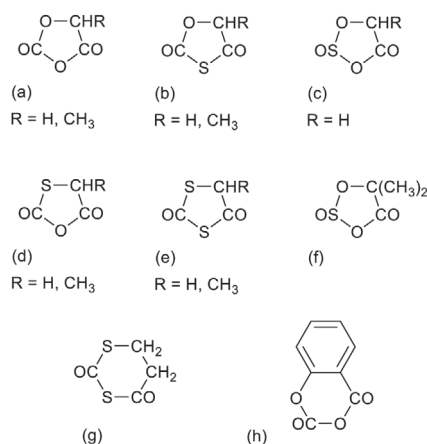


Scheme 13. Sulfur analogs of α -amino acid NCA and β -amino acid NCAs.

syntheses of cyclic polymers whenever initiation via zwitterions is possible. Yet, such a suggestion is misleading as demonstrated by the pyridine-initiated polymerization of pivalolactone (**Scheme 14**). The zwitterionic linear chains, characterized by MALDI-TOF mass spectrometry, proved to be stable up to 160 °C.^[25] Hence, it may be concluded that formation of cyclic polymers via zwitterionic polymerization will only be successful when the cationic chain ends have the structure of N-, P-, or carbene-stabilized acylium ions, whereas the corresponding alkyl ions form rather stable chain ends.



Scheme 14. Zwitterionic polymerization of pivalolactone initiated by pyridine (or substituted pyridines).

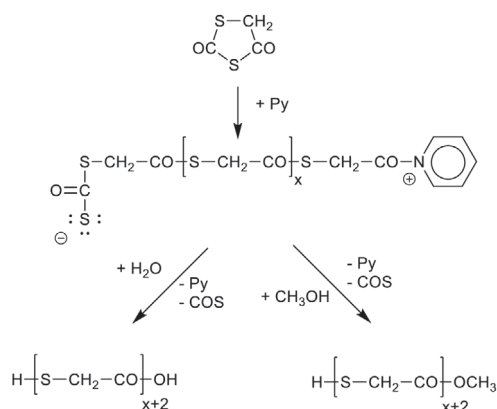


Scheme 15. Sulfides, carboxyanhydrides, and anhydrosulfides of hydroxy- and mercapto-carboxylic acids.

2.2. Zwitterionic Polymerizations of Cyclic Anhydrides of Various Hydroxyl- or Mercapto Carboxylic Acid

Various cyclic anhydrides resembling α - or β -NCAs, but based on hydroxy- or mercapto carboxylic acids, were prepared (**Scheme 15**), and in most cases, pyridine-catalyzed polymerizations were performed. Research in this direction began with the work of Elias and Bührer.^[26,27] Those authors studied syntheses and properties of poly(thioglycolide) and poly(thiolactide) via polymerizations of mercaptoacetic acid SCA (oxathiolane 2,5-dione) and mercaptolactic acid SCA (4-methyl-1,3-oxathiolane-2,5-dione, (d) in Scheme 15). Pyridine-catalyzed polymerizations were conducted, but formation of cyclic polymers was neither expected nor proven and polymerization mechanisms were not formulated. Shortly thereafter, Kricheldorf et al. reported on tertiary amine-catalyzed polymerizations of dithiolane-2,4-dione and 5-methyldithiolane-2,4-dione, ((e) in Scheme 15).^[28,29] A zwitterionic polymerization mechanisms was discussed, but the poor performance of pyridine and the much higher effectiveness of trialkyl amines as catalysts, suggested that deprotonation of the monomers in α -position followed anionic ROP was the most likely mechanism.

However, the first author launched a detailed reinvestigation of the pyridine-catalyzed ROP of dithiolane-2,4-dione in 2007 and identified cyclic poly(thioglycolide) as the main reaction product by means of MALDI TOF mass spectrometry, when the polymerization was finished in the molten state.^[30] A zwitterionic mechanism was proposed as explanation of this result. However, at room temperature in solution, rapid crystallization of poly(thioglycolide) prevented cyclization less effectively, and linear chains having reactive end groups were buried inside crystallites or immobilized on their surface. Upon washing with water or methanol, therefore, linear chains having COOH or methyl ester end groups were the main products (**Scheme 16**). Cyclic poly(thioglycolide)s were also found as reaction products of thermal polymerizations above the melting temperature of the polymer (<160 °C). A self-catalyzed zwitterionic polymerization was formulated (**Scheme 17**) in analogy to the thermal polymerization of Sar-NCA (Scheme 12). Pyridine-catalyzed polymerization of the six-membered 1,3-dithiane-2,4-dione ((g), in Scheme 15) were also reported, but without

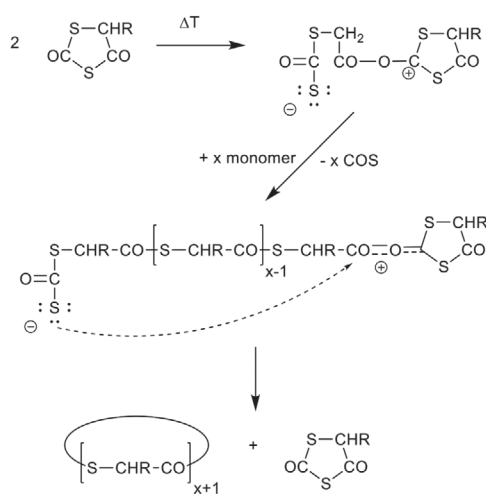


Scheme 16. Pyridine-catalyzed zwitterionic polymerization of thioglycolic acid anhydrosulfide below 160 °C.

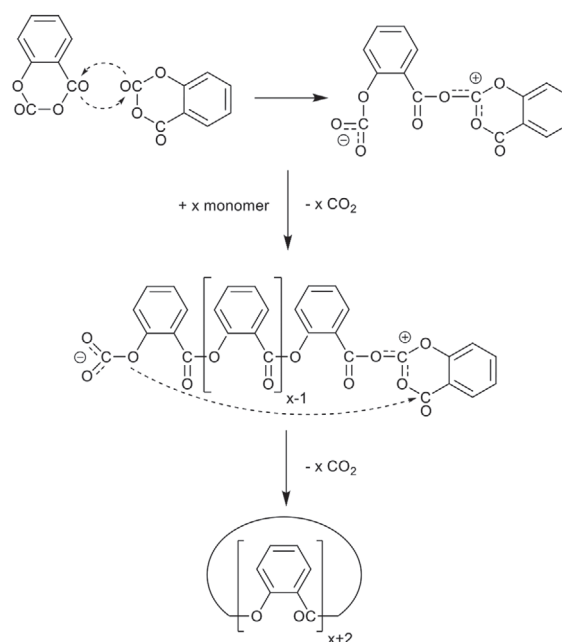
identification of cyclic polyesters and without discussion of a zwitterionic polymerization mechanism.^[31]

Whereas nothing is known about ZIPs of glycolic acid OCA ((a), R = H, in Scheme 15), pyridine-catalyzed polymerization of lactic acid OCAs ((a), R = CH₃, in Scheme 15) was reported, but without identification of cyclics and without discussion of a zwitterionic polymerization mechanism.^[32] However, low molar mass cyclic poly(salicylate)s were obtained in pyridine-catalyzed and thermal polymerizations of salicylic acid OCA ((h) in Scheme 15) and explained by a zwitterionic polymerization mechanism (Scheme 18).^[33]

Finally, thermal polymerizations of α -hydroxy carboxylic acid anhydrosulfites (2-oxo-2-thia-1,3-dioxolanes), such as (f) in Scheme, 2.8 should be discussed. The kinetic of the thermal polymerization of various anhydrosulfites was studied by Thighe and coworkers.^[34–37] A first order kinetic was found in all cases. Those authors concluded that elimination of SO₂ occurs with intermediate formation of α -lactones ((I) in Scheme 19), but a polymerization mechanism was not formulated. Furthermore, neither spectroscopic information about the intermediate formation of the energy rich α -lactones



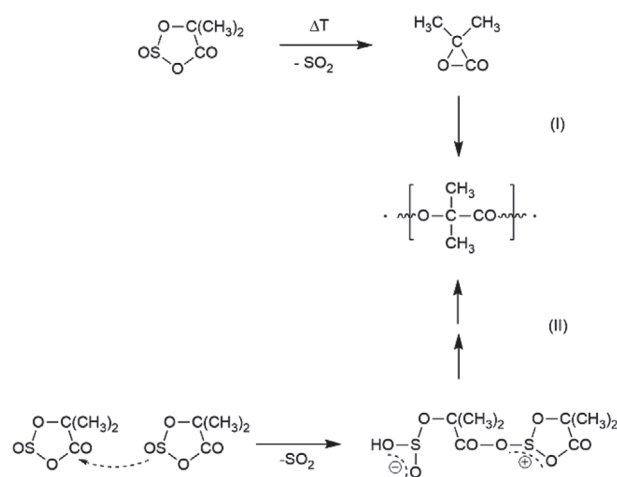
Scheme 17. Thermal polymerization of thioglycolic acid anhydrosulfide.



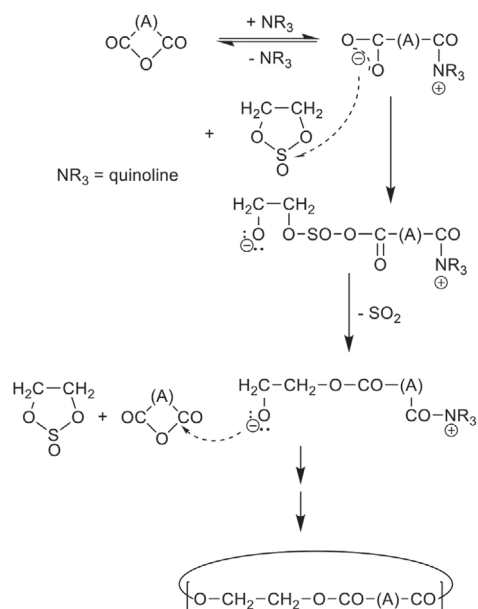
Scheme 18. Hypothetical mechanism of the thermal polymerization of salicylic acid carboxy anhydride.

nor any information about topology and end groups of the resulting polyesters was forwarded. A more recent study including mass spectrometry revealed that cyclic polyesters are indeed the predominant reaction products.^[38] A self-catalyzed zwitterionic polymerization mechanism was proposed which is also compatible with a first order kinetic ((II) in Scheme 19).

In summary it may be concluded that with the exception of *N*-substituted NCAs the few ZIPs of cyclic anhydrides studied by mass spectrometry demonstrated, that these ZIPs were not satisfactory from the preparative point of view, because the cyclics were “contaminated” with significant amounts of linear chains.



Scheme 19. Alternative polymerization mechanism of a hydroxy carboxylic acid anhydrosulfites.



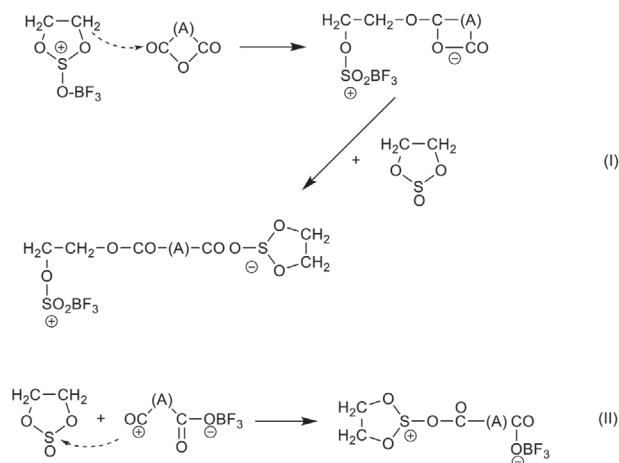
Scheme 20. Hypothetic mechanism of a quinoline catalyzed zwitterionic copolymerization of ethylene sulfite and cyclic anhydrides.

2.3. Zwitterionic Polymerizations of Cyclic Esters and Carbonates

A first attempt to synthesize cyclic aliphatic polyesters via a zwitterionic polymerization was reported in 2001.^[39] The “polycondensation” of ethylene sulfite with aliphatic dicarboxylic anhydrides was studied using either quinoline or boron trifluoride as catalysts. Low molar mass polyesters mainly consisting of cyclics were obtained. Since high temperatures (180 °C) and long times (18 h) were required to achieve high conversions, side reactions were not unexpected. Several zwitterionic polymerization mechanisms were discussed with the most likely variant formulated in **Scheme 20**. Since the CO groups of the anhydrides are the strongest electrophiles in the reaction mixture a heterolytic cleavage by quinolone is the only plausible start reaction. Catalysis by BF₃ is a more complex system and the two most likely alternatives are outlined in **Scheme 21**. Either the first attack of the catalyst goes to the ethylene sulfite (route (I)) or to the anhydride (route (II)). Regardless which mechanism is correct, a zwitterionic polymerization based on the stabilization of the anionic chain end is a rare case.

Analogous experiments were performed with ethylene carbonate or trimethylene carbonate instead of ethylene sulfite, but the preparative results were not better.^[40] A conspicuous difference concerns BF₃-catalyzed polymerization, because, in contrast to catalysis with quinolone, BF₃ also catalyzed a cationic ROP of the carbonates, so that cycles or linear chains containing short blocks of oligocarbonates were formed.

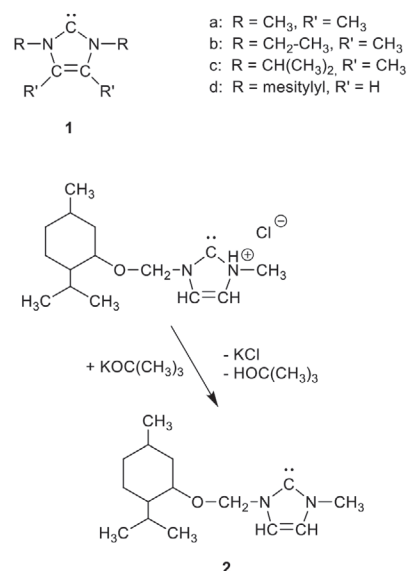
A substantial progress toward syntheses of cyclic polyesters was made when the research group of Hedrick and Waymouth used *N*-heterocyclic carbenes as catalyst (1a–d in **Schemes 22** and **23**).^[41–48] These carbenes belong to the strongest nucleophiles known so far and their nucleophilicity suffices to promote zwitterionic polymerizations of lactides, lactones, and cyclic carbonates even at room temperature or below.



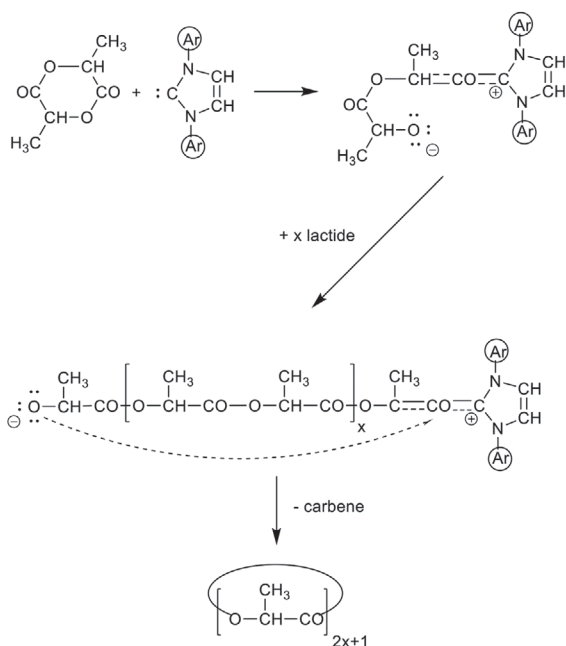
Scheme 21. Alternative zwitterionic polymerization mechanism of BF₃OEt₂: catalyzed 1:1 copolymerization of ethylene sulfite and dicarboxylic acid anhydrides.

However, their first paper in this field focused on ZIP of *L*-lactide evidenced that ZIP of this monomer with carbenes is not attractive from the preparative point of view. The polylactides were partially racemized due to the high basicity of the carbenes and of the alkoxide chain ends, and the molecular weights (*M_w*) were all below 35 000 g mol⁻¹.^[41,43] As discussed below, the carbene-catalyzed ZIP was considerably more successful, when other cyclic esters served as monomers.

Quite recently Tan and coworkers found, that when the reaction temperature is lowered to –70 °C, racemization of *L*-lactide is almost completely avoidable.^[49] The exclusively formed even-numbered cyclics indicate a total suppression of transesterification reactions such as “backbiting.” These experiments were also performed with *rac*-*D,L*-lactide and a high stereoselectivity (up to 90%) was also found. Yet, this progress was combined with the penalty of a relatively low conversions (<60%) and *M_w*’s below 9 000 g mol⁻¹.



Scheme 22. *N*-heterocyclic carbenes (NHCs) discussed in this review.

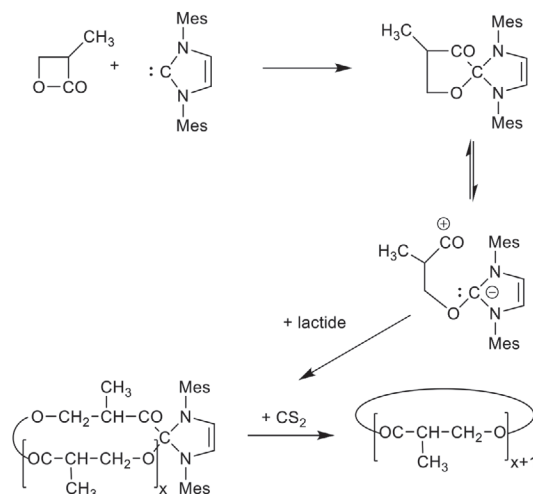


Scheme 23. Synthesis of cyclic poly(lactides) by carbene-catalyzed zwitterionic polymerization.

Syntheses of cyclic poly(lactides) by means of a *N*-heterocyclic carbene were also reported by Prasad et al.^[50] Those authors claimed that an in-situ generation and application of a carbene (**2** in Scheme 22) is advantageous, because carbenes are sensitive to air and moisture. However, the MALDI-TOF mass spectra presented as evidence of the cyclic architecture had such a poor quality that “contamination” with 25% of linear chains is not excluded. A comparison of intrinsic viscosities with linear poly(lactides) was not performed. Furthermore, the melting temperatures below 160 °C indicate significant racemization. In other words, the claimed advantage of this “in situ catalyst system” is not justified by the experimental facts.

ZIPs of various lactones also proved feasible with *N*-heterocyclic carbenes as catalysts. In the case of propiolactone and β -butyrolactone, surprisingly a spirocyclic reaction product could be isolated from the equimolar reaction of lactone and carbene (**Scheme 24**) and characterized by various spectroscopic methods.^[42] This spirocycle proved to initiate the polymerization of additional monomer and thus, was considered to represent the first step of the polymerization process. An equilibrium between covalent (dormant) and zwitterionic (active) form of the spirocyclic reaction products was assumed. Cyclic poly(lactones) free of catalyst were not obtained as primary polymerization products. Their liberation required addition of CS_2 and thus, this polymerization does in fact not obey the definition of a ROPPOC process but represents a borderline case of ZIP and REP. Molecular weights (M_w) up to 10 000 g mol^{-1} and retention of the configuration were reported.

When larger lactones, such as δ -valero- or ϵ -caprolactone were polymerized with *N*-heterocyclic carbenes spirocyclic intermediates were not identified and cyclic polyesters were formed spontaneously.^[44–46] Hence, these ZIPs clearly meet the requirements of ROPPOC syntheses. M_w values up to 70 000 g mol^{-1} were achieved for poly(δ -valerolactone) and up to 230

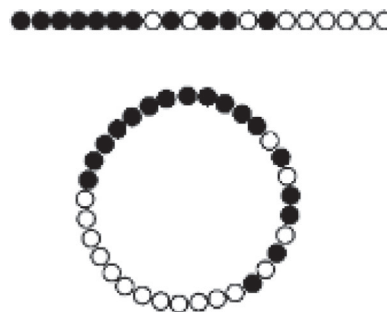


Scheme 24. Mechanism of the heterocyclic-carbene-initiated ZIP of β -butyrolactone.

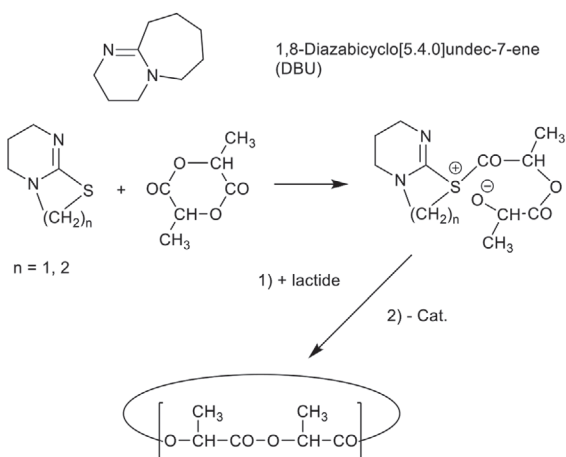
000 g mol^{-1} for poly(ϵ -caprolactone). In connection with the experimental work comprehensive computer-modeling studies of the polymerization mechanism were performed.

In addition to *N*-heterocyclic carbene-catalyzed zwitterionic homopolymerization of lactones, the Hedrick–Waymouth group also studied the copolymerization of δ -valerolactone (VA) and ϵ -caprolactone (CL).^[48] Kinetic measurements demonstrated a faster homopolymerization of VA and a faster incorporation of VA into the copolyesters. M_w 's up to 110 000 g mol^{-1} were obtained and the intrinsic viscosities proved nearly complete cyclization. In the absence of significant transesterification copolyesters with a blocky sequence were obtained as indicated by the ^{13}C NMR signals of the OCH_2 groups. Furthermore, melting temperatures (T_m) slightly lower than those of linear two-block copolymers were found. From these results, those authors interpreted that “gradient copolyesters” were formed mainly consisting of long blocks of VA and CL (chemical heterogeneity of second order, see **Scheme 25**). However, the schematic formula given in Scheme 25 does not agree well with the NMR data which indicate an average block length of only 3 units (2 is typical for a random sequence). Furthermore, no information about the chemical heterogeneity of first order was provided.

In addition to *N*-heterocyclic carbenes the Hedrick–Waymouth group examined the usefulness of bicyclic diamines as



Scheme 25. Schematic illustration of s.c. “gradient copolyesters” prepared by ZIP of δ -valerolactone and ϵ -caprolactone. Reproduced with permission.^[48] Copyright 2011, Wiley-VCH.

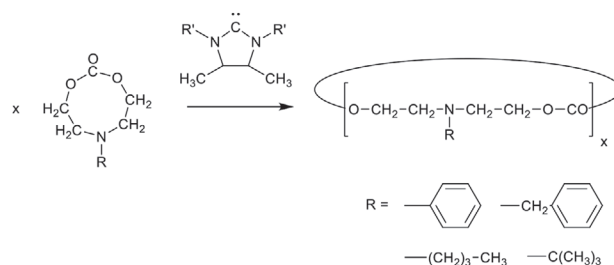


Scheme 26. Structure of the DBU catalyst and zwitterionic polymerization of L-lactide catalyzed by bicyclic isothioureas.

ZIP catalysts for lactide and lactones. A first study based on the amidine DBU (**Scheme 26**) was not much successful, because a side reaction (deprotonation) caused formation of considerable amounts of linear polylactides. This side reaction did not occur when analogous bicyclic isothioureas were used as catalysts (**Scheme 26**).^[51] With these isothioureas M_w 's up to 82 000 g mol⁻¹ were obtained, and both MALDI TOF mass spectra and intrinsic viscosity measurements agree with nearly quantitative cyclization. In this regard, the results obtained with bicyclic isothioureas are significantly better than those obtained with carbenes. However, no information about optical purity was disclosed and not DSC measurements were reported. Considering the high basicity of the catalysts and the long reaction times (23–135 h), preservation of 100% optical purity is absolutely unlikely. An interesting result concerning the polymerization mechanism is the finding, that precipitation of reaction mixtures at low conversion into moist methanol yielded linear chains having methyl ester and COOH end groups in addition to the cyclics. Brown et al. interpreted this finding as evidence for the existence of open-chain zwitterions in the reaction mixture.^[46] This result and interpretation confirm the classification of ZIPs as part of the ROPPOC approach, as discussed in the Introduction.

NHC-catalyzed ZIPs of various eight membered cyclocarbonates were reported by Chang et al. in 2016.^[52] The success of the ZIPs depended very much on the substituent of the carbonates in **Scheme 27**). The *N*-phenyl group prevented polymerization and the cyclic dimer was the main reaction product. *N*-Alkyl substituted cyclocarbonates yielded cyclic polymers and in the case of the *N*-benzyl group M_w 's up to 176 000 g mol⁻¹ were obtained. The intrinsic viscosities (MHS plots) indicated nearly complete cyclization. Furthermore, copolymerization with δ -valerolactone were performed with M_w 's up to 91 000 g mol⁻¹. Due to the higher rate of incorporation of δ -valerolactone, copolymers with a blocky sequence were obtained as indicated by ¹³C NMR spectroscopy.

Finally, a paper of Phomphrai and coworkers describing syntheses of cyclic poly lactides by means of a tin(II) complex derived from a bisphenol (**Scheme 28**) needs discussion.^[53] Those authors proposed a ZIP ((a) in **Scheme 28**) saying that the lone electron pair of the Sn(II) atom plays the role of a carbene.



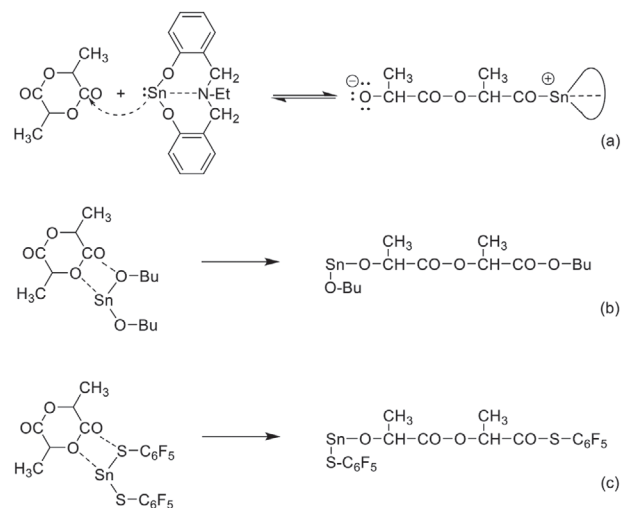
Scheme 27. Carbene-catalyzed zwitterionic polymerization of cyclic carbonates.

However, an experimental evidence for a ZIP mechanism was not provided. Characteristic for a ZIP mechanism is partial racemization of L-lactide, because the anionic chain end (and perhaps the catalysts) is basic enough to deprotonate the monomer.

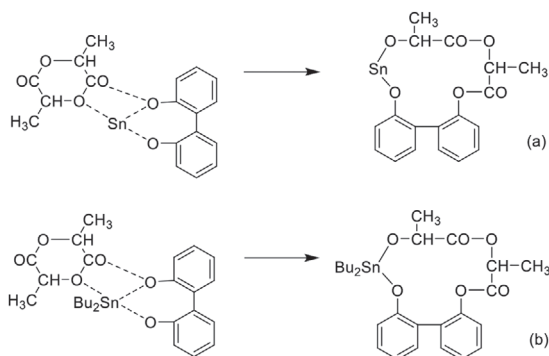
However, in the case of the “Phomphrai catalyst” the tertiary amine group may also cause racemization, so that partial racemization does prove a ZIP mechanism. The authors did not disclose any information about the optical purity of their polylactides. In this connection it is noteworthy that tin bisbutoxide reacts with lactide by a coordination insertion mechanism (B).^[54,55] Furthermore, the bis(pentafluorothiophenolate) of Sn(II) also reacts by a coordination insertion mechanism.^[56] The cyclic tin(II) bisphenoxide^[57] and the cyclic dibutyltin bisphenoxide^[58] (**Scheme 29**) gave nearly identical results, namely high molar mass cyclic poly(L-lactide)s (M_w up to 300 000 g mol⁻¹) with full optical purity, a result which is incompatible with a ZIP mechanism. Since the dibutyltin compound cannot catalyze a ZIP mechanism, a ring-expansion polymerization based on a coordination-insertion mechanism is the only satisfactory explanation. All these results suggest that it is at least questionable, that the “Phomphrai catalyst” catalyzes a ZIP mechanism.

2.4. Zwitterionic Polymerization of Cyclosiloxanes

In 2013, Waymouth and coworkers reported on the ZIP of 2,2,5,5-tetramethyl-2,5-disilacyclopentane (TMSOC) catalyzed



Scheme 28. a) Hypothetical and b+c) proven mechanisms of initiation steps resulting from reactions of various Sn(II) compounds with lactide.



Scheme 29. Initiation steps of ring-expansion polymerizations with cyclic Sn(II) and Sn(IV) bisphenoxides.

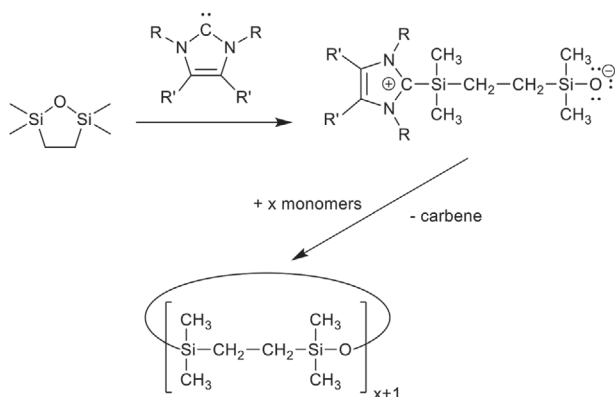
by various *N*-heterocyclic carbenes (**Scheme 30**).^[59] These polymerizations were performed in THF or DMSO at room temperature and proceeded faster in THF. With the most reactive carbenes weight average molecular weights >500 000 g mol⁻¹ were achieved within a few minutes. Comparison of the intrinsic viscosities with those of linear analogs prepared by initiation with alcohols gave ratios around 0.67–0.70 suggesting that the vast majority of these polycarbosiloxanes had a cyclic architecture. For the polymerization mechanism, the authors discuss an equilibrium between open-chain zwitterions and a cyclic dormant species.

Another contribution to this working field came recently from Liu and coworkers.^[6] A spirocyclic octamethyl siloxane was polymerized in THF by means of 1,5,7-triazabicyclo[4.4.0]dec-5-en (TBD), whereupon cyclic methyl-substituted polysiloxanes having M_w 's up to 10⁶ g mol⁻¹ were obtained (**Scheme 31**).

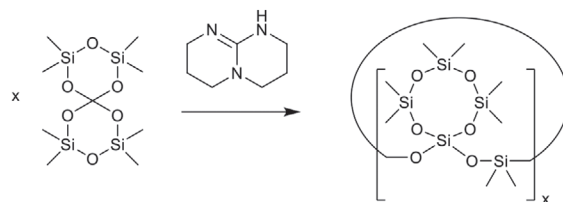
3. ROPPOCs Based on One Ionic and One Covalent Chain End

3.1. Cyclic Polyesters

In 2008, Kricheldorf et al. reported that heating of L-lactide with neat imidazole in bulk resulted in a ROPPOC polymerization

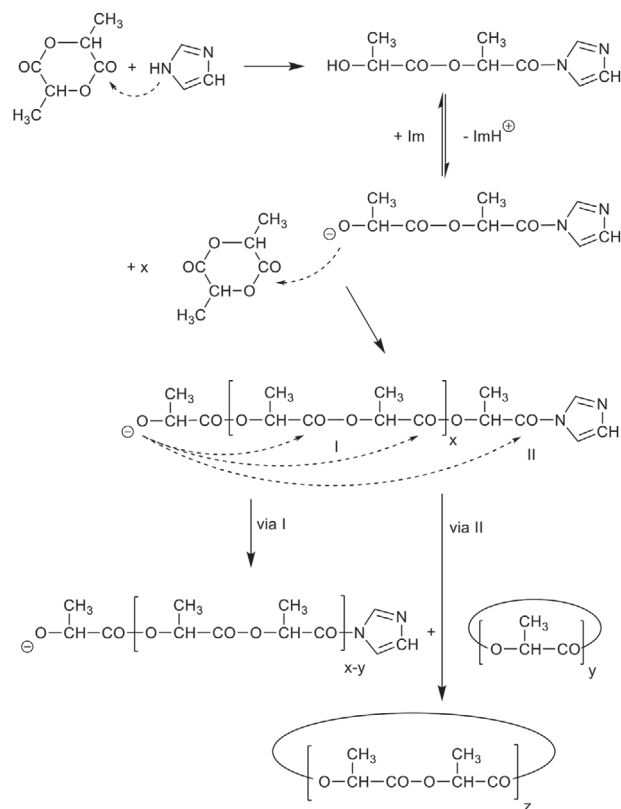


Scheme 30. Zwitterionic polymerization of 2,2,5,5-tetramethyl-2,5-disila-*N*-cyclopentane.

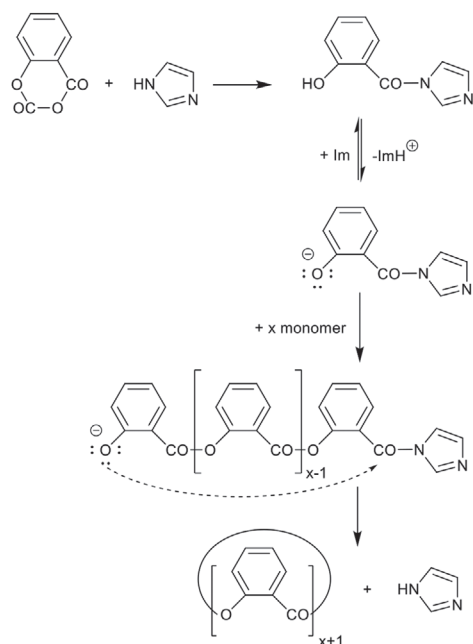


Scheme 31. Zwitterionic polymerization of a spirocyclic siloxane by means of DBU.

yielding cyclic polylactides with M_w 's up to approx. 60 000–70 000 g mol⁻¹.^[4] When conducted at 100 °C with short reaction times (4 h) the reaction product consisted of even-numbered cycles as indicated by MALDI-TOF mass spectrometry. With increasing time (studied up to 48 h) more and more odd-numbered cycles were formed and after 8 h at 150 °C full equilibration of even- and odd cycles was reached. More acidic heterocycles such as benzimidazole, 1,2,4-triazole, uracil, or hypoxanthine did not catalyze a polymerization of lactide. These results together with significant racemization suggest the polymerization mechanism outlined in **Scheme 32**. The first step is a nucleophilic attack of the imidazole onto the CO group of lactide followed by an anionic polymerization with end-to-end cyclization. Reaction of imidazole with the initially formed cyclics results in ring-opening followed by backbiting equilibration. The failure of more acidic heterocycles is a consequence of their lower basicity which does not suffice to deprotonate the OH end group. This approach presents for the first time a preparation of cyclic polyesters from



Scheme 32. Imidazole-catalyzed ROP of lactide with formation of cyclic polylactides.



Scheme 33. Imidazole-initiated ROPPOC synthesis of cyclic polysalicylate.

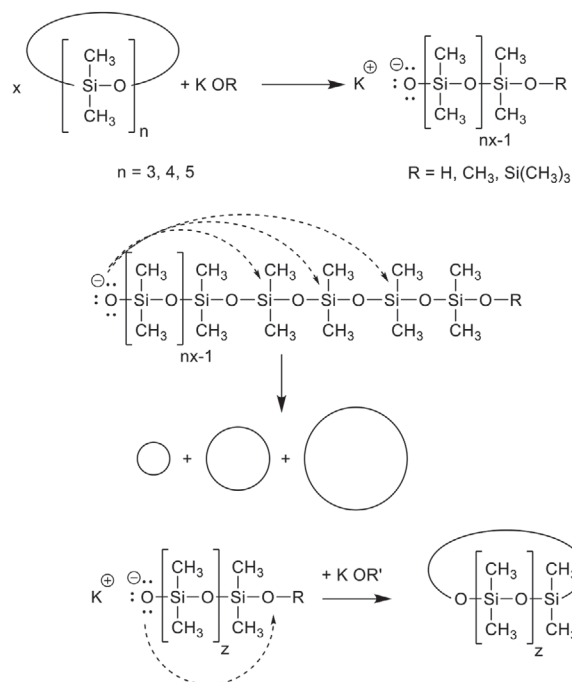
lactides or lactones by means of an organocatalyst in bulk, a procedure which is advantageous over ZIPs in THF from the viewpoint of sustainability and upscaling. Yet, the large quantities of pure and dry imidazole which are needed, and the substantial racemization are disadvantageous.

Another example of imidazole catalyzed formation of cyclic polyesters is the ROPPOC of salicylic acid OCA (**Scheme 33**).^[27]

From the mechanistic point of view, it was interesting to detect imidazole activated linear chains by mass spectrometry, but the “contamination” with linear chains and the low molecular weights of all reaction products are negative aspects from the preparative viewpoint. An example of a carbene-catalyzed polymerization involving only one ionic chain end was reported by Schnee et al. in 2017.^[60] Those authors used a *N*-heterocyclic carbene masked with trimethyl or triethyl compounds of aluminum, gallium or indium in combination with *rac*-*D,L*-lactide as monomer. ROPs in THF at 20–30 °C yielded linear chains having one carbene acylium ion end group and a covalent Al–O–CH end group instead of an anionic chain end. Upon heating in toluene to 90 °C end-to-end cyclization occurred, and low molar mass cyclic poly(*D,L*-lactide)s ($M_n < 10\,000\text{ g mol}^{-1}$) were obtained

3.2. Cyclic Polysiloxanes

The anionic polymerization of cyclosiloxanes has intensively been studied by various research groups.^[61–63] Usually, alkoxide anions or silanolates were used as initiators, and all these initiators gave stable end groups. The formation of cyclic oligomers and low molar polymers, which has intensively been explored by Semlyen and coworkers, was attributed to “backbiting” from the anionic chain end (**Scheme 34**).^[64,65] Yet, when a more reactive covalent end group is used, perhaps derived from an acidic



Scheme 34. Anionic ROP of cyclic siloxanes followed by backbiting and a hypothetical end-to-end cyclization.

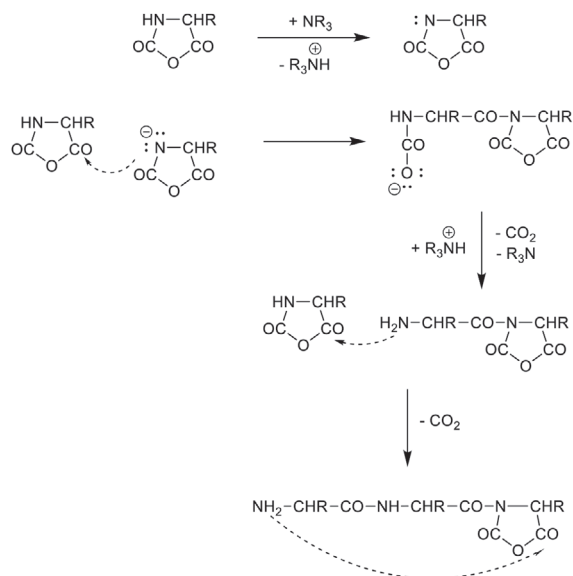
phenol (KOR' in **Scheme 34**), end-to-end cyclization might also occur, so that polysiloxanes almost completely consisting of cyclic species should be formed. However, such a study has not been found by the authors yet.

4. ROPPOCs Based on Two Covalent Chain Ends

4.1. Cyclic Polypeptides

As shortly mentioned in Section 2.1, all kinds of amino acid NCAs can be polymerized with pyridine as catalyst, but in the case of *N*-unsubstituted NCAs, the initial formation of a zwitterion is not necessarily followed by a ZIP (**Scheme 10**). A clear decision, if the chain growth proceeds by a zwitterionic mechanism or via covalent end groups does not exist, but two arguments strongly support a non-ionic mechanism. First, prototropic reactions are orders of magnitude faster than all reactions of heavier atoms and groups. Second, carbamates of tertiary amines are unstable at room temperature (in contrast to carbamates of secondary or primary amines) and decarboxylation of the carbamic acid shifts the equilibrium irreversibly toward amino end groups (**Scheme 35**).

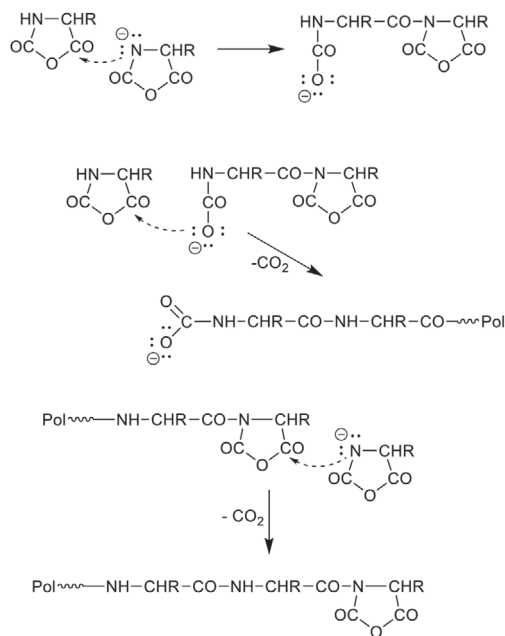
Furthermore, experiments with ethyl diisopropyl amine have shown, that cyclic polypeptides are formed as sole or predominant reaction products, when trialkyl amines are used as catalysts, even when their nucleophilicity is close to zero due to steric hindrance.^[66] For these polymerizations the mechanism formulated in **Scheme 36** was proposed. It has been demonstrated by several syntheses of *N*-substituted NCAs, such as those outlined in **Scheme 37**, that tertiary amines are indeed capable to deprotonate the NH-group of NCAs.^[67,68] However,



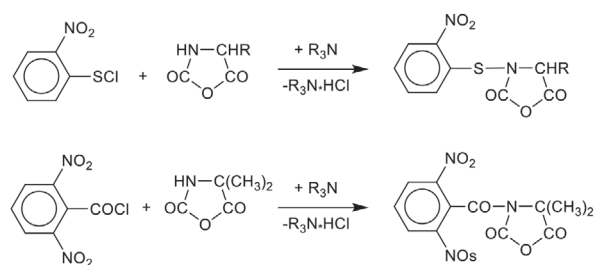
Scheme 35. Tertiary-amine-promoted ROPPOC of α -amino acid NCAs via two covalent chain ends.

it is unproven and unlikely that the chain growth proceeds exclusively via carbamate anions, because carbamates of tertiary amines are unstable and rapidly decarboxylate even at room temperature. Hence, the more likely mechanism is a chain growth via primary amino end groups (Scheme 35).

Therefore, these polymerizations are presented here and not in Section 3. However, they represent a borderline case, and it will be difficult to find out, to what extent the propagation proceeds via amino or via carbamate end groups. The same authors also reported on formation of cyclic polypeptoids by imidazole catalyzed polymerizations of NCAs.^[69] Initiation and



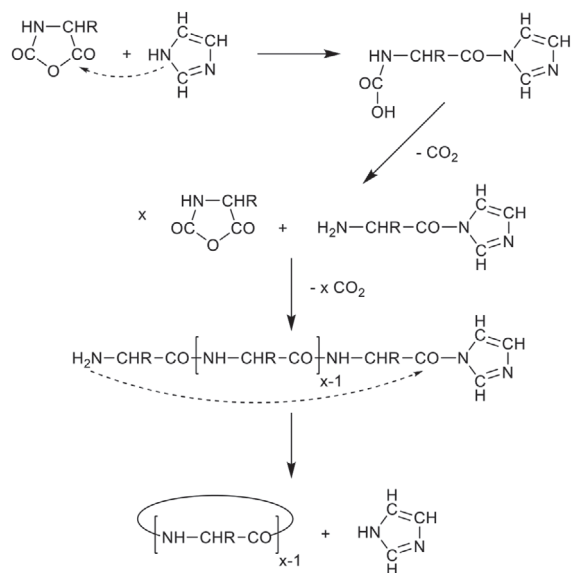
Scheme 36. Tertiary-amine-catalyzed anionic polymerization of α -amino acid NCAs.



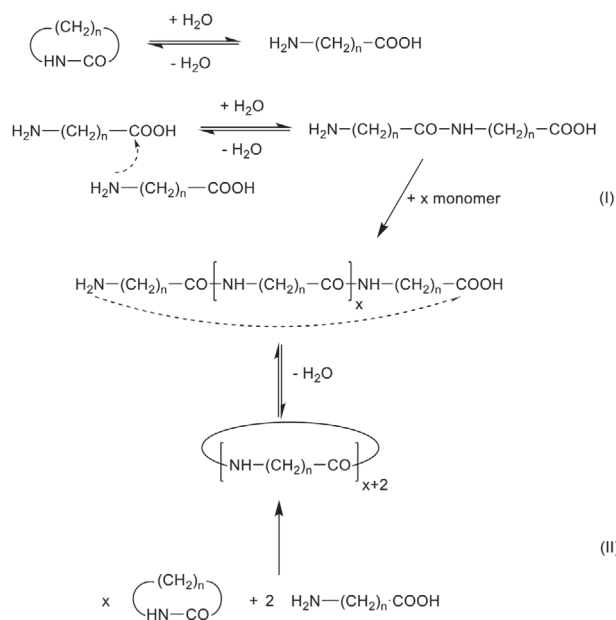
Scheme 37. Tertiary-amine-promoted *N*-substitution of α -amino acid *N*-carboxyanhydrides.

propagation steps are the same as those of aliphatic primary or secondary amine-initiated polymerizations, namely a nucleophilic attack of amino (end) groups onto CO-5 of the NCAs.

The MALDI-TOF mass spectra surprisingly revealed that with Sar-NCA the best results, meaning cycles free of linear chains, were obtained for NCA/imidazole ratio of 1:1, whereas higher ratios resulted in contamination with linear chains. However, the inverse pattern was found for D,L-Leu and D,L-Phe NCAs. Here, the best results were obtained with an NCA/imidazole ratio of 10/1 (and not at 1/1). The results obtained with L-Ala-NCA were different, because CO₂H or CO₂Me terminated linear oligomers were the main products depending on whether the reaction mixture was poured into water or methanol (Scheme 38). This finding suggests that linear chains having imidazolide end groups were buried in the crystallites of the β -sheet lamellae which precipitated rapidly from the reaction mixture. In the case of Sar, D,L-Leu and D,L-Phe-NCA it is the relatively good solubility of the short polypeptide chains in the reaction medium which prevented rapid precipitation. In other words, regardless of mechanistic details, the preparative success of the ROPPOC approach to cyclic polypeptides depends mainly on the solubility of the oligopeptides in the reaction mixture.



Scheme 38. Imidazole-initiated ROP of *N*-NCAs.

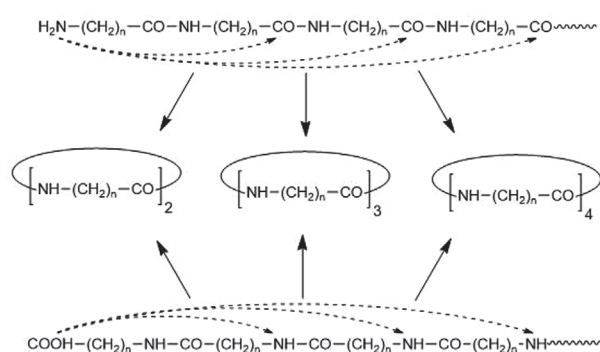


Scheme 39. Simplified mechanism of polycondensation of ω -amino acids and ROPPOC of the corresponding lactam.

4.2. Cyclic Polyamides

Aliphatic polyamides can be prepared in various ways, but the oldest and technically used synthetic method is the polycondensation of diamines and dicarboxylic acids or of ω -amino alkanolic acids. For the technical production of Nylon-6 or Nylon-12, the ω -amino alkanolic acids are almost completely replaced by the corresponding lactams for two reasons. First, the technical synthesis of lactams is less expensive than that of ω -amino alkanolic acids. Second, liberation and removal of rather large amounts of water is avoided. The ω -amino alkanolic acid plays the role of catalyst and its amount can be used to control the average molecular weight. Instead of an ω -amino acid the corresponding amount of water may be added which causes a rapid hydrolysis of lactam at temperatures > 200 °C. (**Scheme 39**). When the temperature is high enough and when the time is sufficiently long, reaction mixtures containing little or much lactam yield the same reaction mixture, provided that the conversion of the reactive end groups is identical. For example, a mixture of 50 mol% lactam and 50 mol% of ω -amino acid corresponds to a polycondensation of ω -amino acid with 50% conversion of the functional groups and a mixture of 90 mol% of lactam and 10% ω -amino acid corresponds to a polycondensation of ω -amino acid with 90% conversion of functional groups. The extent of cyclization depends, in turn, on the conversion of functional groups. Hence, identical products under equilibrium conditions despite variation of the monomer mixture illustrate a standard law of chemistry which says that an equilibrium is independent on the reaction pathway.

Experimental evidence that polymerizations of lactams catalyzed by ω -amino acids obey the definition of ROPPOCs was obtained by the first author from a reinvestigation of the synthesis of Nylon-6 in bulk, so that these nylon syntheses may be considered as the oldest examples of ROPPOCs.^[70] There,



Scheme 40. Formation of cyclic oligomers by backbiting.

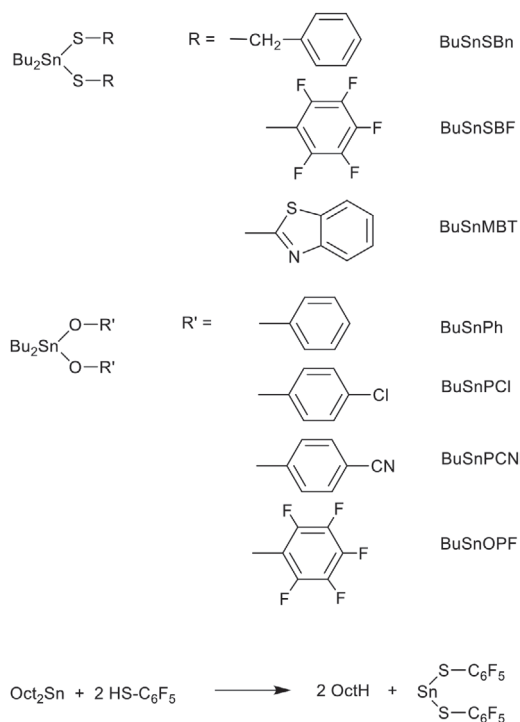
the amino end group can react with the carboxylic end group (**Scheme 39**) and yield small and large cyclic polyamides by end-to-end cyclization. Smaller cycles are also formed by “backbiting” from both chain ends (**Scheme 40**).

The molecular weights, and thus, the conversion was optimized (250 °C/48 h). By precipitation and repeated extraction approx. 28 wt% of the reaction product were removed and identified as monomer and cyclic oligomers and low molar mass polymers. The MALDI TOF mass spectra of the remainder still displayed peaks of cyclics bare of any linear species and cycles up to 10 000 Da were detected (the technical limit of the measurements at this time). Unfortunately, the authors were at that not able to characterize the high molar fraction by measurement of the intrinsic viscosity by GPC with triple detection.

Nearly identical results were obtained from copolycondensation of 7-amino heptanoic lactam and 1,6-diamino hexane and suberic acid.^[71] The resulting Nylon-7/-7,7 copolyamides showed better solubility in trifluoroethanol than the corresponding homopolyamides but looked like homopolymers from the viewpoint of mass spectrometry. The significance of these results for the proper understanding of the Jacobson–Stockmayer theory is discussed in Section 5.

4.3. Cyclic Polyesters

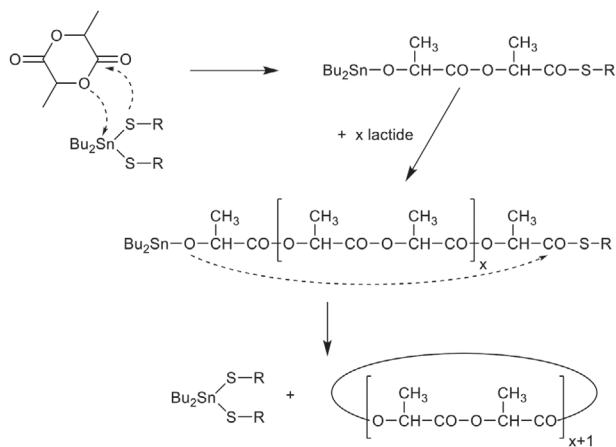
Catalysts suited for ROPPOC syntheses of cyclic polyesters from lactide or lactones via two covalent end groups have only been described over the past 3 years. The first report in this direction were about three dibutyltin dimercaptides presented in **Scheme 41** (with abbreviations BuSnSBn, BuSnSPF, and BuSnMBT).^[72] All these catalysts have in common, that they do not enable polymerization at room temperature in solution. Nevertheless, they have the important advantage that they allow for polymerization of L-lactide in bulk at temperatures above 100 °C without racemization. With BuSnBn Lac/Cat ratio, temperature and time were varied, but even under optimum conditions the MALDI TOF mass spectra displayed peaks of a considerable fraction of linear chains terminated by thiobenzyl ester end groups in agreement with the mechanism outlined in **Scheme 42**. However, the fraction of cycles was much higher than that of poly lactides catalyzed by dibutyltin bisbenzyl oxides (**Figure 1**). This comparison indicates that the benzyl thioester end group is more electrophilic than the benzyl ester end group



Scheme 41. Catalysts used for ROPPOC of L-lactide.

in agreement with the fact, that the human organism activates the acetyl group as a thioester of Coenzyme-A. Furthermore, the end-to-end cyclization is thermodynamically more favored, because a Sn–O bond is replaced by a thermodynamically more stable Sn–S bond.

When BuSnSBn was replaced by BuSnSPF or BuSnMBT almost completely cyclized poly(lactides) were obtained (**Figure 2**). With the MBT catalyst M_w values up to 45 000 g mol^{-1} were achieved, but with BuSnSPF cycles up to 100 000 g mol^{-1} and in more recent study up to 145 000 g mol^{-1} were obtained.^[73] The cyclic topology was proven by MALDI TOF mass spectrometry and absence of end groups, but more recently also a comparison of intrinsic viscosities (MHS



Scheme 42. Simplified reaction mechanism of a ROPPOC of L-lactide catalyzed by a dibutyl tin(II) catalyst.

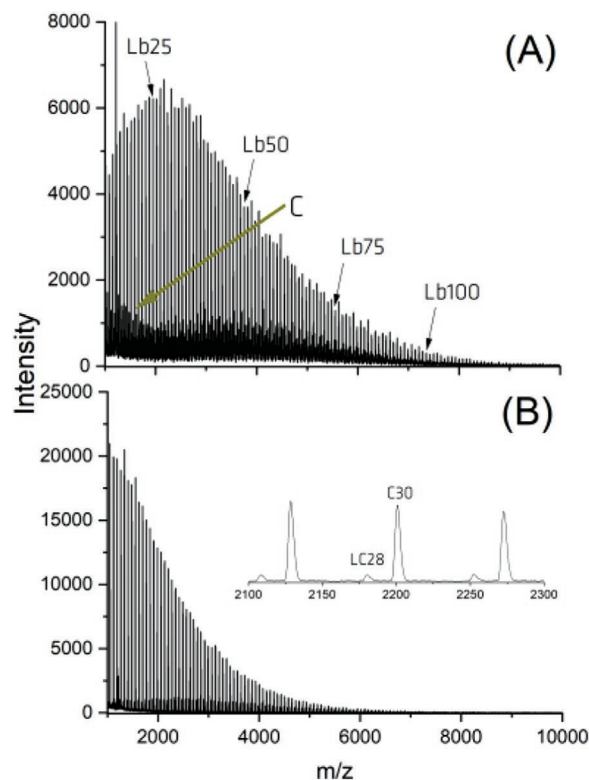


Figure 1. MALDI-TOF mass spectra of poly(L-lactide)s prepared via ROP(POC) in bulk at 160 °C/4 h: A) with $\text{Bu}_2\text{Sn}(\text{OC}_6\text{H}_5)_2$, B) with $\text{Bu}_2\text{Sn}(\text{OC}_6\text{H}_4\text{Cl})_2$. Reproduced with permission.^[72] Copyright 2017, Wiley-VCH.

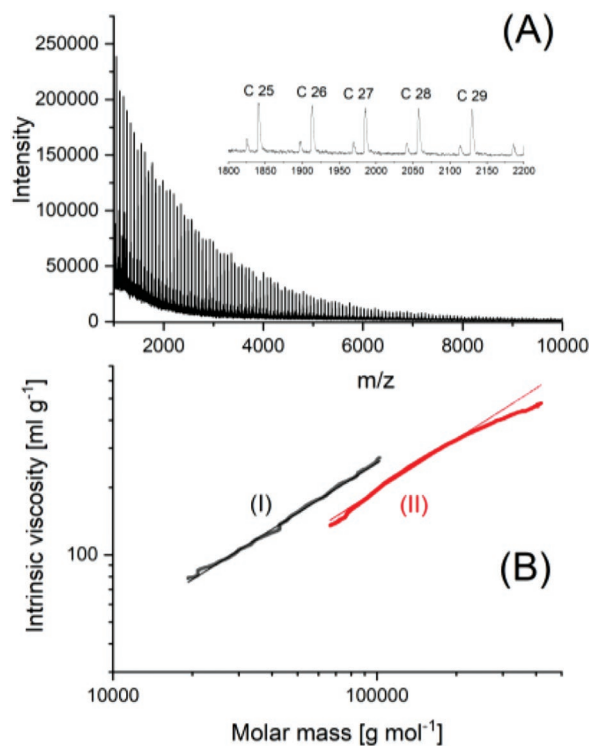


Figure 2. MALDI-TOF mass spectrum and MHS measurement of a poly(lactide) prepared in bulk at 160 °C/4 h with $\text{Bu}_2\text{Sn}(\text{SC}_6\text{F}_5)_2$ as catalyst. Reproduced with permission.^[75] Copyright 1979, Wiley-VCH.

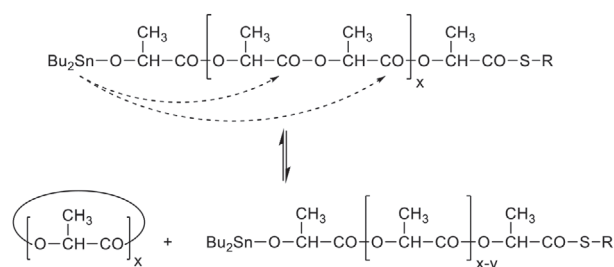
measurements) proved that also the high molar mass fraction is cyclic. A conspicuous feature of all these polymerizations was the finding that the molecular weights decreased with the higher Lac/Cat ratios and the mass spectra displayed more and more peaks of linear chains. A satisfactory explanation of this phenomenon has not been found so far.

In a subsequent study dibutyltin bisphenoxides were used as catalysts (Scheme 41), which were prepared from dibutyltin oxide and phenols.^[74] The acidity of these phenols was varied over a broad range, from phenol itself up to pentafluorophenol. It was expected that the reactivity (electrophilicity) of the phenyl ester end groups formed upon reaction with lactide increases in the same order and this expectation was confirmed by the experiments. Under standard conditions (160 °C/1 h) a large fraction of linear chains was observed in the mass spectra of BuSnPh- and BuSnPCl-catalyzed polylactides. BuSnPCN yielded a considerably lower fraction of linear chains, but mass spectra bare of linear species were only obtained with BuSnOPF. The rate of polymerization increased in the same order. The cyclic topology of the high molar mass fraction of BuSnOPF catalyzed samples was confirmed by MHS measurements.

With BuSnOPF again the phenomenon was observed that the highest molecular weight (M_w up to 90 000 g mol⁻¹) and mass spectra free of linear species were best achieved at low Lac/Cat ratios (e.g., 100/1). The high reactivity of BuSnOPF also allowed for polymerizations in solution, whereupon the molecular weights could be reduced to M_w 's around 25 000 g mol⁻¹ at a monomer concentration of 0.5 mol L⁻¹. This result is important, because ROPPOCs do not allow for a control of the molecular weight via the Lac/Cat ratio.

Furthermore, it was found that simple commercial organotin chlorides may be useful as ROPPOC catalysts.^[3] In the series Bu₃SnCl, Bu₂SnCl₂, BuSnCl₃ the reactivity increased in the given order, but BuSnCl₃ yielded complex reaction products mainly consisting of linear species. In contrast, the least reactive catalyst, Bu₃SnCl produced cyclic polylactides, which according to MALDI TOF mass spectra and MHS measurements were free of linear chains, but reaction times up to 1 d at 160 °C were required. These results were reproduced twice with different batches of L-lactide. When Me₂SnCl₂, Bu₂SnCl₂, and Ph₂SnCl₂ were compared, the reactivity increased in the given order. The most reactive catalyst (Ph₂SnCl₂) gave the best results with respect to molecular weight purity of the cyclic polylactides. Yet, regardless if Bu₃SnCl or Ph₂SnCl₂ served as catalysts, the best results require again low Lac/Cat ratios (<600/1 in the case of Bu₃SnCl). Therefore, this phenomenon proved to be characteristic for this ROPPOC approach and was independent of the structure of the catalyst. The mechanism outlined in Scheme 3 was proposed as most likely explanation of the experimental results.

All the covalent ROPPOC catalysts have in common that they produced equal quantities of even and odd-numbered cycles, due to rapid ring–ring equilibration via intracircular backbiting. Yet when L-lactide was polymerized with BuSnOPF at 100 °C (the lowest possible temperature for polymerization of L-lactide in bulk) even-numbered chains having pentafluorophenyl ester end groups were the main reaction products. This finding proved that the polymerization indeed proceeded by a mechanism analogous to that formulated in Scheme 42, and that the



Scheme 43. Formation of cyclic oligolactides via backbiting from the nucleophilic chain end.

larger cycles formed at higher temperatures were the result of end-to-end cyclization and not by “backbiting” (Scheme 43).

All these experiments have also in common that isolated catalysts were used the structure of which was confirmed by elemental analyses and ¹H NMR spectroscopy. However, a couple of experiments conducted with an in situ prepared Sn(II) catalyst were also reported. For these experiments SnOct₂ was mixed with pentafluorothiophenol and L-lactide and at 160 °C clean cyclic poly(L-lactide)s were obtained after 4 h. Most likely, the SnOct₂ reacted with the thiophenol according to the equation outlined in Scheme 41, and the resulting tin(II) thiophenolate reacted with L-lactide in analogy to the mechanism formulated in Scheme 42. When the preparative usefulness of the covalent catalysts (Scheme 40) for the synthesis of cyclic polylactides is compared with that of zwitterionic catalysts, the following conclusions may be drawn:

- In contrast to ZIP catalysts, the covalent catalysts enable to perform polymerizations in bulk, and thus, allow for upscaling, to reduce the costs, and meet the requirements for sustainability.
- Higher molecular weights can be achieved.
- No racemization occurs even at 180 °C (at times < 4 h)
- The molecular weights can be varied by variation of the catalyst and by polymerization in solution.
- The cytotoxicity of organotin compounds is unfavorable, but so long as the toxicity data of the organic ZIP catalysts are unknown, it is not justified to attribute to them a lower toxicity. The search for a nontoxic catalyst which yields medium and high molecular weight cyclic polylactides and polylactones free of racemization seems to be of primary interest.

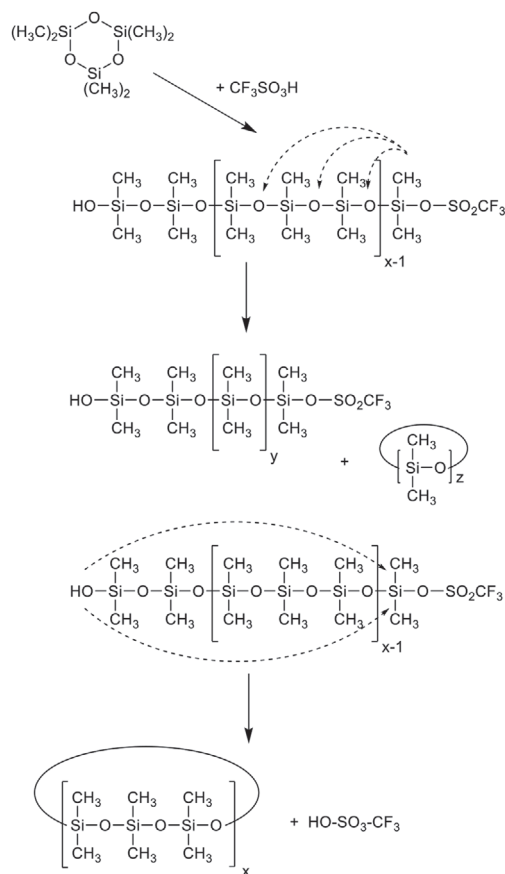
Finally, it should be mentioned that syntheses of cyclic polyesters and other polymers via reversible ROPPOCs possess broad molecular weight distributions, above all, when prepared in bulk. Over the past 20 years, numerous papers have appeared describing syntheses of linear polylactides and polylactones with extremely low dispersities ($\mathcal{D} < 1.29$) and consider this result as important success. However, none of those authors has reported which commercial application requires such low dispersities and the authors of this review were unable to find such an application.

For all applications based on thermal processing from the melt (extrusion, fiber spinning, injection molding, bottle blowing), low dispersities are a serious disadvantage. High-dispersity polymers possess a more favorable balance of low melt viscosity and better mechanical properties. Therefore, high

dispersities of the polymers prepared by reversible ROPPOC's are an advantage and not a shortcoming for almost all potential applications.

4.4. Cyclic Polysiloxanes

Cationic polymerizations of cyclosiloxanes were explored in much detail by several research groups,^[61,75–78] and for most catalyst systems a correlation with the ROPPOC method is hard to find. However, the polymerization catalyzed by trifluoromethane sulfonic acid (triflic acid) which was found to be particularly effective, needs discussion. Chojnowski and coworkers have studied the kinetic of this ROP in dichloromethane in much detail and reached the following conclusion.^[76] First, in the case of hexamethyltrisiloxane rapid exothermal polymerization yields high molecular weight polysiloxanes, but due to a slower equilibration yielding cyclic oligomers, the molecular weight considerably decreases upon storage of the reaction mixture at room temperature for several hours. Second, based on ¹H NMR spectroscopy it was concluded that the triflic acid cleaves the Si–O bonds and yields covalent triflate end groups as highly reactive intermediates (Scheme 44). Provided that the OH end group can react with the triflate group by end-to-end cyclization, this cationic polymerization meets the definition of ROPPOC. Since Chojnowski did neither have the MALDI TOF



Scheme 44. Acid-catalyzed ROP of dimethyl-cyclo-trisiloxane with hypothetical end-to-end cyclization.

method at hand nor SEC with triple detection, information about the extent of cyclization was not available at that time.

Recently, the authors have reinvestigated the triflic acid catalyzed ROP of hexamethyl cyclotrisiloxane in bulk at temperatures of 70 and 120 °C, with variation of time (up to 7d) and with SiMe₂/Cat ratios of 1000/1, 2000/1, 4000/1, and 6000/1. Again, a rapid polymerization was found, but a subsequent decrease of the initially formed high molecular weights was not observed even after 7 d at 120 °C. The *M_w* values roughly paralleled the Si/Cat ratios and *M_w*'s up to 10⁶ were achieved. These results were a first indication that linear polysiloxanes were formed. Nonetheless, the MALDI-TOF mass spectra exclusively displayed peaks of cyclics (up to 8 000 Da), which were equilibrated after a reaction time of 1d. However, comparison of the intrinsic viscosities with that of a commercial linear poly(dimethyl siloxane) did not reveal any difference, what means that the high molecular weight part of the triflic acid-catalyzed polysiloxanes was linear. Therefore, this study has not been published yet.

5. ROPPOC Syntheses of Cyclic Polymers and the Jacobson–Stockmayer Theory

In 1950, Jacobson and Stockmayer (J+S) published two papers presenting experimental results and a theoretical treatment of what is known today as reversible polycondensations.^[79,80] In the 20 years before, Carothers^[81] and Flory^[82] had published the first theory of step-growth polymerizations considering the course of a polycondensation as an irreversible process, although their experimental work was mainly based on reversible polycondensations. This difference was not understood before the Jacobson–Stockmayer papers had appeared. Carothers and Flory had postulated that cyclization reactions do not play any role for the course of step-growth polymerizations. However, Jacobson and Stockmayer demonstrated that in certain polycondensations, such as syntheses of polyesters by polycondensation of dicarboxylic acids and diols, cyclic oligomers are formed by s.c. “backbiting” reactions. The general principle is shown in Scheme 45.

“Backbiting” means that an active chain end attacks bonds in the backbone of the growing polymer with elimination of cyclics (as also shown in Schemes 32, 33, and 43). This “backbiting” is reversible, what means that it is combined with ring-opening growing steps of the intermediately formed cyclics. Furthermore, this ring–chain equilibrium automatically entails ring–ring and chain–chain equilibration.^[79]

The number fraction of the individual cycles was calculated to decrease with their degree of polymerization according



Scheme 45. General principle of backbiting forming cyclics in a reversible reaction.

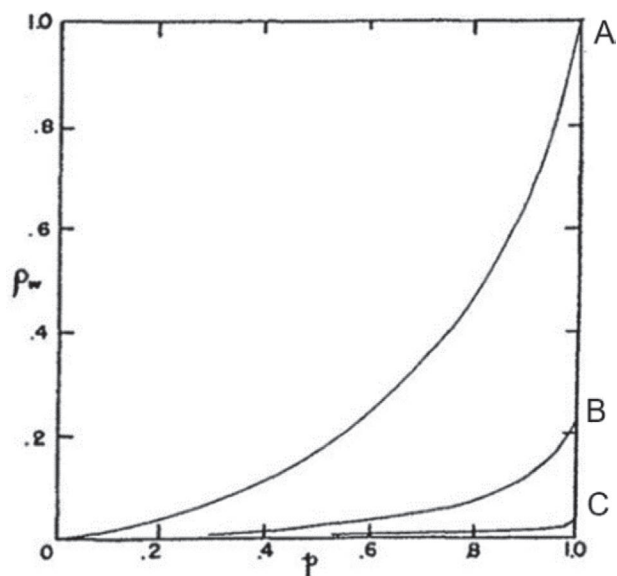


Figure 3. Weight fraction of cyclics (r_w) versus conversion (p) for $a_2 + b_2$ polycondensations calculated for reversible $a_2 + b_2$ polycondensations (case IIIa) with three different initial monomer concentrations: A) $B'/c = 0.5$; B) $B'/c = 0.05$; C) $B'/c = 0.005$ (polycondensation in bulk). Reproduced with permission.^[83] Copyright 1950, American Institute of Physics.

to $DP^{-2.5}$. Therefore, formation of cycles having high molecular weights was not expected, and Stockmayer agreed with Flory in that formation of large cycles (e.g., degree of polymerization >10) by end-to-end cyclization does not occur. In his influential book *Principles of Polymer Chemistry*, Flory accepted Stockmayer's modification of his polycondensation theory and confirmed and expanded calculations published by J+S.^[83] According to their mathematical equations the initial monomer concentration (IMC) plays a decisive role for the course on a reversible polycondensation. Below a s.c. critical concentration 100% conversion results in formation of 100 weight% of cyclics, whereas above this concentration total cyclization is impossible. Stockmayer and Flory have calculated that for polycondensations in bulk an " $a_2 + b_2$ " monomer combination will yield approx. 4 wt% of cycles at 100% conversion and " $a - b$ " monomers will yield approx. 8% because the cyclization probability is twice as high for $a - b$ systems. The diagram of **Figure 3** illustrates this scenario. However, these percentages are the result of mathematical calculations and were never confirmed by experiments.

In the 1970s Gordon et al.^[8,84] and Stepto et al.^[9,10] elaborated and compared three mathematical theories concerning the kinetic course of irreversible step-growth polymerizations. All three theories agreed in that cycles are formed by end-to-end cyclization and their number fraction increases with higher conversions until all reaction products are cycles at 100% conversion regardless of the initial monomer concentration (**Figure 4**). The experimental evidence for the correctness of these theories was later contributed by Horbach et al.^[85] via end group analyses and by Kricheldorf et al. on the basis of MALDI TOF mass spectra.^[2]

Considering that end-to-end cyclization of long polymer chains is normal in irreversible polycondensations, it is hard to

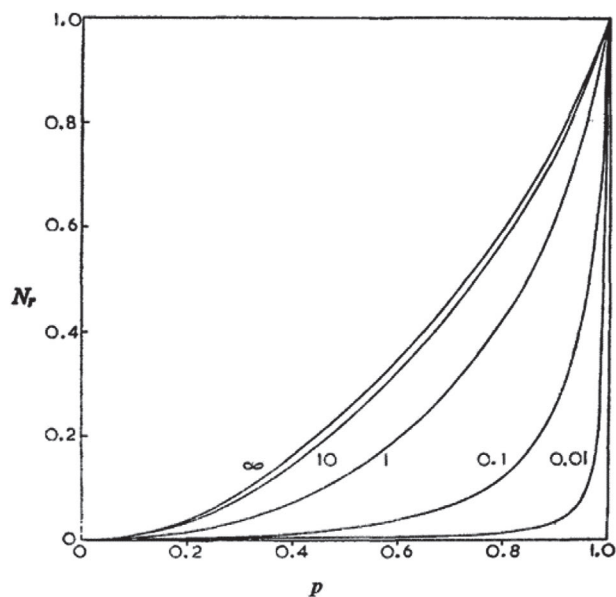


Figure 4. Number fraction of cyclics versus conversion calculated for irreversible polycondensations with different initial monomer concentrations. Reproduced with permission.^[13] Copyright 1951, Royal Society of Chemistry.

understand end-to-end cyclization should not occur in reversible polycondensations, because the existence of backbiting does neither reduce the reactivities of the end groups nor modify the conformational properties of the polymer chains. The ROPPOC experiments with lactams discussed in Section 4.2 were a first demonstration that the mathematical equations of J+S do not match the experimental reality. The contradiction to the JS theory stands on two legs. First, the weight fraction of cyclics is at least by a factor of five higher than calculated (curve C, **Figure 3**). Second, cyclics up to a DP of 90 were detected, and at least the majority of these cycles must have been formed by end-to-end cyclization. This conclusion is based on the fact that both end groups are more reactive than the amide groups in the backbone, and when compared at identical DP, a reaction between both end groups must be faster than the reaction of one end group with an amide group in the chain.

The ROPPOC syntheses of cyclic poly(ϵ -lactide) discussed in Section 4.3, complete the critique of the JS theory with the following results:

- As illustrated by **Figure 1A,B**, the reactivity of the ester end group is decisive for the extent of cyclization a result, which clearly indicates the existence of end-to-end cyclization. This aspect was not considered in the JS theory.
- The MALDI TOF mass spectra of several polylactides demonstrate that cyclization has occurred up to DPs around 100, and since the end groups were more reactive than the ester groups in the backbone at least the majority of cycles must have been formed by end-to-end cyclization.
- The MHS measurements of polylactides prepared by three different classes of catalysts prove that even chains with DPs up to 3000 have cyclized as exemplarily demonstrated by **Figure 1B**.

$$p = N_0 - \frac{N_t}{N_0} \quad (4)$$

with N_0 , N_t = number of functional groups at the beginning and after a certain reaction time t .

$$[L_a]_t = [L_a]_0 \times (1 - p) \quad (5)$$

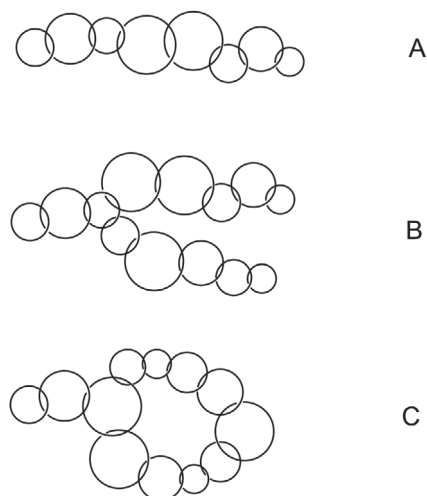
with $[L_a]_0$, $[L_a]_t$ = molar concentration of all linear species at the beginning and after a certain reaction time t .

Furthermore, two theoretical arguments against the calculation of the diagram presented in Figure 3 should be discussed. Equation (4) is the definition of conversion of the end groups in all step-growth polymerizations, regardless if reversible or irreversible. Therefore, 100% conversion is defined by the total consumption of all end groups with the consequence that linear chains have completely disappeared, and all reaction products have necessarily a cyclic topology. Equation (5) says that the molar concentration of all linear species decreases with the conversion until all linear species have disappeared at 100% conversion. At conversions >99% the molar concentration of the linear species dramatically decreases, so that even cyclization of long chains is favored by the Ruggli–Ziegler dilution principle. More experimental and theoretical arguments were presented in a recent publication.^[73] In summary, the experimental results of the ROPPOC syntheses described in Sections 4.2 and 4.3 agree with several theoretical considerations in that the mathematical equations of the JS theory are not correct. Nonetheless, the basic concept of the JS theory is reasonable, and this theory was and still is an extremely fruitful contribution to the understanding of step-growth polymerizations.

6. About the Formation of Polycatenanes

According to the mathematical theories of Gordon and Temple^[8,84] and Stepto and coworkers^[9,10] cyclization competes with chain growth in kinetically controlled (irreversible) polycondensations, and at 100% conversion all reaction products are cycles. As discussed above, the weight fraction of cycles also increases up to 100% in reversible polycondensation. At conversions above 99% not only number and weight fraction of cycles rapidly increases but also their average molecular weight and thus, the ring size. Hence, it is justified to speculate that above 99% conversion a threading of linear chains through neighboring cyclics may dramatically increase, so that more and more oligo- and polycatenanes are formed. These polydisperse polycatenanes do not necessarily possess a quasi-linear architecture ((A) in Scheme 46), they may also be branched (B) or may even have a supercyclic topology (C) and close to 100% conversion formation of 3D architectures must be taken into account.

The ROPPOC syntheses of cyclic polyesters performed in bulk represent the best experimental approach to formation of polycatenanes via polycondensation. Particularly interesting is the comparison with ring-expansion polymerization of the same monomer, because in the case of REP no linear intermediates are formed, so that catenization cannot take place (Scheme 43). For polycatenanes a lower hydrodynamic volume may be expected than for cyclic polymers of identical molecular weight.



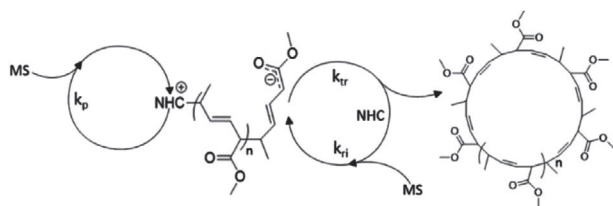
Scheme 46. Various topologies of polydisperse catenanes, which may, in principle, be formed in an ROPPOC.

Hence a comparison of intrinsic viscosities measured under identical conditions for polymers or polymer fractions of identical molecular weight should provide at least a rough estimation, if the ROPPOC approach involves formation of a significant fraction of polycatenanes. The authors have performed numerous Mark-Houwink-Sakurada plots using SEC measurements of polylactides using the triple detection method. No difference between cyclic polylactides prepared by ROPPOC catalysts or by REP catalyst has been found. Since this analytical approach is rather inaccurate, it does certainly not exclude that the ROPPOC polylactides contained < 5% of catenanes. More precise analytical methods will hopefully be developed in the future.

Therefore, a low concentration of oligo- and polycatenanes means that this kind of compact architecture is thermodynamically unfavorable. For large cycles steric hindrance of threading and thus, enthalpic effects are unlikely. The entropy seems to play the predominant role. Two opposite trends need to be considered. First, formation of a small fraction of catenanes represents a gain in entropy for the entire reaction mixture, because it enhances the diversity of molecules. Second, unfavorable conformations and intramolecular interactions will result in a weak positive reaction enthalpy. The balance between entropic and enthalpic effects will largely depend on the structure of individual polymers, because dipole-dipole interactions and rotational barriers depend strongly on the chemical structure.

7. ROPPOC Related Synthetic Strategies

Recently, Takasu and coworkers have reported a new synthetic strategy yielding cyclic vinyl polymers on the basis of a zwitterionic polymerization combined with intramolecular (and perhaps also intermolecular) condensation steps.^[86–88] Since no cyclic monomers were used, this synthetic strategy does not obey the definition of ROPPOC, but it resembles ROPPOC in fundamental aspects. Vinyl monomers such as methyl methacrylate, allyl methacrylate or methyl sorbate were used. A complex of a *N*-heterocyclic carbene and monomer was combined



Scheme 47. Synthetic strategy presented by Takasu et al. to form cyclic vinyl polymers by zwitterionic polymerization. Reproduced with permission.^[86] Copyright 2017, American Society of Chemistry.

with methylaluminum-bis-(2,6-di-tert-butyl-4-methylphenoxide) to yield the catalyst, which initiated an anionic polymerization as the first stage of the entire polymerization process followed by the much slower cyclization of the resulting polymeric zwitterion. This cyclization step involves elimination of the carbene and thus, obeys the definition of a condensation step. M_n values in the range of 7 000–26 000 g mol⁻¹ with dispersities in the range of 1.1–1.5 were achieved. Most polymerizations of methyl sorbate gave lower M_n 's and higher dispersities. Solvents such as toluene, THF and DMF were compared. **Scheme 47** presents an exemplary illustration. In the case of allylmethacrylate, mercaptanes were added to the pendant allyl groups, so that sun-shaped polymers were obtained.

8. Conclusions and Perspectives

The ROPPOC approach has turned out to be a versatile synthetic strategy which allows for syntheses of various cyclic polymers. Although the roots of this approach go back to the middle of the nineteenth century, the vast majority of the results discussed above have been elaborated over the past 15 years. Therefore, this approach may still be considered to be a rather new synthetic strategy. An important advantage and interesting aspect are its versatility, because biopolymers such as polypeptides, biodegradable polyesters such as polylactides and commercial, stable polymers such as polyamides and polysiloxanes can be prepared with cyclic topology in a simple one-step process. Further research will certainly broaden its application and improve the results for other monomers.

Another interesting aspect is its similarity to the biosynthesis of cyclic biopolymers. In both cases, the reaction pathway begins with a polymerization yielding a long linear chain which finally undergoes cyclization via activated end groups. High dilution or fixation of the linear chains to enzyme complexes favors cyclization over intermolecular condensation.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

cyclization, polycondensation, ring-opening polymerization, zwitterions

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