Milestones in development of a ring-opening polymerization of the heterocyclic monomers — view from a personal perspective

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This article is dedicated to Professor Stanislaw Penczek on the occasion of his 80th birthday

Abstract: Ring-opening polymerization (ROP) studies of cyclic acetals, ethers, esters, and esters of phosphoric acids developed in Centre of Molecular and Macromolecular Studies in Łódź is concisely reviewed. Main attention is paid to results of a more general importance for polymer science, as seen from a personal perspective of the authors of this article. Mostly thermodynamics and kinetics in connection with mechanism of the ROP is discussed.

Keywords: heterocyclic monomers, ionic polymerization, coordination polymerization, ring-opening polymerization, kinetics of polymerization, thermodynamics of polymerization.

Kamienie milowe w rozwoju badań polimeryzacji z otwarciem pierścienia monomerów heterocyklicznych — spojrzenie z perspektywy osobistej

Streszczenie: Dokonano zwięzłego przeglądu badań polimeryzacji z otwarciem pierścienia cyklicznych acetali, eterów, estrów i estrów kwasu fosforowego rozwijanych w Centrum Badań Molekularnych i Makromolekularnych w Łodzi. Szczególną uwagę poświęcono wynikom, które na podstawie osobistego poglądu autorów niniejszego artykułu, mają bardziej ogólne znaczenie w nauce o polimerach. W dyskusji położono nacisk na termodynamikę i kinetykę polimeryzacji w powiązaniu z jej mechanizmem.

Słowa kluczowe: monomery heterocykliczne, polimeryzacja jonowa, polimeryzacja koordynacyjna, polimeryzacja z otwarciem pierścienia, kinetyka polimeryzacji, termodynamika polimeryzacji.

With exception of special cases such as cyclic olefins metathesis, vinyl cyclopropane or bicyclobutane polymerization all ring-opening polymerizations (ROP) are limited to heterocyclic monomers. Heteroatom (*e.g.* oxygen, sulfur, nitrogen or phosphorus) containing groups: ether, acetal, carboxylate, sulfide, amide or phosphate are the "vulnerable points" which could readily react with intitiators and propagating active species. In some cases these groups could be additionally activated in result of protonation or binding cationic or anionic species that enhance monomer reactivity towards hydroxyl or amine polymer chain end-groups [1].

Obvious consequence of polymerization of heterocyclic monomers is presence of the reactive heteroatom containing groups along the polymer chains. Therefore, in a large majority of ROP one should take into consideration possibilities of reactions of these groups with propagating active centers. The mentioned above reactions could proceed inter- and intramolecularly, in the latter case leading to formation of cyclic oligomers [2]. The complete set of propagation and transfer reactions is shown in Scheme A.

From Scheme A it follows that ROP of heterocyclic monomers, which begins with a simple initiation and propagation reactions, may end with a system containing in addition to linear molecules a set of cyclics of a various size (see Scheme B).

At equilibrium, fraction of strained cyclic oligomers, including monomer (M) considered formally as the smallest cyclic "oligomer", may strongly depend on temperature. This does not apply to larger, usually non-strained, cyclics and their content in the polymerizing mixture is not temperature dependent. For polymerizations in which only linear chains and monomer are present at equilibrium the monomer concentration ($[M]_e$) can be described by the formula:

$$\ln[M]_e = \frac{\Delta H_p}{RT_e} - \frac{\Delta S_p^\circ}{R} \quad (1)$$

where: ΔH_p, ΔS_p° — enthalpy and standard entropy of polymerization, respectively.

For processes with standard initial monomer concentration (*e.g.* $[M]_0 = 1$ mol/dm^3), $T_e = T_{cr} = \Delta H_p/\Delta S_p^\circ$ (where T_{cr} denotes the critical temperature when at equilibrium

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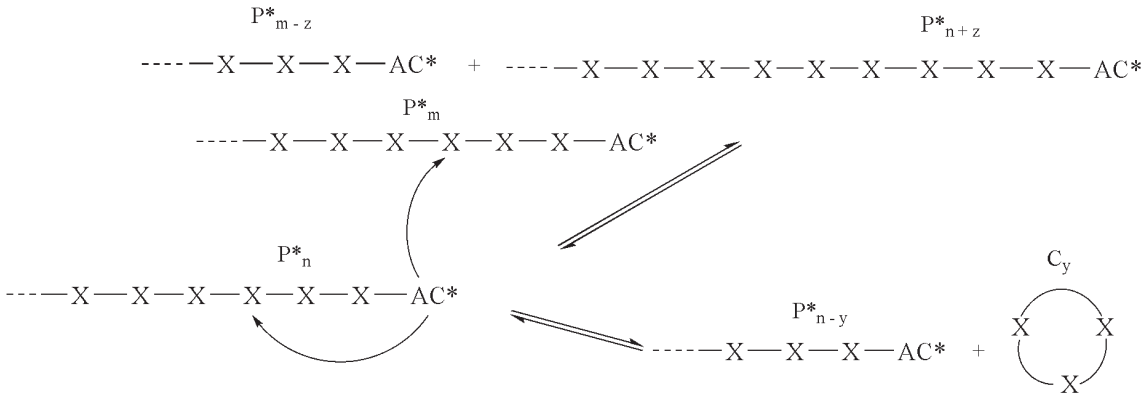
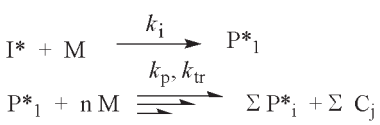


Scheme A

where: X — heteroatom or group containing heteroatoms, — — -[C(R)H]$_n$- moiety, AC* — the active center, P*$_n$ — the linear propagating chains with degree of polymerization equal n, C_y — cyclic oligomers with degree of polymerization equal y, C_1 — monomer (M).



Scheme B

where: I* — initiator molecule, k_i, k_p, and k_{tr} — rate constants of initiation, propagation and transesterification, respectively.

the linear, high-molecular weight polymer is absent, *i.e.* when $[M]_e \approx [M]_0$). For the majority of polymerizations $\Delta H_m < 0$ and $\Delta S_m < 0$ (where ΔH_m and ΔS_m are the enthalpy and entropy change per mole of monomer reacted, respectively) and $T_c = T_{cr}$ means a ceiling temperature above which the high-molecular weight polymer is not formed. For much more rare systems with $\Delta H_m > 0$ and $\Delta S_m > 0$, $T_f = T_{cr}$ is a floor temperature below which the high-molecular weight linear polymer can not be formed. Polymerization of larger ring-size carboxylate esters (*e.g.* tri- or pentadecanolactone) [3, 4] is subjected to thermodynamic restrictions of the latter kind.

Detailed analysis of the kinetics of ROP with cyclization revealed that for the systems with fast propagation and slow cyclization the complete monomer conversion into linear molecules is possible, before a significant amount of cyclic oligomers is formed [5, 6]. Practically, a concept of "Reactivity-Selectivity Principle" [7] led us to a conclusion, that the less reactive are initiating/propagating species the more pronounced is depression of the undesired transesterification side reactions.

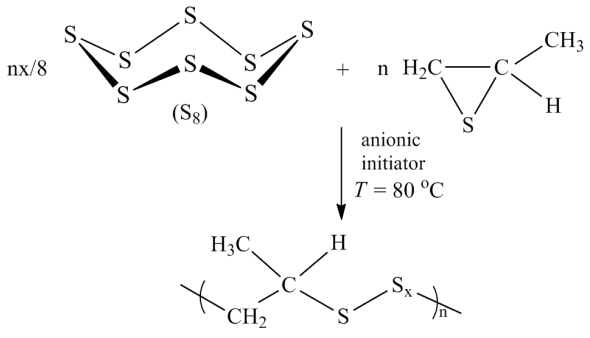
Inter- and intramolecular transfer reactions result also in significant broadening of molecular weight distribution. The dependence of $\overline{M}_w/\overline{M}_n$ on monomer conversion strongly depends on the ratio of the propagation and transfer rate constants. Detailed discussion of this subject was given in a paper by Penczek *et al.* [8] who determined values of the mentioned above ratios of the propagation and chain transfer rate constants at which narrow molecular weight distribution is maintained even for a high (*e.g.* 95 %) monomer conversion.

Presence of heteroatom containing reactive groups along the chain [*e.g.* –C(=O)O–] makes some polymers especially prone to degradation during processing. For example, it is commonly known that injection molding of polylactide is often accompanied with the difficult to control degradation resulting in a polymer with lower $\overline{M}_n$, broader molecular weight distribution and, in many instances, contaminated with lactide. On the other hand, degradability may be also beneficial. In contrary to polyolefins, the aliphatic polyesters are used for fabrication of goods which after serving for the needed time can be composted eventually degrading hydrolytically and enzymatically to water and CO_2 and in this way reducing the plastic waste impact on environment. Due to degradability the polylactide containing polymers found application in medicine as drug carriers, temporary implants and supports in tissue engineering.

Chemical structure of heteroatom containing groups affects also intermolecular interactions which may improve polymer properties. Polyamides with intermolecular hydrogen bonding are a special example when polymers with $\overline{M}_n$ even as low as $2 \cdot 10^4$ have good mechanical properties.

The presented above considerations show that synthesis of desired polymers by ROP of heterocyclic monomers requires deep understanding of the complex polymerization process, including not only determination of the major and side reaction routes but also determination of the relevant rate constants and their dependence on chemical structure of propagating species, monomer, properties of reaction medium, and temperature.

Apart from carbon only few elements are able to form linear polymeric chains. This is also a feature of sulfur atoms. The most stable form of elemental sulfur, the eight-membered unstrained ($\Delta H_p > 0$) ring (S_8), polymerize on heating (T_f = 159 °C in bulk) due to its $\Delta S_p° > 0$ [9]. However, the resulting polymeric sulfur (polyS) is ther-



Scheme C

modynamically unstable at the moderate temperatures and gradually converts back to S_8 *via* unzipping mechanism employing macroradicals (…-SSS*) formed by "spontaneous" homolytic splitting of the polyS chain. Stabilization of polyS chains against this undesirable depropagation should be possible by interruption of linear chain of sulfur atoms by, for example, carbon atoms sequences. This idea has successfully been realized in our laboratory by application of anionic copolymerization of S_8 with cyclic three-membered sulfides as it is shown in Scheme C [10].

This process results in stable, high-molecular weight ($\overline{M}_n \leq 5 \cdot 10^4$) polysulfides with sulfur content up to 85 wt. %. Homopropagation of cyclic sufide is practically absent, but the advanced intramolecular segmental exchange reactions (*cf.* Scheme A) lead to a certain distribution of the length of the polysulfur sequences in the copolymer repeating units. There was a controversy whether the resulting product is a genuine thirane/S_8 copolymer or rather consists of a mixture of polythiirane and the unreacted sulfur. Finally, the copolymer structure has been proven by application of the Raman spectroscopy, that unequivocally shows presence of the linear polysulfide sequences in the product [11, 12].

During the last 45 years such investigations carried out by Professor Stanislaw Penczek and his co-workers resulted in a comprehensive understanding of the mechanism, thermodynamics, and kinetics of the polymerization of cyclic ethers (oxetane and tetrahydrofuran), cyclic acetals (1,3-dioxolane, 1,3,5-trioxane), aliphatic cyclic esters of carboxylic acids (β-propiolactone, β-butyrolactone, δ-valerolactone, ε-caprolactone, lactides), and aliphatic cyclic esters of phosphoric acids (2-alkoxy-2-oxo--1,3,2-dioxaphosphorinane, 2-alkoxy-2-oxo-1,3,2-dioxaphospholane, 2-hydro-2-oxo-1,3,2-dioxaphosphorinane, and *N*,*N*-diethylamino-1,3,2-dioxaphosphorinane). In the subsequent sections of this paper the main findings of these studies will be summarized.

MECHANISM OF POLYMERIZATION OF CYCLIC ETHERS AND ACETALS

Cyclic ethers and cyclic acetals constitute important classes of heterocyclic monomers. Some polymers derived from those monomers are produced on a large industrial scale such as for example poly(ethylene oxide), poly(propylene oxide), polytetrahydrofuran (in form of oligodiols) or polytrioxane. At the same time studies of kinetics and mechanism of polymerization of cyclic ethers and cyclic acetals contributed to our present knowledge of polymerization processes, not limited to specific field of ionic ring-opening polymerization but having more general significance. Notable example is given in professor Krzysztof Matyjaszewski contribution to this issue where he is showing how his earlier studies of cationic polymerization of tetrahydrofuran paved the way for recent developments in controlled radical polymerization (reversible-deactivation radical polymerization following the IUPAC terminology) [13].

Ionic polymerization of cyclic ethers and acetals was thoroughly reviewed recently [14, 15]. Therefore, in the present paper we will concentrate mainly on those selected aspects of cationic polymerization of cyclic ethers and cyclic acetals to which our laboratory have mostly contributed and which, in our opinion, are important for understanding mechanisms of ROP in general.

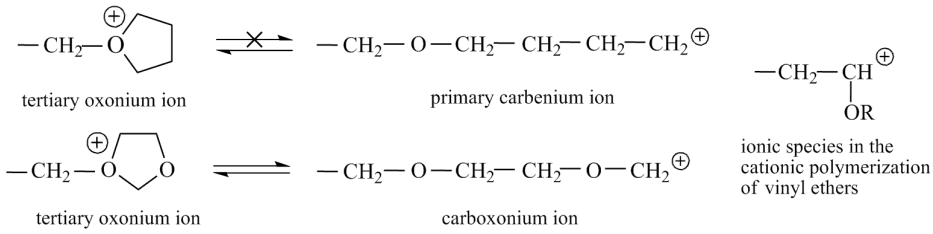
One of those important issues are equilibria between various possible forms of growing species in polymerization; the consequences of understanding ion-ester equilibria in the cationic polymerization of a model cyclic ether: tetrahydrofuran are discussed in Matyjaszewski's article in the present issue.

Other general problem which may be addressed by studying the cationic polymerization of cyclic ethers and cyclic acetals is the mechanism of formation of cyclic fraction of polymeric products. Understanding of cyclization phenomena is important from both fundamental and synthetic point of view, especially if the synthesis of end-functional polymers is attempted. In this section we will briefly describe how the studies of model cyclic ethers and acetals helped to resolve some questions related to cyclization phenomena in cationic ring-opening polymerization.

Cationic polymerization of 1,3-dioxolane

Typically, active species in cationic polymerization of cyclic ethers are tertiary oxonium ions located at the chain end. Because oxygen atoms are present in both monomer and polymer unit, propagation is usually accompanied by cyclization. In the cationic polymerization of cyclic acetals [1,3-dioxolane (DOX) as model monomer] situation is more complex. While in the case of cyclic ethers unimolecular opening of cyclic tertiary oxonium ion can be excluded as it would lead to highly reactive primary carbenium ion, in the case of DOX unimolecular opening would lead to stabilized carboxonium ion, as illustrated in Scheme D (note the similarity of carboxonium ion to active species of cationic polymerization of vinyl ethers).

Thus, the first question that has to be answered to understand the mechanism of cyclic acetal polymerization



Scheme D

is the nature of active species: are they oxonium ions or carboxonium ions (or both coexisting in equilibrium). This was solved by ^{1}H NMR studies of model systems. These studies revealed that carboxonium ions do exist in the system but their fraction is low (~0.3 % at –70 °C in liquid SO_2) [16, 17]. However, their contribution to propagation is not negligible because they are two orders of magnitude more reactive than oxonium ions. The conclusion was, that from both points of view, namely the proportion of a given active species and their contribution to chain growth, the tertiary oxonium ions predominate.

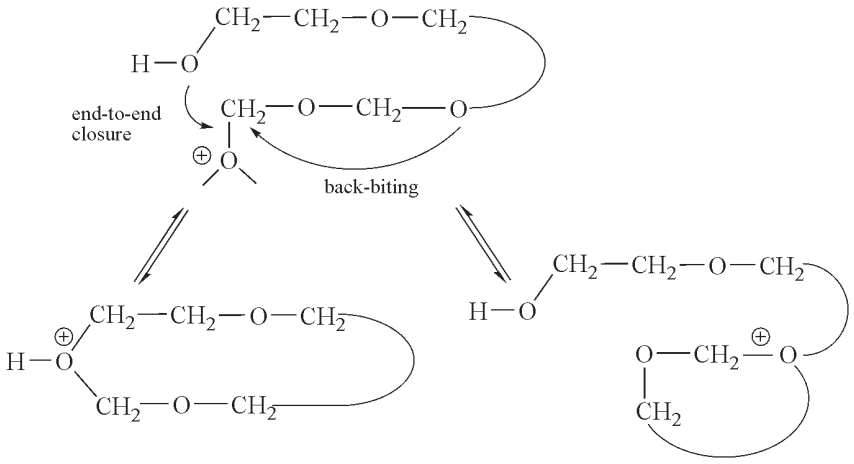
There was, however, more general problem in cationic polymerization of cyclic acetals, that had to be solved. In an early patent [18] it was suggested that polymers of DOX are exclusively cyclic. Later on P. H. Plesch from Keele University elaborated this idea and to explain this observation proposed that polymerization of DOX proceeds by ring-expansion mechanism [19]. This view was opposed by group from Mainz University [20] claiming that polymerization proceeds on linear active species and cyclic fraction is formed by back-biting [21]. This controversy dominated the field for years.

To solve this controversy we used ion-trapping method, developed in our group, based on trapping of active species with reactive tertiary phosphine and subsequent determination of structure of resulting phosphonium ion by ^{31}P NMR [22]. In ^{31}P NMR spectra of polymerizing reaction mixture after trapping with $P(Bu)_3$ signals of both tertiary and quaternary phosphonium ions were observed, their proportion depending on polymerization conditions namely on the ratio of monomer to initiator concentration (strictly speaking on the length of the chain at the moment of phosphine addition). The higher this ratio, the higher was the fraction of quaternary phosphonium ions formed from tertiary oxonium ion active species and the lower the fraction of tertiary phosphonium ions formed from secondary oxonium ion active species.

How this observation can be explained? We have argued that propagation proceeds on linear species *i.e.* macromolecules terminated with tertiary oxonium ion active species. Tertiary oxonium ions located at the chain-ends may react not only with acetal oxygens along the chain (back-biting) but also with HO- group located at the other chain-end (head-group formed as result of initiation with protic acid).

Such end-to-end reaction leads to the structure which is indistinguishable from the structure postulated for ring-expansion mechanism, as shown in Scheme E. Probability of the end-to-end cyclization decreases with increasing chain length and this explain changes of fraction of secondary and tertiary oxonium ion active species with changing chain length.

End-group analysis confirmed linear structure of polymers. If polymers with relatively high-molecular weight were analyzed, there was a reasonable agreement between expected and observed content of end-groups [23—25]. Thus ring expansion mechanism for cationic



Scheme E

polymerization of cyclic acetals was finally disproved although some experimental observations on which it was based (high content of cyclic fraction at specific conditions of polymerization) were essentially correct [26].

Cyclization in cationic polymerization of cyclic ethers and acetals

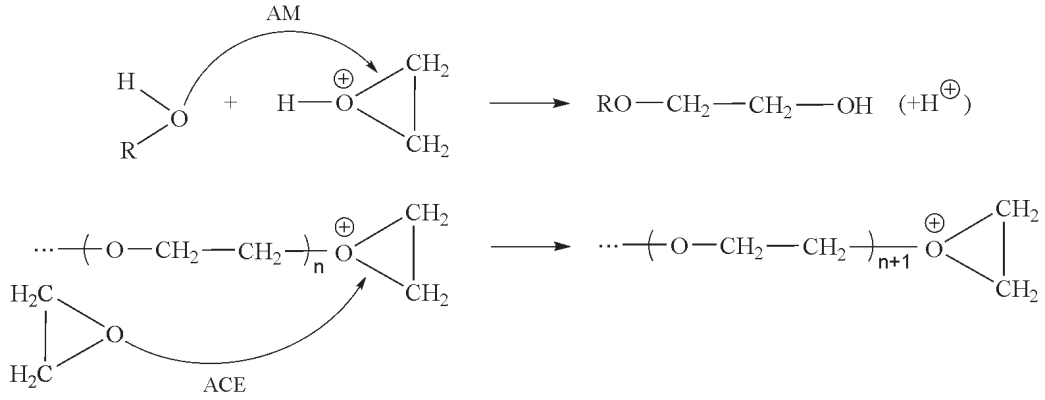
On the first look, cyclization in cationic polymerization of cyclic ethers and acetals cannot be avoided because even if conditions are created that end-to-end cyclization is negligible (high [monomer]/[initiator] ratio) there is still back-biting reaction leading to formation of cyclic oligomers. From the synthetic point of view, especially if synthesis of end-functionalized polymers is attempted, the presence of cyclic fraction that does not contain end-groups is detrimental. In some systems, for example in cationic polymerization of 3-membered cyclic ethers (oxiranes) back-biting proceeds so effectively that practically the only products are cyclic oligomers (dimers in the case of ethylene oxide [27, 28] trimers to hexamers in the case of propylene oxide [29]).

Back-biting in cationic ring-opening polymerization of heterocyclic monomers is inevitable if active species are located at the chain-end. Exceptions are systems in which cyclization by back-biting is much slower than propagation so that polymerization may be terminated before cyclic fraction starts to be formed [30]. Looking into the possibility to overcome this problem we turned our attention to mechanism known as activated monomer (AM) mechanism postulated earlier for anionic polymerization of lactams and *N*-carboxyanhydrides (NCA) [31]. In contrast to conventional polymerization mechanism of ionic polymerization in which growing chain end is charged and monomer is neutral, in AM mechanism situation is reversed; growing chain-end is neutral while monomer is charged (therefore activated).

Activated monomer mechanism in the cationic polymerization of cyclic ethers

In the late 1980's we started to investigate cationic polymerization of oxiranes carried out in the presence of compounds containing hydroxyl groups in order to find an explanation for observation that in such systems the amount of cyclic oligomers is substantially reduced [32].

An explanation has been proposed based on the mechanism shown in Scheme F which bears resemblance to mentioned earlier AM mechanism in that sense that propagation proceeds by the reaction of protonated (activated) monomer with terminal hydroxyl group of growing macromolecule (thus growing chain-end is not charged) as shown in Scheme F for cationic polymerization of ethylene oxide.



Scheme F

where: ROH — low-molecular weight alcohol and/or poly(ethylene oxide) growing chain, AM — activated monomer mechanism, ACE — active chain-end mechanism.

The scope of AM mechanism as applied to cationic ring opening polymerization was discussed in detail in a review paper [33]. The presence of hydroxyl group containing compound does not exclude propagation by conventional mechanism called active chain end (ACE) mechanism. In a series of kinetic experiments we have shown that propagation rate constant k_{AM} is higher than propagation rate constant k_{ACE} about 5 times (for polymerization of propylene oxide and epichlorohydrin) [34, 35].

Thus, although AM type propagation is preferred, this preference is not sufficient to ensure the high enough contribution of the AM mechanism. To enhance the contribution of propagation according to the AM the slow monomer addition was applied, in which the instantaneous [monomer]/[–OH] ratio is low, favoring AM propagation.

A series of telechelics and macromonomers was synthesized by AM polymerization of propylene oxide and epichlorohydrin using slow monomer addition approach [36, 37]. Resulting medium molar mass polymers had required functionality and low dispersity; polymerization

degrees were close to those predicted on a basis of [reacted monomer]/[–OH] concentrations ratio. Thus, cationic AM polymerization of cyclic ethers shows features of a living process although it results in the limited molar mass range of the resulting polyethers.

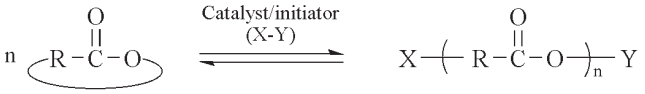
Studies of cationic polymerization of cyclic ethers proceeding in the presence of hydroxyl group containing compounds opened new interesting synthetic possibilities. There are several cyclic ethers available that contain hydroxyl group as substituent for example hydroxymethyloxirane (glicydol), 3-ethyl-3-hydroxymethyloxetane or 3,3-bishydroxymethyloxetane. In the presence of cationic initiators those compounds should polymerize by AM mechanism (with possible contribution of ACE mechanism) and due to the participation of HO-group in propagation such polymerization should lead to highly branched polymers. Indeed, studies of cationic polymerization of unprotected glycidol revealed that polymerization proceeds with high contribution of AM mechanism and branched polymers are formed [38, 39]. This approach was later extended to polymerization of 3-ethyl-3-hydroxymethyloxetane [40—43], 3,3-bishydroxymethyloetane [44], and 2-hydroxymethyltetrahydrofuran [45]. Cationic polymerization of monomers containing both functions, *i.e.* cyclic ether group and hydroxyl group in the same molecule offers therefore a facile way for preparation of highly branched, multihydroxyl polymers.

Thus, as indicated earlier, cationic ring-opening polymerization of cyclic ethers and cyclic acetals offers a possibility for studying phenomena that have more general significance in polymer chemistry. On the other hand by this method several industrially important polymers are made including polyacetal thermoplastics made by cationic ring-opening polymerization of 1,3,5-trioxane (cyclic acetal). The original technology for the latter process had been developed in Poland, in the Industrial Chemistry Research Institute in Warsaw with cooperation of our group headed by professor Stanisław Penczek. This technology is used for manufacturing of polyacetal (under the brand name Tarnoform®) in Azoty Tarnow with production capacity > 10^4 tons per year.

MECHANISM OF ROP OF ALIPHATIC CYCLIC ESTERS

ROP of aliphatic cyclic esters leads, according to Scheme G, to aliphatic polyesters, a rediscovered class of polymers important in practice that show useful mechanical and thermal properties, compatibility with natural environment (including human body) and are able to undergo hydrolytical and biological degradation after desired exploitation time. Besides, ROP of cyclic esters is a convenient model system for studies of the living polymerization mechanisms.

Polymerization of this class of monomers was reviewed by us several times [46—48]. In the present paper only a more general phenomena accompanying ROP of



Scheme G

where: R = $-(CH_2)_2-$, $-(CH_2)_3-$, $-(CH_2)_5-$, $-[CH(CH_3)C(=O)OCH(CH_3)]-$ for β-propiolactone (PL), γ-butyrolactone (BL), ε-caprolactone (CL), and dilactide (LA), respectively.

cyclic aliphatic esters elucidated in our laboratory are concisely reported.

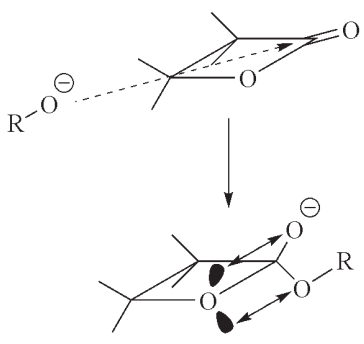
Studies of thermodynamics of polymerization of this class of monomers, carried out in our laboratory, included determination of the standard thermodynamic parameters of polymerization of L,L-dilactide [49], dioxan-2-one [50], analysis of copolymerization the otherwise non-homopolymerizable, γ-butyrolactone [51, 52], and copolymerization of LA after reaching polymer--monomer equilibrium [53].

Below some mechanistic and kinetic aspects of ROP of cyclic esters are discussed on a selected examples of polymerizations of PL, CL, and LA monomers.

Propagation in anionic polymerization of aliphatic esters: β-lactones case

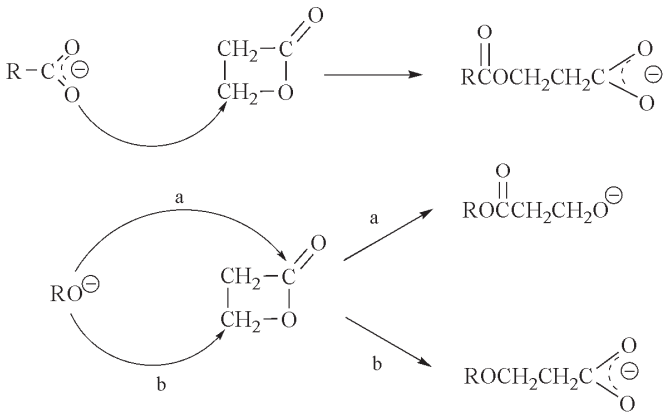
β-Lactones should be considered as a special subclass of cyclic esters. They are highly strained. For the most investigated PL values of ΔH_p and $\Delta S_p°$ are equal -82.3 kJ/mol and -74 J/(mol K), respectively (determined thermochemically [54]). In contrary to lactones with larger rings the molecule of PL is flat, what has a significant influence on polymerization mechanism. As it is shown in Scheme H, an attack of a nucleophile (*e.g.* RO^-) on the acyl carbonyl atom in PL is sterically hindered. Moreover, an addition of RO^- anion to the carbonyl carbon atom changes its hybridization from sp^2 to sp^3 and in the new conformation the additional repulsive interactions occur between the free electron pairs of the endocyclic oxygen atom and the ≡C-O-R and ≡C-O^- groups.

Obviously, the direction of the attack shown in Scheme H is practically ineffective for the $RCOO^-$ anions



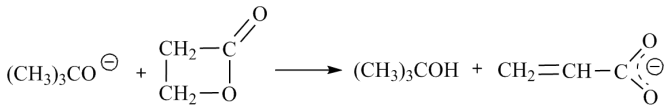
Scheme H

which are more bulky and less nucleophilic than the RO^- ones. Therefore, the $RCOO^-$ anion can attack exclusively the carbon atom in β position with resulting addition and alkyl-oxygen bond cleavage facilitated by the high ring strain. In this reaction the carboxylate active species are formed. The more nucleophilic RO^- anions may attack not only β-carbon atoms but, in spite of the mentioned above hindrance, also the carbonyl carbon atoms, with resulting acyl-oxygen bond cleavage and formation of the …-O^- species reacting with the new monomer molecules (Scheme I).



Scheme I

Because during each step some part of the alkoxide active centers is converted to carboxylate ones thus, shortly after initiation, only the carboxylate active species are present in the system [55—57]. In the case of the bulky alkoxide anions [*e.g.* $(CH_3)_3CO^-$] the initiation proceeds differently, namely by proton abstraction. However, also in reaction shown in Scheme J the carboxylate anions are formed [58]. Thus, regardless whether the alkoxide or carboxylate anions initiate polymerization of β-propiolactone, the eventual propagating species are carboxylate anions.



Scheme J

In anionic polymerization of PL, like in many anionic polymerizations, the active center can be present in form of ion pairs and free ions being in an equilibrium. Position of this equilibrium depends on counterion, solvent and temperature. In polymerization of β-lactones ion pairs and free ions react with monomer (propagation) with their own propagation rate constants ($k_p^{\mp}$ and k_p^- for ion pairs and free ions, respectively, Scheme K).

For potassium cations complexed with dibenzo-18--crown-6 ether (K^+DB18C6) in CH_2Cl_2 and in DMF both, ion pairs and free ions were present in the system and contributed to propagation.

In anionic polymerization the propagation rate constants for contact ion pairs are much lower than for the free ions. The rates of propagation for solvent separated

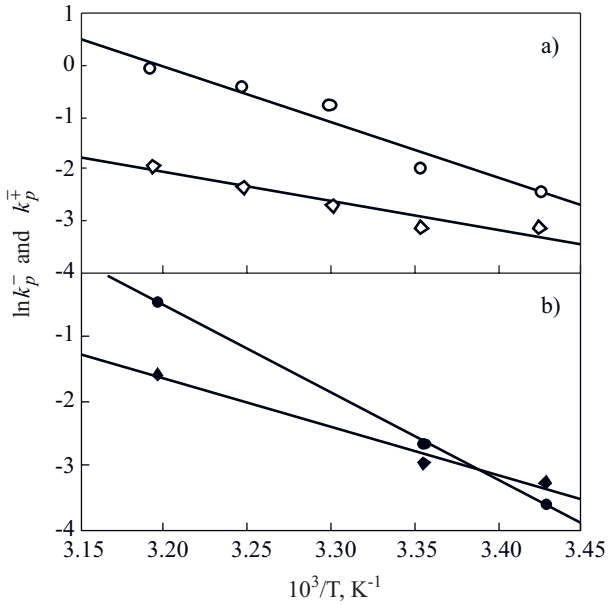
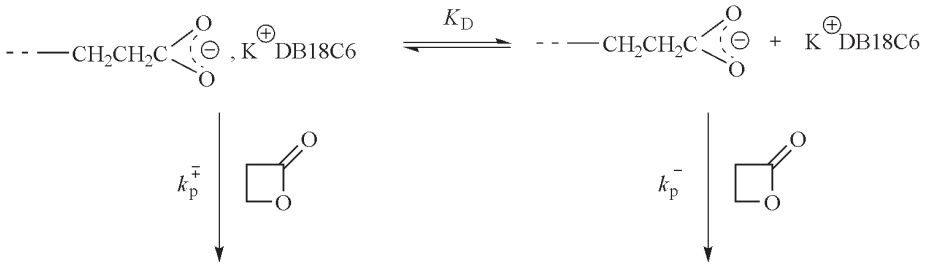


Fig. 1. Semiempirical dependences of the constants of propagation on ions (k_p^-) and ion pairs ($k_p^{\mp}$) on reciprocal of the absolute temperature for the polymerization of β-propiolactone initiated with $CH_3CH_2COO^-K^+$DB18C6 and carried out in DMF: a) k_p^- (○), $k_p^{\mp}$ (◇), $[PL]_0$ = 0.5 mol/dm^3; b) k_p^- (●), $k_p^{\mp}$ (◆), $[PL]_0$ = 1 mol/dm^3



Scheme K

ion pairs (ion pairs in which a solvent, monomer or molecule of complexing agent separate ions) can be close to those for free ions but usually do not reach their values. In the case of the polymerization of PL, when free ions are strongly solvated with solvent and polar monomer molecules (dipole moment of PL equals 4.17 D), the formation of activated complex requires additional energy for removal of at least some solvating molecules from the immediate proximity of free ions [59, 60].

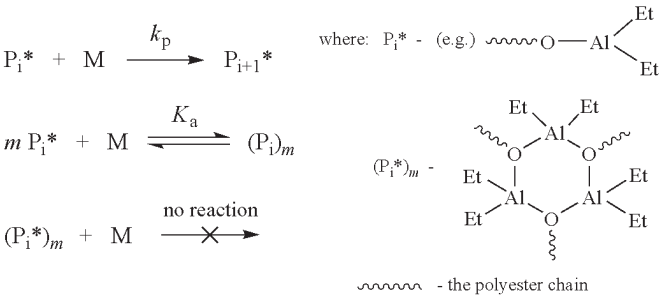
Therefore, as it could be seen in Fig. 1, at low temperatures the rate constants of propagation on free ions become close to those on ion pairs. For the polymerization in polar DMF and with the initial monomer concentration equal 1 mol/dm^3, below 22.3 °C, unexpectedly, the rate constant for propagation on free ions becomes even lower than that on ion pairs. Apparently, at these conditions energy of solvation of ions is so strong that enthalpy of activation on these species is higher than for ion pairs.

Propagation in coordination polymerization of aliphatic esters: importance of aggregation of active centers

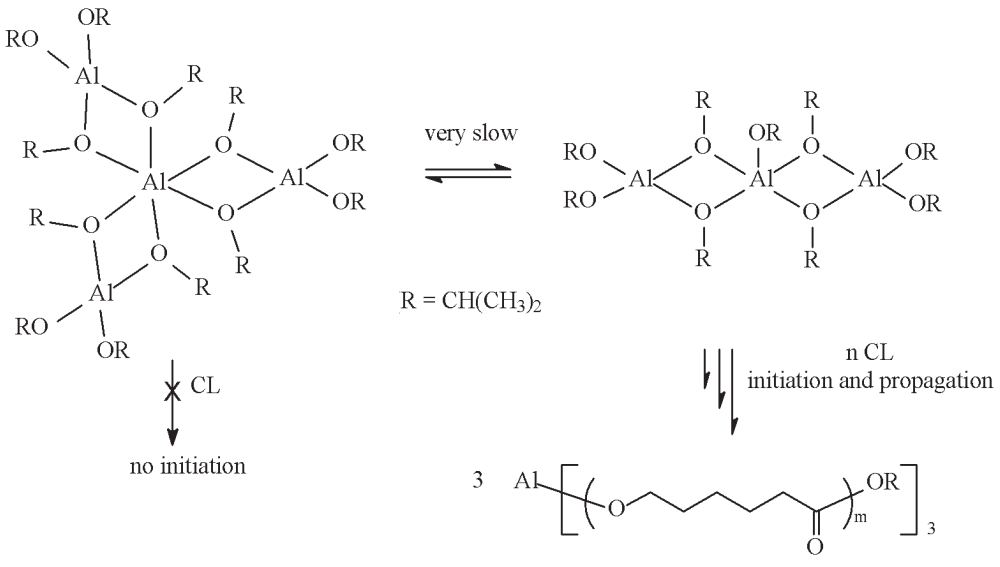
In contrast to PL, which polymerizes with soft and moderately reactive carboxylate anions, less strained cyclic esters (*e.g.* ε-caprolactone and lactides) require stronger nucleophiles to propagate and in consequence usually are plagued by side reactions. On the other hand, it has been found that coordinate ROP of CL or LA initiated with covalent, polarized metal alkoxides (*e.g.* derivatives of Zn, Al or Sn) may proceed in the perfectly controlled way due to a high selectivity, that is with practically quantitative elimination of the undesired side reactions.

Alkoxides (both ionic and covalent species) tend to exist in different aggregated forms, and it may happen that one form is more reactive than the other one. If, in addition, the exchange between these forms is slow, in comparison with the rate of initiation, then only this reactive form is engaged in initiation, leaving the other form(s) even intact, when the polymerization is over. As it has been shown in our laboratory, this is the case of polymerization of CL and LA initiated with aluminum isopropoxide [(*i*-PrO)$_3$Al], consisting of a trimer (reactive) and tetramer (unreactive) at least at ambient temperatures (Scheme L) [61]. This observation closed a 25 years-old discussion on an important, from the point of view of $\overline{M}_n$ control and block copolymers synthesis, question — how many polyester chains growth starts one Al(OR)$_3$ molecule?

Depending on a structure of the resulting active centers (mostly on the number of growing polyester chains located at one metal atom) propagation may also be accompanied by aggregation of the alkoxide species. In the (*i*-PrO)$_3$Al trimer/CL system the macroalkoxide species assume exclusively the three arm unimeric structure, whereas for dilalkylaluminum alkoxides (R$_2$AlOR')/CL dimeric and trimeric aggregates prevail at higher concentration of active centers [62—64]. In the majority of the reported cases aggregates are not reactive and the corresponding kinetic scheme reads as it is shown in Scheme M.



Scheme M



Scheme L

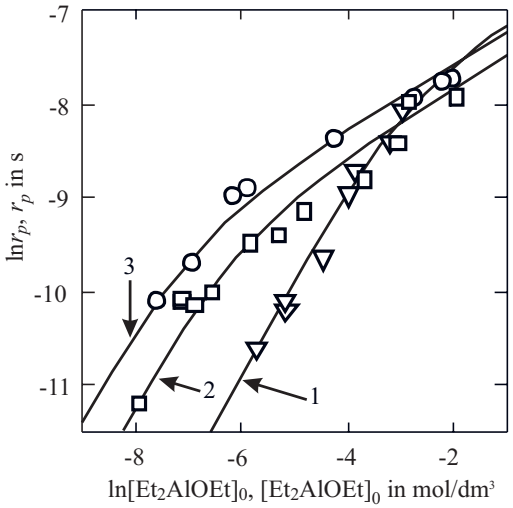


Fig. 2. External order in initiator (Et_2AlOEt) concentartion dependencies of r_p = d[M]/[M]dt obtained in polymerization of ε-caprolactone at 25 °C for conditions: $[CL]_0$ = 2 mol/dm^3, solvents — CH_3CN (1), THF (2), C_6H_6 (3) (points — experimental, lines — computed numerically assuming kinetic scheme M according to [64])

Aggregation may be diagnosed from the external kinetic order in active centers. In the example illustrated in Figure 2 for higher concentrations range of initiator (and then of the resulting active centers) this order, equivalent numerically to slope of the plot, is equal to 1/3 what is indicative of the unreactive trimeric aggregates formation (Scheme M, m = 3). For a lower concentration of active centers the slope of the plots reaches eventually the value of 1, showing that the unimeric (deagregated) species strongly prevail.

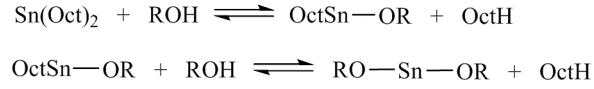
More detailed analysis of results presented in Fig. 2 leads to the conclusion that both the rate constant of propagation (k_p) and the equilibrium constant of aggregation (K_a) decrease with increase of solvent polarity (*i.e.* its solvating power) [64].

Besides, aggregation leads to an increase of the coordination number of Al atom (cf. structures in Schemes L and M). Indeed, this was confirmed by an analysis of the ^{27}Al NMR spectra of the polymerizing mixtures [46—48].

The interexchange rates between aggregated (dormant) and unimeric (propagating) species in CL/R_2AlOR' system are high enough to govern even growth of all macromolecules, as can be judged from $\overline{M}_w/\overline{M}_n$ values determined for the resulting poly(CL) being in the range from 1.03 to 1.13 [65].

Polymerization of ε-caprolactone and L,L-dilactide coinitiated by tin(II) octoate

For a long time the mechanism of initiation of higher lactones and lactides with covalent Sn or Zn carboxylates was under dispute. In one of the suggested mechanisms it was proposed that tin(II) octoate, reacts with a coinitiator [*e.g.* water, alcohol, or hydroxyacid (ROH)] and giving this way the corresponding alkoxide according to Scheme N.



Scheme N

where: Oct — 2-ethylhexanoate (octoate) group, OctH — 2-ethylhexanoic (octanoic) acid.

The hydroxyl group containing compound may be present as an impurity or may be purposely added to the system. Then, the resulting tin(II) mono- and/or dialkoxide initiates and propagates in the usual manner, as the other metal alkoxides. However, there was no a direct proof for such a mechanism and several other mechanisms have been proposed. The most often cited was the "trimolecular mechanism", in which first the catalyst-monomer complex is formed [66].

The latter mechanism has conclusively been shown not to operate since it excludes the presence of Sn atoms in the growing macromolecules covalently bound. The MALDI ToF mass spectrometry measurements carried out in our laboratory for the cyclic ester/ROH/Sn(Oct)$_2$ system revealed presence of the tin(II) alkoxides in the growing polyester chains [67]. Moreover, kinetic studies also strongly supported the carboxylate-alkoxide ligands exchange mechanism [68—70].

In the example illustrated in Figure 3 are compared the rates of LA polymerization in two systems, namely that initiated with Sn(Oct)$_2$/BuOH and with

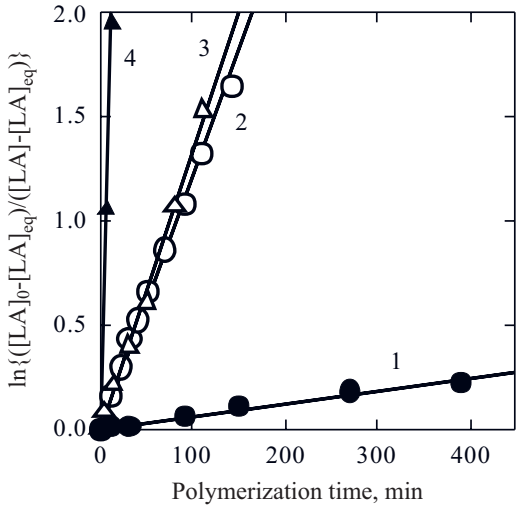


Fig. 3. Comparison of kinetics of L,L-dilactide (LA) polymerization initiated by tin octoate [Sn(Oct)$_2$] (1), Sn(Oct)$_2$/BuOH (2), Sn(OBu)$_2$/octanoic acid (OctH) (3), and Sn(OBu)$_2$ (4) for conditions: $[LA]_0$ = 1.0 mol/dm^3, $[Sn(OBu)_2]_0$ = $[Sn(Oct)_2]_0$ = 0.05 mol/dm^3, $[OctH]_0$ = $[BuOH]_0$ = 0.10 mol/dm^3, THF solvent, 50 °C (according to [66])

$Sn(OBu)_2$/OctH [66]. Polymerization with $Sn(Oct)_2$ with no alcohol added is very slow (plot 1). It is certainly coinitiated by compounds containing hydroxyl group, adventitiously present in the system as impurities.

Polymerization initiated with $Sn(OBu)_2$ was 240 times faster than that with $Sn(Oct)_2$ „alone" (plot 4). In the next two experiments $[Sn(Oct)_2]_0$ and $[Sn(OBu)_2]_0$ were equal one to another (0.05 mol/dm^3) and 0.1 mol/dm^3 of BuOH and OctH were added, respectively. As it is seen in Fig. 3 (plots 2 and 3), polymerization rates in the $Sn(Oct)_2$/BuOH and $Sn(OBu)_2$/OctH systems are practically the same, what strongly supports the proposed mechanism of the actual initiator formation (Scheme N).

Molecular weights control in processes initiated with multivalent metal alkoxides

A number of well-defined macromolecules with well controlled size and the end-groups were prepared with Al and Sn(II) initiators. $\overline{M}_n$'s of poly(ε-caprolactone) (PCL) could be controlled up to $\leq 5 \cdot 10^5$ with dialkylaluminum alkoxide initiators [71].

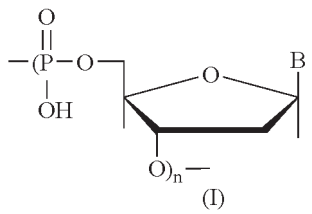
After understanding a difference between aluminum tris-isopropoxide (i-PrO)$_3$Al trimer and tetramer (*cf*. Scheme L), the isolated trimer has become the most versatile initiator for the controlled polymerization of cyclic esters. It provides fast and quantitative initiation, moderately fast propagation [k_p = 0.6 dm^3/(mol·s) comparing to 0.039 dm^3/(mol·s) for Et_2AlOEt (25 °C, THF)] [61, 62] and relatively good selectivity (with regard to transesterification). Thus, (i-PrO)$_3$Al in the form of a trimer looks to be ideally suited for the synthesis of aliphatic polyesters, since apart from a good selectivity it provides a direct control of polymerization degree of the resulting polyester, by simply adjusting the monomer/initiator concentrations ratio. On the other hand, there is an upper limit of $\overline{M}_n \approx 3 \cdot 10^5$ of PLA and PCL which can be obtained with (i-PrO)$_3$Al, whereas with $Sn(OBu)_2$ $\overline{M}_n \approx 10^6$ has been reached [72].

$Sn(Oct)_2$ is probably the most often used catalyst in the polymerization of cyclic esters. This is mostly due to its commercial availability, physical state (liquid), and higher chemical stability in comparison with the alkoxides. Polymerization degree of the polyester formed in the cyclic ester/$Sn(Oct)_2$/coinitiator (ROH or RNH_2) systems is given by the monomer/initiator concentrations ratio due to the fast initiation and exchange reactions: the chain transfer to water, alcohol, or amine and then to the resulting macroalcohol. Using the standard high vacuum technique and $Sn(Oct)_2$ of 99.0 mol. % purity we were able to prepare both PCL and PLA with $\overline{M}_n$ up to $\approx 9 \cdot 10^5$. Thus, $\overline{M}_n \approx 10^6$ looks to be a limit of $\overline{M}_n$ of the aliphatic polyesters prepared *via* the ROP, by using the usual techniques and this limit is, most probably, related to the impurities concentration level.

These selected examples of research conducted in our laboratory show that also polymerization of cyclic esters is an useful model system for studies of thermodynamics, kinetics, and mechanism of ROP in general. Besides, results of these studies allowed to elaborate conditions for the living or at least controlled polymerization, what opened then a possibility of preparation of aliphatic polyesters that have the predetermined molecular weights, end-groups or macromolecular architecture.

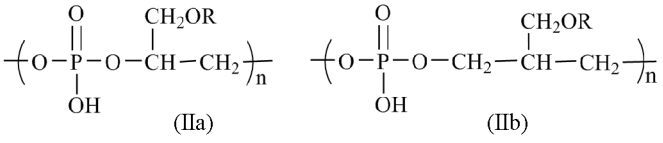
POLYESTERS OF PHOSPHORIC ACID: FROM NATURAL POLYMERS TO THEIR MODELS BY ROP

Phosphorus can be introduced into the polymer backbones and/or to the side chains in a variety of chemical methods. Phosphorus bound to hydrogen, carbon, sulfur, or nitrogen atoms will impart properties so much differing from each other that any generalization is hazardous. There are two fields, where the presence of the phosphorus atoms in the chains is essential, namely biopolymers and their models and flame retardants.



B - nucleic acid base

The most prominent phosphorus polymers are nucleic (NA) [formula (I)] and teichoic acids (TA) [formulas (IIa) and (IIb)]. Backbones of NA and TA are composed of hydrolytically stable diesters of phosphoric acids.

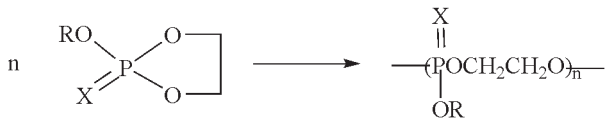


R - alanyl, sugar

In the early 1970's our laboratory started the synthesis of poly(alkylene phosphate)s — the very simple analogs of NA and TA. It was supposed that these polymers could have interesting properties. The mechanism of polyphosphates formation by ROP was also extensively studied [73—75].

The first high-molecular weight linear poly(alkylene phosphate)s, devoid of side groups, were prepared with either coordinate ROP [76, 77], polycondensation [78] or transesterification processes [79, 80]. For some monomers have been found conditions for the controlled and/or living polymerization [81].

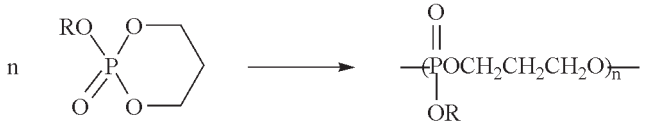
In 1960's only a few papers were devoted to polymerization of five- [82, 83] and six-membered cyclic phos-



(III) or (IV) poly(III) or poly(IV)

Scheme O

where: (III) — X = O, R = CH_3, C_2H_5, *n*-C_3H_7, *i*-C_3H_7, *n*-C_4H_9, *t*-C_4H_9; (IV) — X = S, R = CH_3, ClC_2H_4, C_6H_5.



(Va), (Vb) or (Vc) poly(Va), poly(Vb) or poly(Vc)

Scheme P

where: (Va) — R = CH_3; (Vb) — R = C_2H_5; (Vc) — *n*-C_3H_7, *i*-C_3H_7, *n*-C_4H_9, $Si(CH_3)_3$.

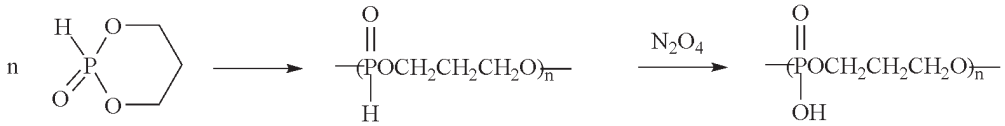
phates [84]. Five-membered cyclic phosphates, like that given by formula (III) in Scheme O (R=CH_3) with anionic [82—84] and cationic [77, 84] initiators provided exclusively polymers with $\overline{M}_n \approx 3 \cdot 10^3$ and with ill-defined structures. Neither kinetics of the process and mechanism of elementary reactions were investigated nor NMR spectra were given. High-molecular weight polymers were only reported for five-membered cyclic thiophosphates given by formula (IV) in Scheme O [85].

Ring opening polymerization

Anionic polymerization of cyclic phosphate esters was studied for 2-alkoxy-2-oxo-1,3,2-dioxaphospholanes [formula (III)] (mainly methoxy and ethoxy derivatives) [77, 86—89] and its 2-thiono derivatives [formula (IV)] a living process [87]. The ability of compound (III**)** to form high-molecular weight polymers may be attributed to the high strain of the five-membered ring: ~29 kJ/mol (data from heat of hydrolysis [91, 92]) and 15±2 kJ/mol (data from the heat of polymerization [88]), which presumably lowers the probability of the side reactions.

Only oligomers with polymerization degree not exceeding 7 were obtained in the anionic polymerization of the six-membered esters, 2-methoxy- and 2-ethoxy-2--oxo-1,3,2-dioxaphosphorinane [formulas (Va) and (Vb) in Scheme P], respectively [82, 84, 93, 94]. The cationic polymerization of five-membered [formula (III)] [77] and six-membered [formula (V)] [95, 96] cyclic phosphates leads also to oligomers only ($\overline{M}_n \leq 2 \cdot 10^3$).

Anionic ROP of the six-membered *H*-phosphonate monomer [formula (VI) in Scheme Q] led to the high-



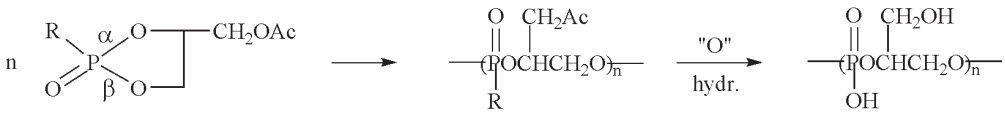
(VI) poly(VI) (VII)

Scheme Q

[85]. High vacuum technique [77, 90] was used for the preparation of high-molecular weight polymers.

The highest molecular weights ($1.5 \cdot 10^5$) was obtained in the polymerization of cyclic phosphate ester given by formula (III, R = CH_3) with Et_2Mg, at -20 °C in methylene chloride [77]. On the other hand it appears that polymerization of the same monomer (III, R = CH_3) with $(i\text{-PrO})_3Al$ (for the concentration range from 10^{-3} to 10^{-2} mol/dm^3) is -molecular weight linear polymer with $\overline{M}_n$ up to 10^5 [90]. Polymer given by formula poly(VI) was easily converted into polyacid [formula (VII)] by oxidation with N_2O_4 [76].

Models of simple teichoic acids [*e.g.* polymer given by formula poly(VIIIa) in Scheme R; $\overline{M}_n = 2.5 \cdot 10^4$] were prepared by using a ROP of cyclic monomers containing the required sequence of elements of the chain squeezed into the corresponding rings. Because of the different open-



(VIIIa) or (VIIIb) poly(VIIIa) or poly(VIIIb) (IX)

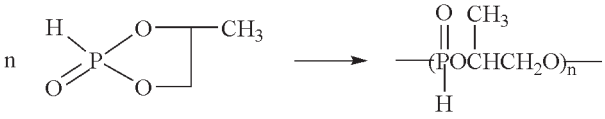
Scheme R

where: (VIIIa) — R = OCH_3; (VIIIb) — R = H.

ings of the ring (cleavage of α and/or β bond) of unsymmetrical substituted compound (VIIIa), in polymer chain three different diads: head-to-head (H-H), head-to-tail (H-T), and tail-to-tail (T-T) were observed [97].

Polymer poly(VIIIb) after oxidation and hydrolysis gave polyphosphate given by formula (IX) — the analog of teichoic acid [97].

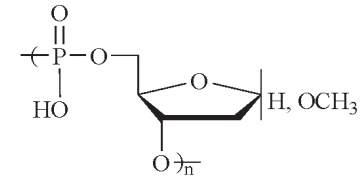
The same initiating system [(*i*-Bu_3)Al] gave high polymers ($\overline{M}_w \leq 8 \cdot 10^4$) in the polymerization of optically active [98], as well as racemic 2-hydro-4-methyl-2-oxo--1,3,2-dioxaphospholane [formula (X) in Scheme S] [98—102]. The structure of the resulting polymer (H-H, H-T, and T-T) was analyzed in detail [103].



(X) poly(X)

Scheme S

In the case of trivalent phosphorus cyclic compounds only the anionic polymerization of 2-diethylamino-1,3,2--dioxaphosphorinane [formula (XI) in Scheme T] [81, 104] and α,β-methyl-2-deoxy-D-ribofuranoside cyclic diethylphosphoramidite [formula (XIII) in Scheme U] [105] were studied.



(XIV)

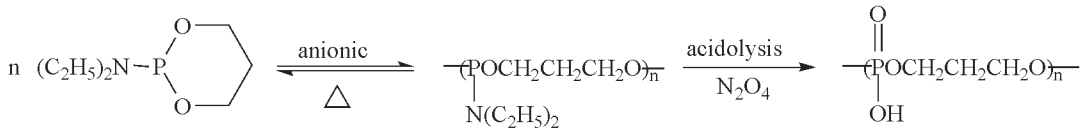
Polymer poly(XI) gave after acetolysis the corresponding poly(*H*-phosphonate) [formula poly(VI)] with characteristic P-H coupling. Its further oxidation led to the polyphosphate given by formula (XII) [76, 81].

Polymer poly(XIII) ($\overline{M}_n = 9 \cdot 10^3$), obtained in polymerization of compound (XIII), was further transformed into polymer given by formula (XIV), the analog of the nucleic acid devoid of base [105]. Polyphosphates containing glucose [74, 106] and THF rings [107] in the main chain were also obtained.

The phosphorus-containing cyclic monomers undergo copolymerization with cyclic organophosphorus monomers as well as with other cyclic or unsaturated compounds. In previous review papers the published data related to this subject have been collected [73, 75, 108].

Kinetics, mechanism and thermodynamics of polymerization

The kinetics and the mechanism of polymerization of cyclic phosphorus compounds was broadly described in reviews papers [73, 75]. The mechanism of initiation and

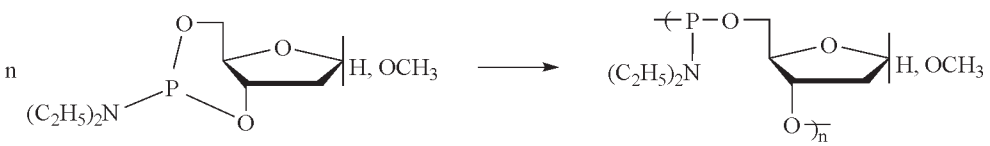


(XI) poly(XI) (XII)

Scheme T

Polymer poly(XI) ($\overline{M}_n \leq 3.2 \cdot 10^4$) obtained by anionic polymerization of compound (XI) had a linear structure without any isomerization detected, according to the ^{1}H NMR, ^{13}C NMR, and ^{31}P NMR spectra. The anionic polymerization of compound (XI) is living and fully reversible [75, 81].

the structure of growing species in the anionic polymerization was reported for two monomers, namely 2-diethylamino-1,3,2-dioxaphosphorinane [formula (XI)] [81] and 2-methoxy-2-oxo-1,3,2-dioxaphospholane [formula (III), R = CH_3] [87]. In the case of six-membered cyclic phosphates [formula (V)] the mechanism of anionic



(XIII) poly(XIII)

Scheme U

and cationic polymerization was studied as well and the formation of only low molecular weight oligomers was elucidated [93, 95, 96].

The thermodynamics of polymerization was studied mainly for tetracoordinated [88, 93, 95, 96] and tricoordinated [81] phosphorus cyclic compounds. The results obtained for various monomers in both anionic and cationic processes are in reasonably good agreement. The size of the exocyclic group in the ester series [formula (V)] does influence monotonically ΔH_p and ΔS_p. Larger substituents decrease polymerizability of cyclic phosphates. The entropy change is only slightly negative for compounds given by formula (Va) (with methyl substituent) and starting from the ethyl monomer [formula (Vb)], polymerization becomes driven by a positive entropy change. This is because the bond angles in cyclic six-membered monomers and those in the open-chain esters are almost identical. Conversion of six-membered cyclic phosphates into a polymer results in a considerable increase in the rotational and vibrational entropy, because of the enhanced flexibility of the exocyclic group in the open-chain polymer unit [74, 75, 109, 110].

Properties and applications

For some model polymers their hydrolytical stability was studied. The rate constants of hydrolysis and the pH — rate profile for poly(trimethylene phosphate) [formula (XII)] and poly(methyl ethylene phosphate) [formula poly(III), R = CH_3] were determined [111].

Poly(1,3-propylene phosphate) [formula (XII); model of teichoic acids] [112, 113] and other poly(alkylene phosphate)s [114—116] were used as components in the studies of active ion transport through liquid membranes. Poly(alkylene phosphate)s, depending on the number of atoms in repeating units, differ in their abilities to complex metal cations. They give conductive complexes with polyaniline [117, 118] and were also applied for the formation of ionic polymeric gels [119].

The equilibrium constants of complexation of Na^+ cations by poly(methyl ethylene phosphate) [formula poly(III), R = CH_3] were determined using ^{23}Na NMR method. The numerical values are close to these known for poly(ethylene glycol) [120].

Dihydrophilic block copolymers with nonionic and ionic blocks with esters of phosphoric acid were prepared and successfully used as modifiers of the crystallization of $CaCO_3$ [121—123] — mimicking biomineralization process [124].

Poly(alkylene phosphate)s mostly soluble in water with a biodegradable backbone are promising for biomedical applications [108].

CONCLUSIONS

The present review covers only selected research topics, developed in the laboratory founded in early 1970's in Łódź by Professor Stanislaw Penczek which in a few subsequent years became one of the leading world laboratories working in the ROP field. Results of these studies significantly contributed to ROP fundamentals. This conclusion can be supported by a numerous reviews on ROP prepared on invitation of the book editors (see, *e.g.*: [2, 9, 14, 15, 46, 47, 73—77, 125—136]).

It would be not possible, in one article of the present issue, to comment all research topics, initiated by Professor Penczek and carried out in our Center. It is perhaps enough to mention that the more recent research includes, for example: stereochemical aspects of lactides copolymerization [137—139], poly(D,D-LA)/poly(L,L-LA) stereocomplexes [140—142], cyclic esters polymerization mediated by the metal-free initiators/catalysts [143, 144], dispersion ROP polymerization [145], biomedical applications of polyesters prepared by ROP [146, 147] or numerical calculations, predicting possible course of polymerization and the resulting products microstructure [135, 136].

Concluding, ROP still remains an active research field, particularly in developing technology of the high tonnage environmentally friendly polymers and in a subtle synthesis of the specialty polymers.

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