

Review

## Ring-Opening Polymerization—An Introductory Review

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We would like to dedicate this article to P. H. Plesch, a pioneer of cationic polymerization and a mentor and friend for many of those who are now at the forefront of this field of science. He passed away 5 March 2013 at the age of 95. We will miss him.

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**Abstract:** This short, introductory review covers the still rapidly growing and industrially important field of ring opening polymerization (ROP). The review is organized according to mechanism (radical ROP (RROP), cationic ROP (CROP), anionic ROP (AROP) and ring-opening metathesis polymerization (ROMP)) rather than monomer classes. Nevertheless, the different groups of cyclic monomers are considered (olefins, ethers, thioethers, amines, lactones, thiolactones, lactams, disulfides, anhydrides, carbonates, silicones, phosphazenes and phosphonites) and the mechanisms by which they can be polymerized involving a ring-opening polymerization. Literature up to 2012 has been considered but the citations selected refer to detailed reviews and key papers, describing not only the latest developments but also the evolution of the current state of the art.

**Keywords:** ring-opening polymerization; RROP; CROP; AROP; ROMP

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### 1. Introduction

Ring-opening polymerization (ROP) is, together with chain (radical and ionic) polymerization and condensation polymerization, one of the three paths to the polymers that are so important to life in the

21st century. Some ROP can be considered as a chain polymerization (addition of monomer to a growing chain end) but many reactions are more complicated and involve, e.g., activated monomers. Particularly ROP has proved to be a useful synthetic route to technologically interesting polymers with very specific, and controllable properties (e.g., refractive index), for preparing synthetic variants to naturally occurring polymers (e.g., chitin, see Section 3.1) or to optimize biodegradable polymers for agricultural, medicinal and pharmaceutical applications (see Section 2.4).

Since this review is intended more as an introduction to the field of ROP, no attempt will be made to describe the particularities of the thermodynamics of these polymerizations. It should however be noted that rather than the driving force for the polymerization being the conversion of a multiple to a single bond, for most ROP the driving force is the ring strain and associated steric considerations. Additionally, there is the consideration of the ring chain equilibrium, which leads to the considerable influence of the initial monomer concentration and temperature on the microstructure of the products. The interested reader is referred to the excellent recent summary by Duda and Kowalski [1].

With some exceptions, such as the ROP of Leuchs' anhydrides (see Section 4.2) or the radical ROP of 2,2-diphenyl-4-methylene-1,3-dioxolane (see Section 2.2), is not accompanied by the elimination of small molecules. Additionally, ROP is not aided by the enthalpy difference between a single and double C–C bond, which counteracts the loss of entropy occurring as a consequence of polymerization via chain polymerization. ROP have in common that the monomers are rings, irrespective of ring size, but the reason why polymerization takes place can vary. Rings composed of 3–8 atoms may polymerize due to the loss of enthalpy associated with the loss of ring strain. Thus, the ring strain for oxiranes [2] is 116 kJ mol<sup>-1</sup> and even for the 7 and 8 membered lactones and lactams [3] the polymerization is driven by an enthalpic contribution even though, in these cases the ring strain is only *ca.* 6 J mol<sup>-1</sup>. Strain-free six-membered rings do not generally polymerize. For rings containing disulfide, silicon or carbonate moieties an additional effect is the increased rotational freedom of these groups in the resulting linear chains which leads to an increase in entropy to give the driving force for polymerization [4].

Many polymers of industrial importance are produced via ROP, e.g., polycyclooctene, polynorbornene, polyethylene oxide, polysiloxane and polyphosphazene. A large family of commercially available polymers called polyethylenimines (many of which are highly branched), are produced via a CROP of aziridine or oxazoline monomers. Polyoxymethylene (POM), derived from trioxane and most of the diols (produced, e.g., via CROP of THF) used in polyurethanes as well as Nylon 6 (poly  $\epsilon$ -caprolactam) are perhaps, in terms of volume, the most significant. More recently, polyglycolides and polylactides (see Section 4.1) [4] are becoming important as packaging materials due to the bio-compatibility and natural decomposition of these materials.

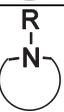
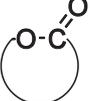
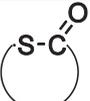
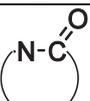
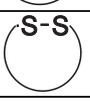
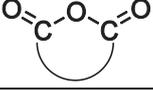
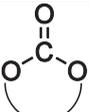
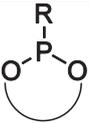
Another important development is the use of metathesis catalysts to open rings with exo functional groups to yield novel polymer structures (Section 5).

Table 1 lists the major groups of ring structures and the mechanism by which they are usually polymerized.

This review is organized according to mechanism rather than molecular types and is designed to demonstrate the usefulness of this type of polymerization to yield novel polymers, particularly for those new to the subject. It is hoped that it will provide a useful start for entering the field rather than

being an exhaustive review of all the literature to date. It is recommended that the interested reader refer to, e.g., the chapters of [5].

**Table 1.** Typical cyclic monomers and their usual polymerization mechanism [4].

Name	Structure	Ring size	Mechanism
Olefin		4,5,8	Metathesis
Ether		3–5,7	Cationic, anionic
Thioether		3,4	Cationic, anionic
Amine		3,4,7	Cationic
Lactone		4,6–8	Anionic, cationic
Thiolactone		4–8	Anionic, cationic
Lactam		≥4	Anionic, cationic
Disulfide		≥8	Radical
Anhydride		5 and ≥7	Anionic
Carbonate		6–8 and ≥20	Anionic
Silicone		6,8 and ≥10	Anionic, cationic
Phosphazene		6	Cationic
Phosponite		3,5–7	Anionic

## 2. Radical Ring-Opening Polymerization

Via a ring-opening polymerization, especially radical ROP (RROP), it is possible to produce polymers with the same or lower density than the monomers. This is interesting for applications where it is desirable to maintain a constant volume during the polymerization such as tooth fillings, coatings and accurate molding of electrical and electronic components. RROP offers novel routes to polyesters

and polyketones particularly using vinyl substituted cyclic monomers (see Section 2.2) [6]. A less common group of monomers which undergo RROP are the bicyclobutanes, whereby the bridge across the four-membered ring can be viewed as a concealed double bond (see Figure 1).

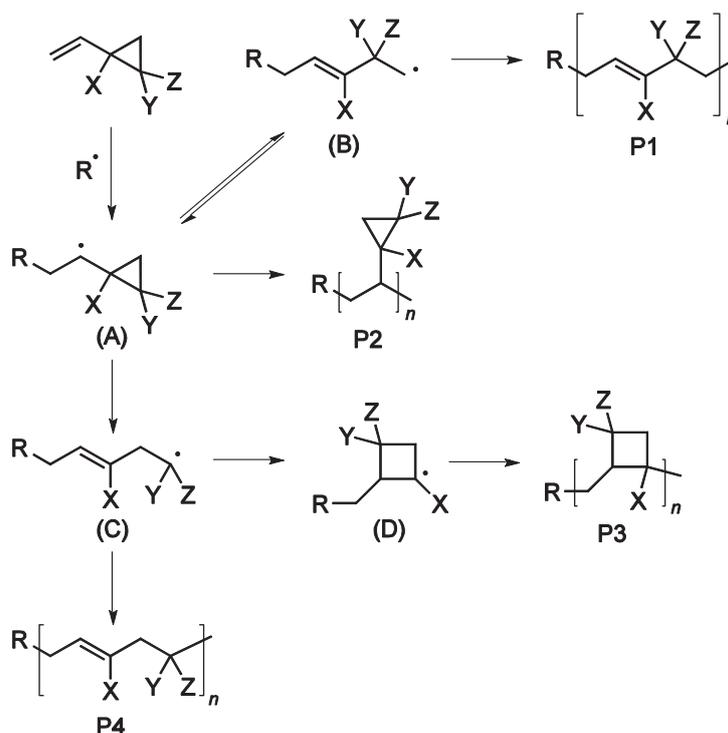
**Figure 1.** The radical ring opening polymerization (RROP) of a bicyclobutane [7].



### 2.1. Vinyl Substituted Cyclic Monomers

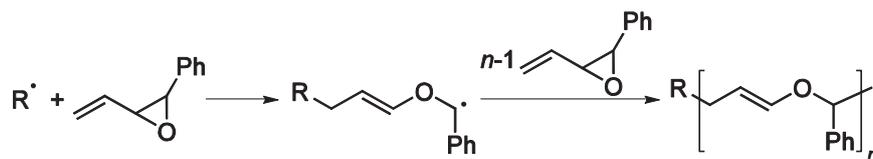
Vinyl cyclopropane and its derivatives have been studied by several groups [8–11]. The three membered ring has considerable ring strain (115 kJ mol<sup>-1</sup>) [2] and the simple RROP thus competes with the vinyl chain polymerization (see Figure 2).

**Figure 2.** The RROP of vinyl cyclopropane showing the competing reaction pathways.

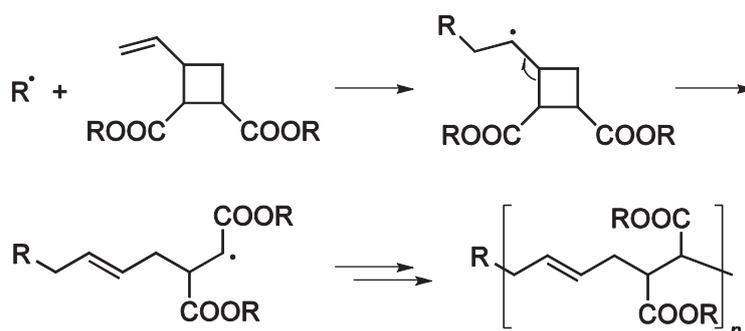


Which of the simple ROP products P1 and P4 predominates depends on the substituents Y and Z and the preference of the ring to open at the CX–CH<sub>2</sub> or the CX–CY bond. The simple vinyl chain polymerization P2 and the intermediate formation of a four-membered ring to yield P3 are additional possibilities.

Vinyl oxiranes yield polyethers via ROP [12–14] (see Figure 3).

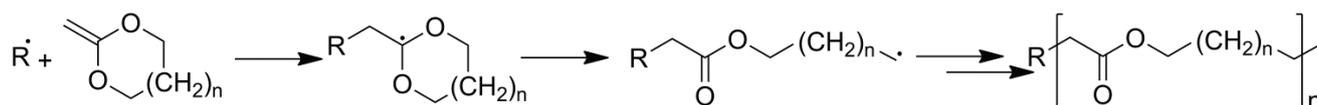
**Figure 3.** The RROP of phenyl (Ph) vinyl oxirane.

Vinyl cyclobutanes can also undergo RROP [15] (see Figure 4).

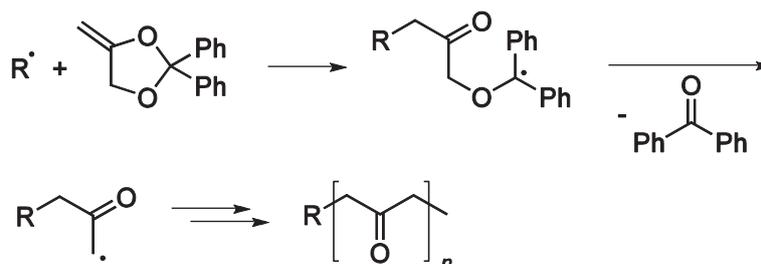
**Figure 4.** The RROP of a substituted vinyl cyclobutane.

## 2.2. Methylene Substituted Cyclic Monomers

The ring-opening of ketene acetals has proved to be a novel route to useful polyesters [16] (see Figure 5) although the sensitivity of the monomers to acid hydrolysis makes their handling difficult.

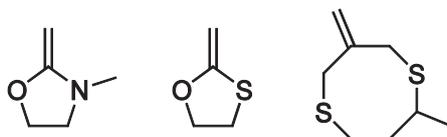
**Figure 5.** The RROP of ketene acetals.

The polymerization of 2,2-diphenyl-4-methylene-1,3-dioxolane [17] yields a polyketone rather than a polyester since benzophenone is eliminated by each ring-opening step (see Figure 6).

**Figure 6.** The radical polymerization of 2,2-diphenyl-4-methylene-1,3-dioxolane to yield a polyketone.

Heterocyclic monomers with nitrogen or sulfur heteroatoms have also been shown to undergo radical ROP (see Figure 7).

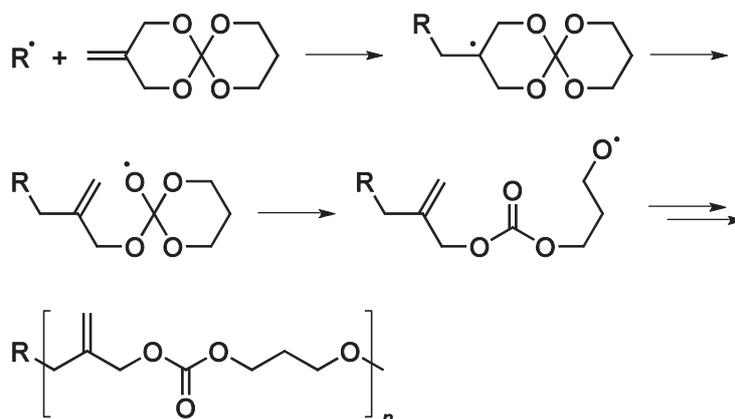
**Figure 7.** Some heterocyclic monomers which have been shown to undergo radical ROP [16,18,19].



### 2.3. Double Ring-Opening

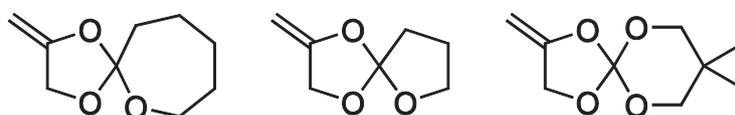
Spiro ortho-carbonates and their analogues have been the subject of considerable interest due to the volume expansion which occurs when the crystalline monomers are polymerized (If the monomers are first melted then a volume contraction takes place) [20]. A typical reaction scheme is shown in Figure 8 [16].

**Figure 8.** The radical ROP of a spiro carbonate.



The spiro ortho esters shown in Figure 9 have also been shown to polymerize, essentially quantitatively, via a radical ROP [21–24].

**Figure 9.** Some other examples for the radical ROP spiro monomers.

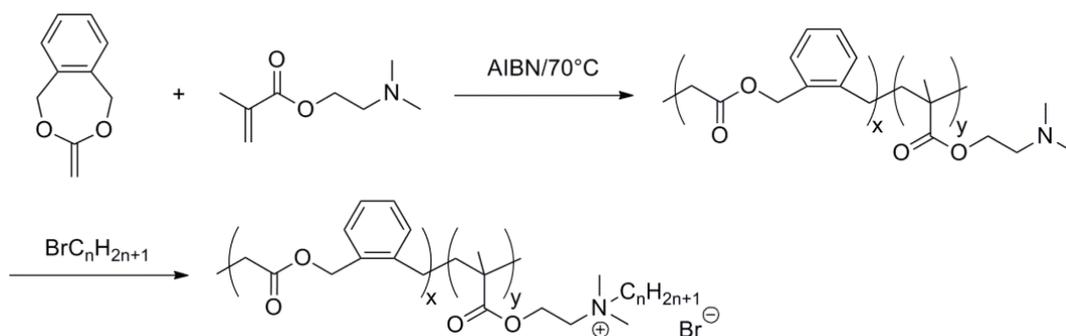


### 2.4. Degradable Polyesters via Radical Ring-Opening Homo- and Copolymerization

The polyester synthesis described above under 2.2 (Figure 5) is not a typical CROP, AROP or RROP in that a rearrangement takes place as each ring opens. Despite the apparently promising work of Bailey [16] the synthesis of polyesters via a RROP of ketene acetals initially received little interest. However, with the increasing interest in biodegradable polyesters and the versatility of RROP with respect to the structures accessible via very different monomers [25] and their copolymerization with conventional vinyl monomers [26–34] has changed the situation significantly.

Figure 10 shows an example of such a copolymerization. It is clear that by varying the monomers or their proportions, or indeed by varying the mode of initiation, e.g., NMP (nitroxide mediated polymerization) [35], RAFT (reversible addition fragmentation transfer polymerization) [36] or ATRP (atom transfer radical polymerization) [37] many and varied polymers can be obtained, optimized for their use in agricultural, medicinal or pharmaceutical fields.

**Figure 10.** An example of a radical ring opening copolymerization of a ketene acetal.

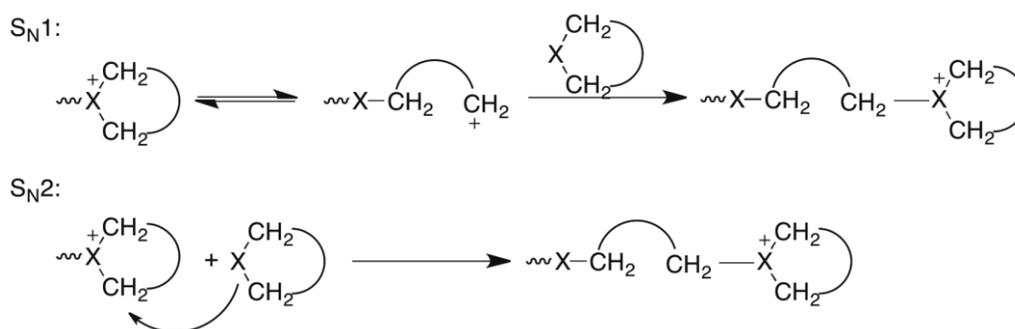


### 3. Cationic Ring-Opening Polymerization

Ring-opening polymerizations involving a positively charged intermediate (Cationic ROP or CROP) provide several important industrial polymers. These include polyacetals, copolymers of 1,3,5-trioxane and oxirane or 1,3,5-trioxane and 1,3-dioxolane, polytetrahydrofurans, copolymers of tetrahydrofuran and oxirane, poly (3,3-bis(chloro-methyl)oxetanes), polysiloxanes, polymers of ethyleneimine and polyphosphazenes [38,39].

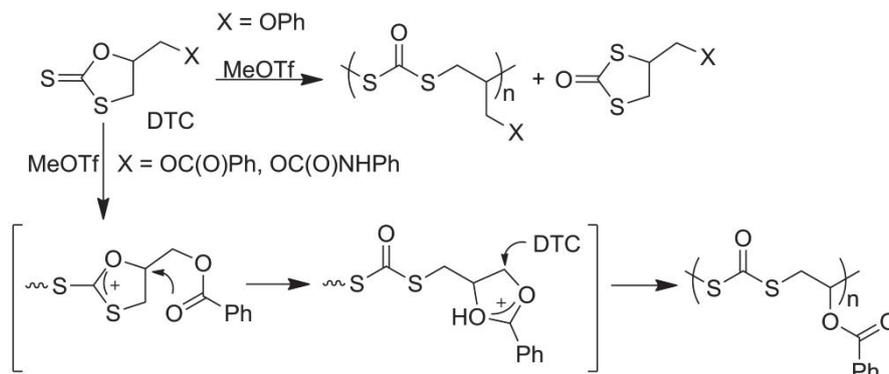
There are essentially two mechanisms that are discussed in the literature [38] for CROP: The first involves a growing chain with a cationic center at the chain end which adds to a monomer molecule via a  $S_N1$  or  $S_N2$  mechanism (Figure 11), whereby X represents an oxygen, a nitrogen or a sulfur atom.

**Figure 11.** CROP involving active chain ends;  $S_N1$  and  $S_N2$  mechanisms.



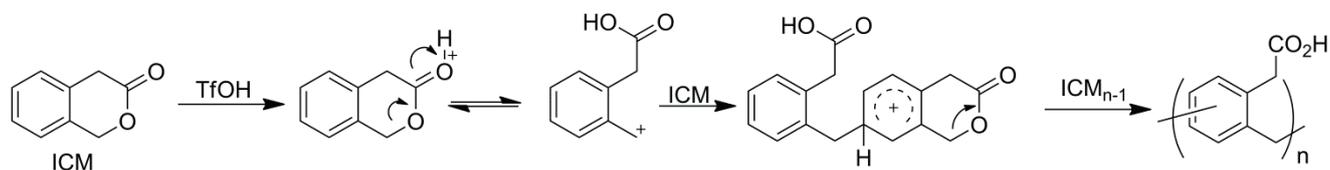
The polymer structure can be further controlled by the use of appropriate side groups. Thus, the exchange of an ether side group for an ester or carbamate (So-called NGP: Neighboring Group Participation) results in a different, well defined, microstructure during the CROP of cyclic dithiocarbonates (Figure 12) with methyl triflate initiator due to effective suppression of the isomerization of the monomer and the stabilization of the growing chain via the ester (carbamate) moiety [40].

**Figure 12.** Controlling the reaction path of a CROP of dithiocarbonates using Neighboring Group Participation (NGP).



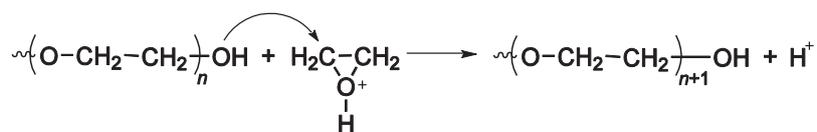
An extreme example of NPG is reported by Suzuki *et al.* [41] TfOH who describe the polymerization of an aromatic lactone in which the lactone is part of a fused ring system (3-Isochromanone). Using a variety of spectroscopic techniques and an elegant analysis, the authors suggest that the resulting polymer, which could be prepared in excellent yield via a bulk polymerization (2 h at 120 °C, 5 mol % triflic acid (TfOH) as catalyst), is formed via an intermediate Friedel-Crafts alkylation step (Figure 13) as a result of the stabilization of the growing chain end in the form of a benzyl cation.

**Figure 13.** The CROP of 3-isochromanone.



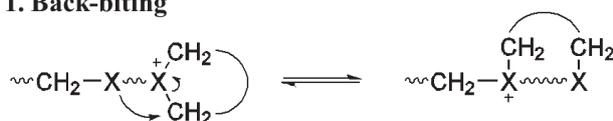
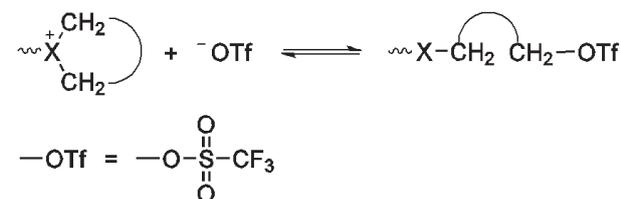
A treatment of the propagation of CROP would not be complete without reference to a long discussion, which can be considered as resolved (*vide infra*), specifically concerning, e.g., 1,3-dioxolanes, as to whether the propagating species are linear tertiary or secondary ions and thus, the mechanism is one of ring expansion or of linear growth. In terms of the microstructure of the polymers produced this is not trivial. In a very detailed analysis Plesch *et al.* [42] showed that under conditions where the concentration of water was less than  $10^{-4}$  mol L<sup>-1</sup> and at relatively low monomer concentration, the secondary oxonium ion predominates and the ring expansion mechanism prevails. In contrast to the suggestions of Plesch, Jaacks [43] and later Penczek [44] postulated, based on extensive experimental results that propagation takes place essentially via open chains. Finally, from even more detailed studies it was found that ring-expansion is favored at low monomer concentrations and the open chain mechanism dominates the propagation at higher monomer concentration [45] (see also [5]). This discussion is worthy of detailed study since it demonstrates the need to carefully examine the experimental techniques and the prevailing conditions before making conclusions about reaction mechanisms, especially where cationic systems are involved.

An alternative, third, mechanism proposed for the propagation of CROP is that the monomer is activated and carries the cationic center; the growth reaction is an electrophilic attack of the activated monomer on the chain end (Figure 14).

**Figure 14.** CROP via an activated monomer mechanism.

For some systems it has been shown that both mechanisms operate simultaneously [46].

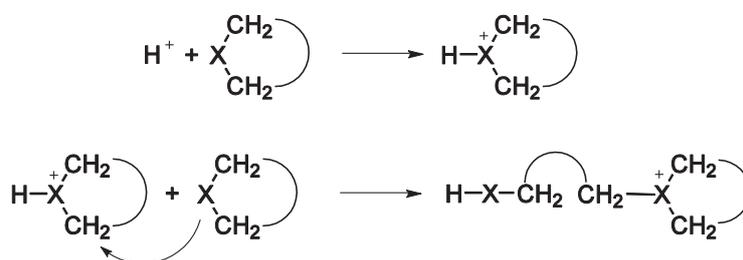
There are at least three types of reactions [38], which compete with the propagation reaction during a CROP as shown in Figure 15.

**Figure 15.** Three principal side reactions during a CROP.**1. Back-biting****2. Ring elimination****3. Counterion collapse****3.1. Initiation**

CROP can be initiated by Brønsted acids, carbenium ions, onium ions, photoinitiators and covalent initiators:

- Brønsted acids:

Protons can initiate the polymerization of numerous heterocyclic monomers, e.g., oxiranes, 1,3-dioxolanes, thiiranes, aziridines, tetrahydrofurans, lactones, 1,2 oxazolines and cyclic siloxanes as shown in Figure 16 assuming an activated chain end mechanism, in analogy to Figure 12 (S<sub>N</sub>2). “Dry” acids such as HCl, H<sub>2</sub>SO<sub>4</sub>, as well as HClO<sub>4</sub> and HOSO<sub>2</sub>CF<sub>3</sub> have frequently been used [40–42].

**Figure 16.** Initiation of a cationic ROP by a Brønsted acid.

Alternatively, the heteroatom poly-acids of the general structure shown in Figure 17 can be employed as initiators [47].

**Figure 17.** General structure of heteroatom poly-acids.



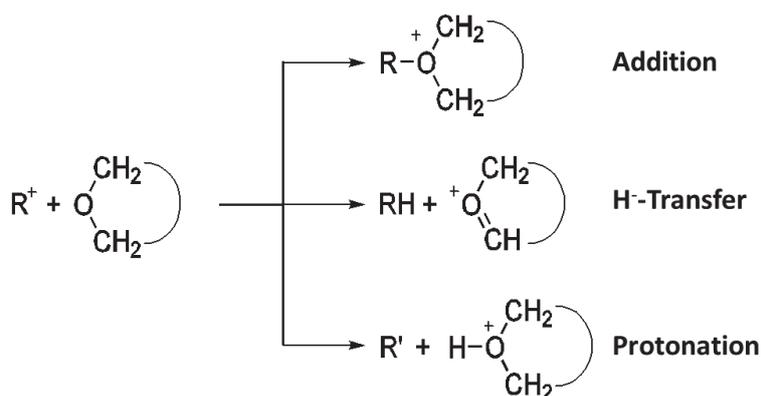
The acids with X = P can be relatively easily prepared from phosphoric acid and the required metal oxide; they are stable in air and are soluble in a variety of organic solvents. Two examples are well documented in the literature:  $\text{H}_3\text{PMo}_{12}\text{O}_{40}$  and  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  [47].

The CROP of epoxides and oxetanes via Brönsted acids are often characterized by an induction period and, although not completely explained, the more recent studies of Crivello's group [48] modifying the kinetics of the photo initiated CROP by the addition of crown ethers (which are similar in structure to the oligomers formed in the early stages of polymerization) or 2,6 di-tert-butyl pyridine do offer a plausible explanation for some of the observed effects. Thus, control of an auto accelerated thermal polymerization is improved by such additives.

- Carbenium Ions:

Initiation of CROP by various carbenium ions has been frequently studied, the general reaction scheme is shown in Figure 18 ( $\text{R}^+ = (\text{C}_6\text{H}_5)_3\text{C}^+$  [49],  $(\text{C}_6\text{H}_5)_2\text{CH}^+$  [50],  $(\text{C}_6\text{H}_5)\text{CH}_2^+$ ,  $\text{H}_2\text{C} = \text{CH}-\text{CH}_2^+$  and  $(\text{CH}_3)_3\text{C}^+$  [38]). The carbenium ions can react with rings of various structures and having various hetero atoms:

**Figure 18.** Initiation of CROP by carbenium ions ( $\text{R} = \text{R}^+(-\text{H}^+)$ ).



- Onium-Ions:

Onium-Ions can be prepared in a separate reaction or *in situ* [51]. Initiation by onium ions follows, in a general sense, the scheme shown in Figure 19; typically the reaction involves the transfer of a carbenium ion and can thus be seen as an extension of the initiation by carbenium ions (*vide supra*).

Typical examples are the reactions of trialkyl oxonium ions with cyclic acetals [38], ethers [52], or sulfides [53] as well as with amines [54].

A variation on this type of initiation is reported by Li and Yu [55] who have reported the use of glycosyl ortho-alkynyl benzoates and a gold triflate salt ( $\text{PPh}_3\text{AuNTf}_2$ ) to prepare poly-THF with glycosyl terminal groups.

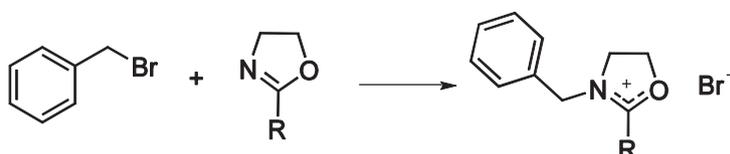
**Figure 19.** Initiation by onium-ions (Z and X may be identical, e.g., oxygen).



- Covalent Initiators:

The polymerization of 2-Alkyl-2-oxazolines can be initiated by classical alkylating reagents, such as benzyl bromide [56] (see Figure 20).

**Figure 20.** Initiation by covalent reagents.

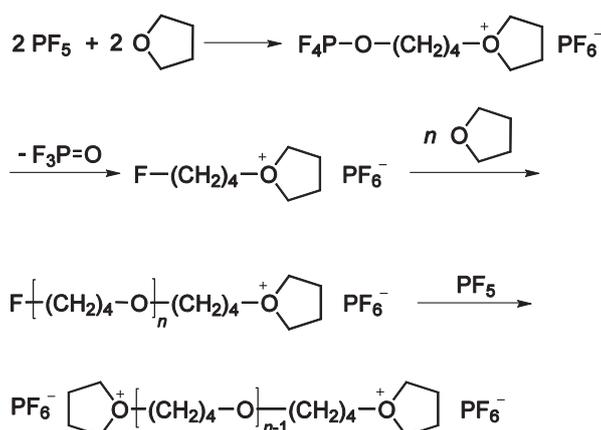


Esters of Brønsted acids (e.g.,  $\text{ROSO}_2\text{CF}_3$  and  $\text{ROSO}_2\text{F}$ ) can also be used as initiators [57–59], whereby the covalent initiators act as precursors for a carbenium ion initiation (*vide supra*). In particular, the use of triflic acid anhydride [57] is worth noting as a route to growing polymers of THF with two active ends.

- Lewis acids:

These compounds require a coinitiator (activator), e.g., an alkyl halide or water, in order to polymerize heterocyclic monomers [2,38,60]. The most frequently employed Lewis acid for the cationic polymerization is  $\text{BF}_3$  and its precursor  $\text{BF}_3\text{OEt}_2$ . However, in order to apply them for the ROP of THF the addition of cationogenic compounds such as acid halides is required. Detailed studies have also been made using  $\text{PF}_5$ , e.g., for the polymerization of THF for which a mechanism supported by  $^{19}\text{F}$  and  $^{31}\text{P}$  NMR spectroscopy has been proposed (see Figure 21) [61].

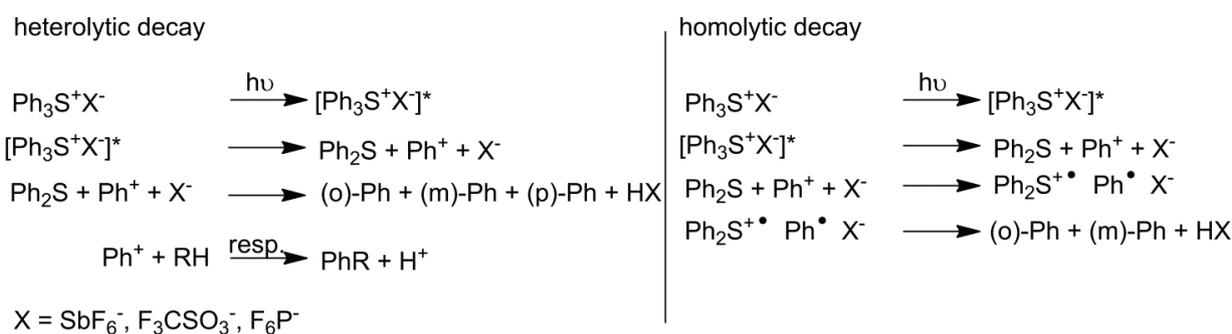
**Figure 21.** Initiation of the CROP of THF by  $\text{PF}_5$ . Chain growth from both chain ends.



- Photoinitiators

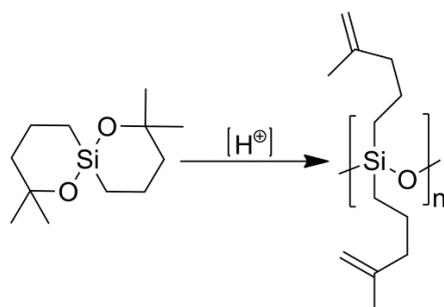
Sulfonium- and iodonium-salts have achieved industrial importance as cationic photo initiators [39]. Both heterolytic and homolytic reaction mechanisms are possible. Taking sulfonium salts as an example, via a heterolytic process the sulfonium salt is raised to a singlet-state, which then relaxes to give  $\text{Ph}_2\text{S}$  and  $\text{Ph}^+$  (from  $\text{Ph}_3\text{S}^+$ ). The  $\text{Ph}^+$  moiety can then react with e.g., an alkyl group (this may be the solvent, polymer or monomer [48,62–65]) to yield a proton and  $\text{PhR}$  (see Figure 22).

**Figure 22.** Formation of an initiator by heterolytic or homolytic splitting of a photoinitiator (\*: Singlet-state).



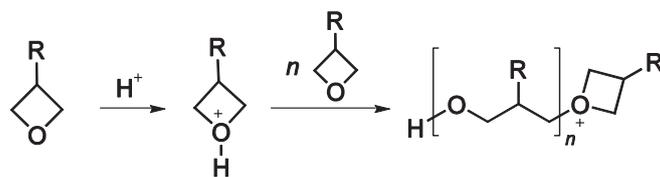
Via the heterolytic splitting of the initiator can be considered as an acid generator or photoacid generator (PAG). Typical examples are triphenylsulfonium triflate and diphenyliodonium triflate. The latter has been studied recently [66] to selectively cleave the carbon-oxygen bonds in a vinyl functionalized oxasilaspirocycle to form both homo- and copolymer polysiloxanes via a double ring-opening CROP (*cf.* Section 2.3, see Figure 23).

**Figure 23.** The formation of a polysiloxane via a double ring-opening cationic polymerization.

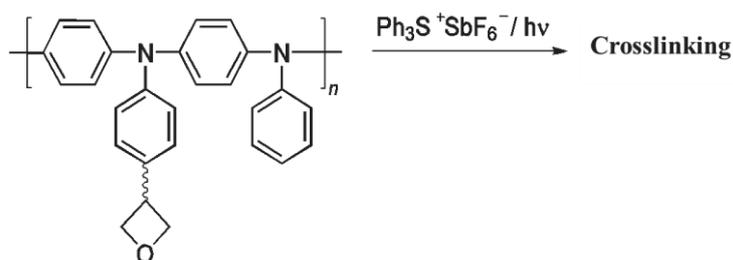


The homolytic splitting of triphenylsulphonium cations leads to a phenyl radical, which then undergoes a Fries photo-rearrangement together with the diphenylsulphonium cation radical to yield by-products such as *p*- and *o*-(Phenylthio)biphenylenes [67]. That some *m*-substituted products are observed can be explained by a heterolytic decomposition followed by an electrolytic aromatic substitution of the diphenylsulphonium cation radical [68]. Photo initiators have proved useful as crosslinking agents for hole (defect) conductors [69,70] (e.g., aromatic amine polymers which can give up an electron to yield a radical cation, an electronic defect) with oxetane side groups, which are employed in the manufacture of OLED. The reaction schemes are shown in Figures 24 and 25.

**Figure 24.** CROP of oxetanes (R = Polymer chain with oxetane side groups (for the source of H<sup>+</sup>, see e.g., Figure 22)).



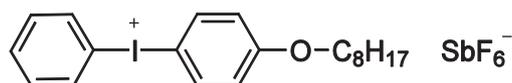
**Figure 25.** The cationic crosslinking of a hole defect polyarylamine.



If the hole defect polymer has numerous oxetane side groups, the ROP leads to crosslinking and the polymer becomes insoluble. The soluble polymer can be coated (e.g., by spin-coating), dried and then photochemically crosslinked so that further coating is possible without dissolving the deposited film [71,72].

The solubility of the photo initiator can be improved by increasing the length of the side chain (e.g., Figure 26).

**Figure 26.** Structure of an iodonium photo initiator [62,65].



Enzymes have also been shown to initiate the ring-opening polymerization of oxazolines (EROP). By employing different sugar molecules having a methyl oxazoline side group a variety of natural and synthetic polysaccharides could be produced, in particular some of the most complicated synthetic polymeric structures and synthetic chitin. The fundamental mechanism, although the enzyme interacts with the intermediates and increases the reaction rate considerably, remains a CROP [73]. It is worth noting that polyoxazolines have been shown to be biocompatible and potentially useful as carriers of pharmaceutically active agents [74]. An additional group of initiators for the CROP of oxazolines are the activated metallocene complexes described by Kourti *et al.* [75]. In this study, zirconium and hafnium metallocenes were activated with pentafluoroborates or their anilinium salts to initiate a CROP of 2-methyl and 2-phenyl oxazolines. That the polymerization is indeed a CROP was corroborated by appropriate blank experiments. However, since the metallocene does not take part in the propagation step the steric control associated with metallocene polymerizations cannot be expected for these systems and the polymerizations appear to show no special kinetic or mechanistic features. However, the authors do note an increase in the MWD and M<sub>n</sub> at close to complete conversion, which may be explained by backbiting reactions (*vide infra*, Section 3.3).

## 3.2. Chain Growth

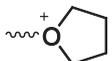
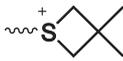
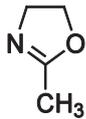
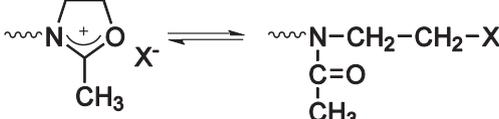
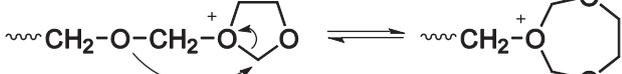
The active species in CROP are oxonium, sulfonium, ammonium or phosphonium ions (see Figure 27).

**Figure 27.** The structure of the growing chain ends in CROP.



The active species can be identified by NMR (see examples in Table 2) and can be quantified e.g., by reacting with e.g., sodium phenolate [76,77] to yield a UV active end group (see Figure 28).

**Table 2.** The structure of the growing chain ends during CROP for a variety of monomers.

Monomer	Structure of the Growing Chain End [51–53,56]
	
	
	
	

**Figure 28.** Termination of CROP by phenolate to allow quantitative determination of the growing chains.



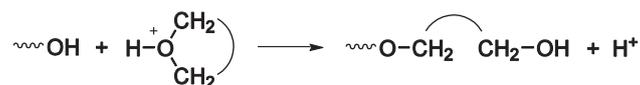
An alternative method for the quantitative determination of the active chain ends is to react these with, e.g., triphenyl phosphine and to analyze the solution by  $^{31}\text{P}$  NMR (see Figure 29) [78]. It is worth noting that these polymers are not suitable for further analysis, as they tend to degrade although the solutions are stable, for days at least, provided they are kept under an inert atmosphere.

**Figure 29.** Reaction of the CROP growing chain ends with a phosphine to allow quantitative analysis.



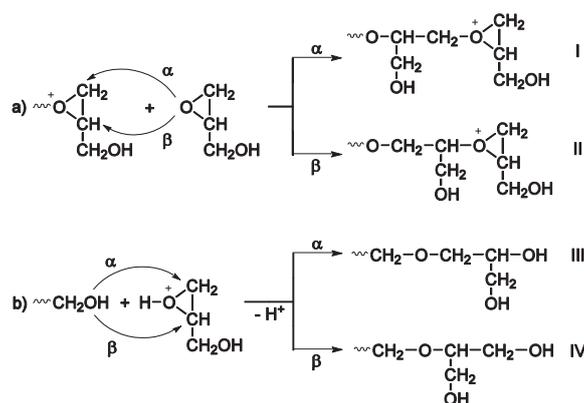
Propagation via an activated monomer [79] can be visualized as shown in Figure 30.

**Figure 30.** Chain growth via an activated monomer.



With asymmetric monomers chain growth via an activated monomer rather than an activated chain end can yield different polymer microstructures as shown in Figure 31.

**Figure 31.** The microstructure of poly-glycidol: (a) Growth via an active chain end and (b) via an activated monomer mechanism.

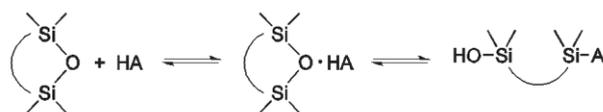


The experimental results suggest that the predominant structure is III [38,79,80] (Figure 31) so that it can be assumed that for this monomer the activated monomer mechanism predominates.

The CROP of hexamethylene cyclotrisiloxane ( $\text{D}_3$ ) is an important industrial process generally catalyzed by trifluoromethane sulphonic acid or metal salts of this acid [81]. For the CROP of cyclic siloxanes two propagation reactions have been proposed [82,83] (see Figure 32).

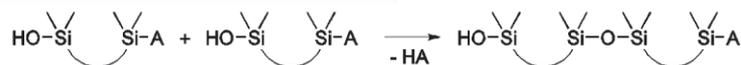
**Figure 32.** Two alternative propagation routes for the ROP of cyclic siloxanes: (a) Step-growth and (b) Chain-growth.

**Initiation**

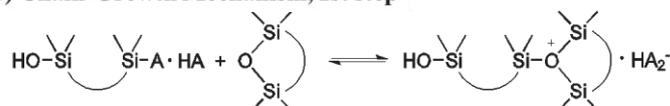


**Chain Growth**

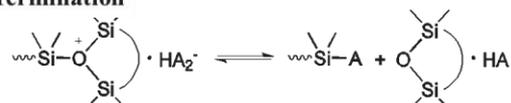
**a) Step-Growth Mechanism, 1st step**



**b) Chain-Growth Mechanism, 1st step**



**Termination**

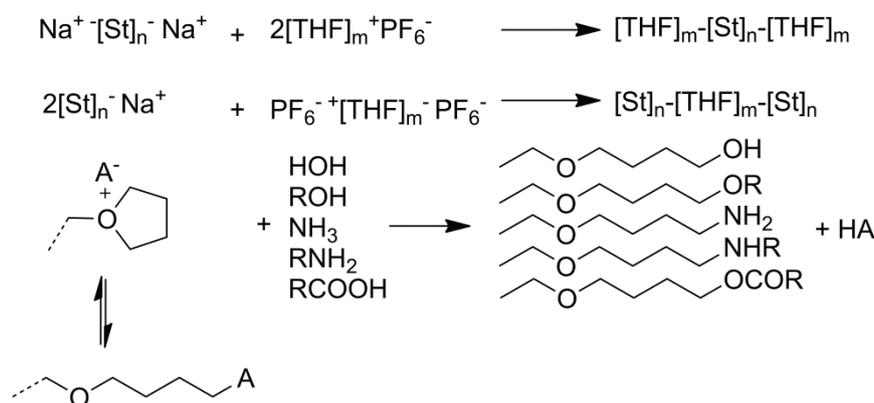


In contrast to the chain growth polymerization of olefins, where the termination leads to an active species being destroyed, the termination of cyclic monomers containing a heteroatom (such as the siloxane shown in Figure 32) leads in the first instance to the chain growth being stopped but the resulting monomer unit can start a new chain as long as monomer is available. Thus, the distinction between the terms transfer and termination becomes gradual. Since the reaction intermediates are extremely reactive, the mechanism of the CROP of cyclic siloxanes is still a matter for discussion [2,38].

### 3.3. Termination

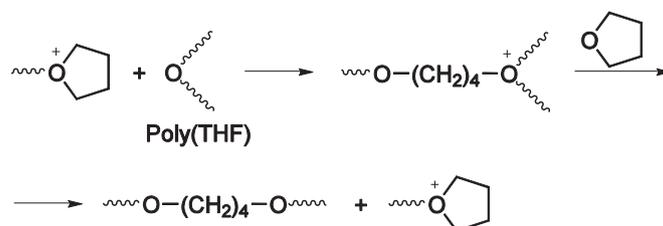
The CROP of some heterocycles, especially cyclic ethers such as THF and oxetane can, at appropriate temperatures and monomer concentrations, be considered as “living” (*i.e.*, without termination). Intentionally adding termination reagents may *e.g.*, be done to enable the end groups to be (quantitatively or qualitatively) analyzed. Examples, already discussed above, are the addition of phenoxy anions [76] or phosphines [78] but polyanions can also be used to yield block copolymers [84]. These reactions are summarized in Figure 33.

**Figure 33.** Intentional termination of CROP.



However, backbiting and/or intermolecular alkylation is intrinsic to such systems (see Figure 34).

**Figure 34.** Transfer (Termination) via an alkyl transfer mechanism.



Since these reactions usually only become predominant when the monomer becomes depleted, only then do they represent chain termination rather than transfer; the charged species cease to grow due to lack of monomer and the second stage of the scheme in Figure 34 does not occur.

In some systems, backbiting seems to be negligible and the systems appear to be living [85]. In this work the authors report the CROP of 3-benzyl-1,3-oxazolidine-2-thione (BOT) to yield a

polythiourethane (Figure 35) using  $\text{BF}_3\text{OEt}_2$  in nitrobenzene solvent and although initiator efficiencies are low (*ca.* 0.1 based on the amount of  $\text{BF}_3\text{OEt}_2$  employed), the  $M_w/M_n$  measured was *ca.* 1.0 for all initiator/monomer ratios studied and both di- and triblock copolymers could be produced with 3-benzyl tetrahydro-1,3-oxazolidine-2-thione (BTOT) as a second monomer. This work is especially worth citing for its use of an unusual end-capping agent ( $\text{Et}_2\text{NCS}^-\text{Et}_2\text{NH}_2^+$ ), which can then be analyzed by NMR, the use of a variety of analytical techniques to confirm the structures as well as for the excellent yields of polymers with improved thermal stability and perhaps interesting optical properties via a CROP. The kinetic analysis also corroborates the idea (*vide supra*) that the ROP is driven by the ring strain; thus, the rate of propagation for the 5 membered BOT ring is twice that of the 6 membered ring in BTOT, although the authors ascribe the difference to the different steric hindrance around the thiocarbonyl groups of the two monomers.

**Figure 35.** The CROP of 3-benzyl-1,3-oxazolidine-2-thione initiated with  $\text{BF}_3\text{OEt}_2$ .

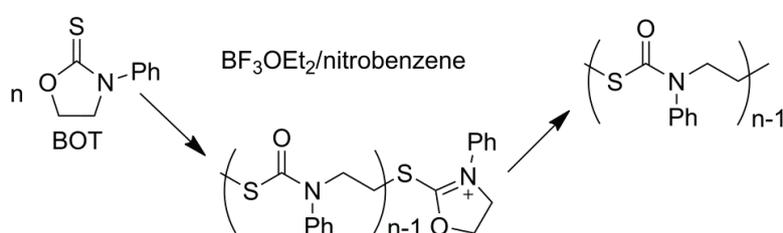
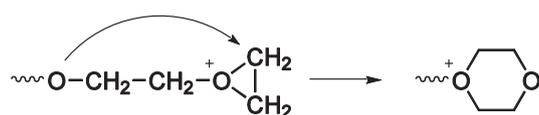


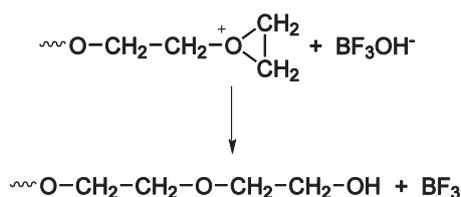
Figure 36 shows this reaction for the ROP of oxirane. The resulting dioxonium ring, in this case, is inert to further chain growth [38,79].

**Figure 36.** Termination via back-biting; ring expansion.



The collapse or decomposition of the counter ion also leads to a termination of chain growth, whereby this reaction (Figure 37) may be an equilibrium reaction and thus, the chain ends considered as dormant rather than terminated.

**Figure 37.** Termination of chain growth due to collapse of the counter ion.



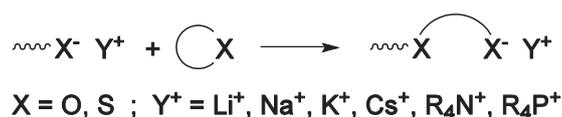
The living nature of CROP has been utilized to form block copolymers from 2-methyl-2-oxazoline, 2-ethyl-2-oxazoline, 2-n-nonyl-2-oxazoline and, e.g., styrene or acrylates. The CROP of the oxazoline was terminated by a carboxylate functionalized chain transfer agent and the second block formed by a reversible addition-fragmentation chain transfer (RAFT) polymerization [86].

CROP reactions are often rather slow and reaction times even at higher temperatures are often of the order of hours. The reaction rate can be increased considerably (up to 400 fold) by the use of microwave rather than simple heating, although it has been shown that the effect is a simple thermal effect [87]. An interesting comparison of continuous micro reactor configurations and a batch reactor for the microwave assisted CROP of 2-ethyloxazoline is reported by the same group [88] who discuss a major effect on the MWD of the products resulting from the residence time distribution of the individual reactors whereby differences in conversion are conveniently assigned to probable inaccuracies in the temperature measurements. Poly (2-oxazolines) are becoming increasingly interesting for biomedical applications [89] and as micellar catalysts [90–92].

#### 4. Anionic Ring-Opening Polymerization

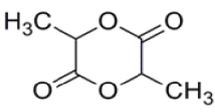
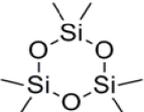
Anionic ROP (AROP) can be described as the nucleophilic attack of the growing chain end on a heterocyclic monomer molecule (see Figure 38). The AROP of  $\epsilon$ -caprolactam to produce Nylon 6 is an important industrial process.

**Figure 38.** The AROP as a nucleophilic addition reaction [93].



Some of the heterocycles that can be polymerized anionically are listed in Table 3 with their corresponding active chain ends.

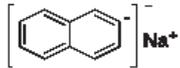
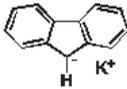
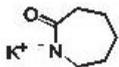
**Table 3.** Anionically polymerizable heterocycles and the corresponding active species [93–99].

Monomer	Structure of the Growing Chain	Reference
	$\sim\text{CH}_2\text{-CH}_2\text{-O}^-$	[94]
	$\sim\text{CH}_2\text{-CH}_2\text{-S}^-$	[95]
	$\sim\text{S-CH}_2\text{-CH}_2\text{-CH}_2^-$	[96,99]
	$\sim\text{O-C(=O)-CH(CH}_3\text{)-O-C(=O)-CH(CH}_3\text{)-O}^-$	[97]
	$\sim\text{Si-O-Si-O-Si-O}^-$	[98]

##### 4.1. Initiation

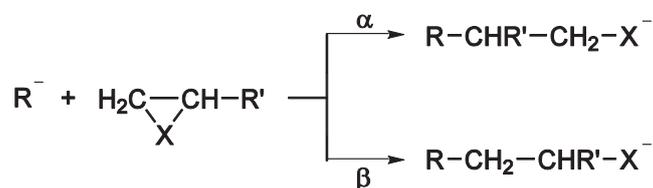
Some of the more important initiators for AROP are listed in Table 4.

**Table 4.** Initiators for an AROP of heterocycles.

Description	Structure	Monomer	Reference
Radical anion		Ethylene oxide	[100]
		Propylene sulfide	[101]
Carbanion	$C_2H_5-Li^+$	Thietane	[99]
	$n-C_4H_9-Li^+$	Propylene sulfide	[102]
		Hexamethylcyclo-trisiloxane	[102]
		Ethylene oxide	[103]
Alcoholate	$CH_3O^- K^+$	Styrene oxide	[104]
		$\beta$ -Propiolactone	
Silanolate	$(CH_3)_3SiO^- K^+$	$\beta$ -Propiolactone	[105]
		$\epsilon$ -Caprolactone	[106]
Carboxylate	$CH_3COO^- K^+$	$\beta$ -Propiolactone	[106]
		Ethylene oxide	[106]
		Propylene oxide	[107]
Thiolate	$C_2H_5S^- K^+$	Propylene sulfide	[107]
Lactam anion		$\epsilon$ -Caprolactam	[108]
Amine	$(C_2H_5)_3N$	Propylene sulfide	[95]
Al-trialkoxide	$Al(O-t-C_3H_7)_3$	$\epsilon$ -Caprolactone	[109,110]
Al-Dialkyl monoalkoxide	$(C_2H_5)_2AlOCH_3$	Lactide	[111,112]
		$\epsilon$ -Caprolactone	

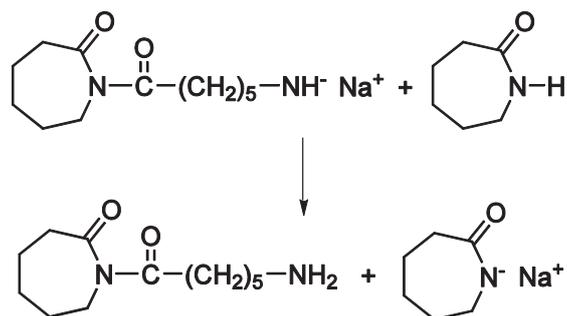
#### 4.2. Propagation

For unsymmetrically substituted rings there are formally two ways the monomer ring can be opened as shown in Figure 39.

**Figure 39.** Nucleophilic ring-opening of asymmetrical heterocycles.

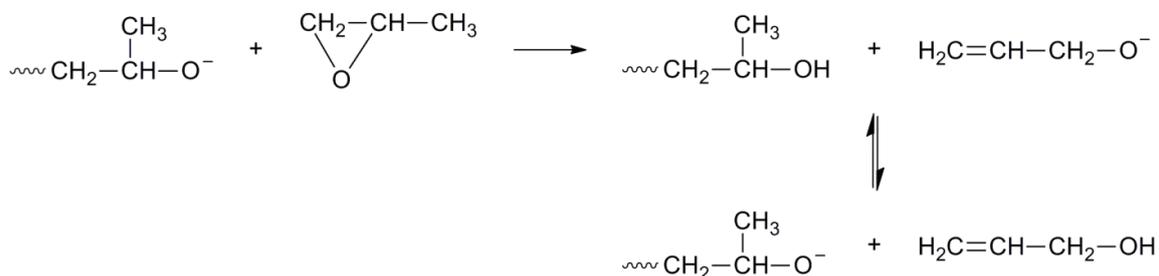
Although not trivial, with careful microstructure and end group analysis the preferred reaction route can be identified [93]. Additionally, simple consideration of the stability of the reaction intermediates can prove helpful. Thus, the carboxylate ion (route  $\beta$ ) is preferred, even for lactones (see Figure 40) [113], and the nucleophilic attack takes place at the least substituted carbon atom.



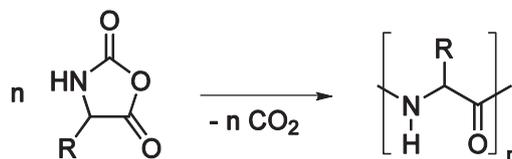
**Figure 44.** Regeneration of the lactam anion.

Whereby the terminated dimer can also react with a lactam anion and thus grow.

An AROP of methyl oxirane (1,2-propylene oxide) is an industrial process for the preparation of oligomers in combination with oxiranes (ethylene oxide). The extensive chain transfer to monomer, typical of substituted oxiranes prohibits the formation of high polymers [117]; the reaction is shown in Figure 45. It should be noted that the allyl alkoxide ion can also generate propagating chains. This leads to less than ideal alcohol group formation where simple end capping reactions are employed (or diol formation with bifunctional initiators).

**Figure 45.** AROP of methyl oxiranes with chain transfer to monomer.

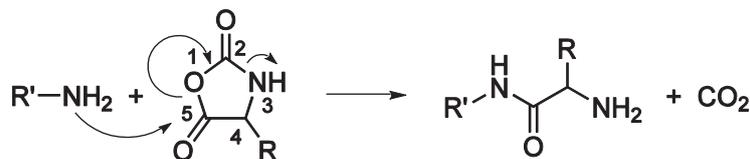
A particularly interesting case of AROP is the condensation ROP of a Leuchs' anhydride (*N*-Carboxy- $\alpha$ -amino acid anhydride), which eliminates a molecule of  $\text{CO}_2$  for each addition step (see Figure 46).

**Figure 46.** Formation of "Nylon-2" from a Leuchs' anhydride.

As initiator, e.g., primary amines can be employed [118] (see Figure 47).

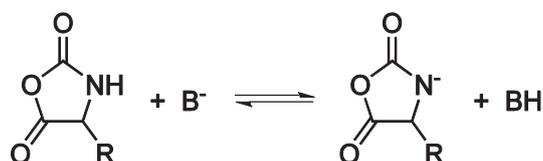
It could be shown by using  $^{14}\text{C}$  labeled monomer that the  $\text{CO}_2$  contains exclusively the C-2 (Figure 47) carbon atom. Thus, the free electron pair of the primary amine nitrogen attacks the monomer at C-5, the carbon with the lowest electron density and the  $\text{CO}_2$  elimination results from sequentially breaking the C-5-O-1 and the C-2-N-3 bonds, whereby the amine nitrogen acts as the base.

**Figure 47.** Mechanism of CO<sub>2</sub> elimination as a result of the attack of a primary amine on a Leuchs anhydride.



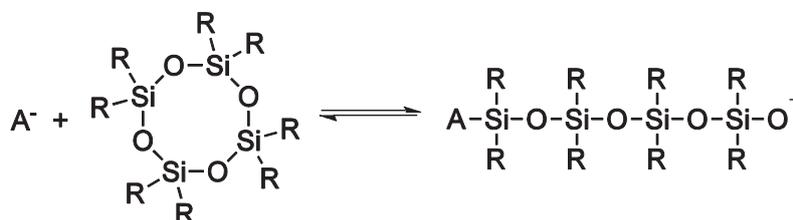
An alternative to a covalent initiator is the use of a base B<sup>-</sup> (e.g., <sup>-</sup>OCH<sub>3</sub>, H<sup>-</sup>, <sup>-</sup>OOCCH<sub>3</sub> [118]) which generates an anion from oxazolidin-2,5-diones as shown in Figure 48. This anion can then initiate chain growth via a nucleophilic attack on another monomer.

**Figure 48.** Formation of an anion from a Leuchs' anhydride using a base.



Cyclic siloxanes can also undergo ROP via anionic intermediates employing alkali metal oxides or hydroxides as initiators [119]. On an industrial scale, octamethylenecyclotetrasiloxane (D<sub>4</sub>) is employed as a starting material. For the propagation step the  $\Delta H_p \approx 0 \text{ kJ mol}^{-1}$ , but due to the increased rotational freedom of the side chains the  $\Delta S_p = +6.7 \text{ J mol}^{-1}$  polymerization does occur. However, depolymerization competes with polymerization and rings and chains are in equilibrium (see Figure 49). The equilibrium is shifted to the ring form with increasing size of the substituents. If other siloxanes with different (e.g., phenyl or methyl) substituents are mixed with D<sub>4</sub> statistical copolymers are obtained [119]. An alternative, employing D<sub>3</sub> (Hexamethylenecyclotrisiloxane) as the monomer, has the disadvantage that the synthesis is more elaborate [120,121].

**Figure 49.** Equilibrium between rings and chains during the AROP of cyclic siloxanes (A<sup>-</sup> = ~Si(R)<sub>2</sub>O<sup>-</sup>).



#### 4.3. Transfer and Termination

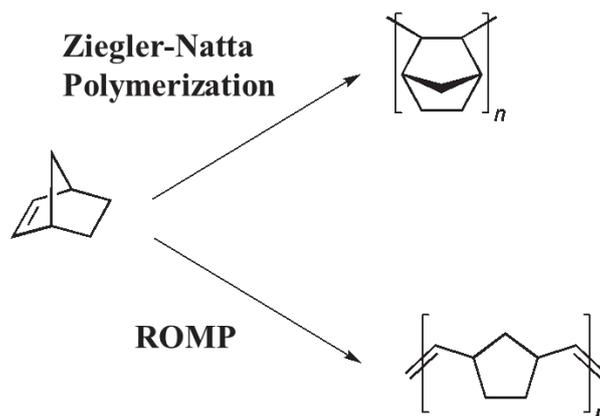
As discussed above (e.g., Figure 34) chain termination reactions are more accurately described as transfer reactions as long as additional monomer is available. The active centers of AROP, e.g., alcoholates or carboxylates are not only nucleophilic but act as bases and can abstract protons from the monomer to initiate new chains. Thus, the polymerization of propylene oxide initiated with alkali metal salts does not give polymers with high molar masses (*Vide supra*). One possibility to increase

the molar mass of the products is to add crown ethers as complexing agents for the counter ions to the polymerization system [122]. The free-ion/ion-pair equilibrium is shifted to the free-ion side; the free-ions preferentially add to monomer rather than abstract a proton.

## 5. Ring-Opening Metathesis Polymerization (ROMP)

Olefin metathesis is a reaction that can be seen to have influenced both organic and polymer chemistry more than any other during the last few decades. Historically, the ring-opening metathesis reaction has its origin in polymer chemistry: In 1955 Anderson and Merckling (DuPont), working with norbornene and  $\text{TiCl}_4/\text{EtMgBr}$  catalysts obtained a polymer containing a highly unsaturated backbone [123] which some years later was identified as the product of a ring-opening polymerization [124] (see Figure 50).

**Figure 50.** Ziegler-Natta polymerization and ring-opening metathesis polymerization (ROMP) of norbornene.



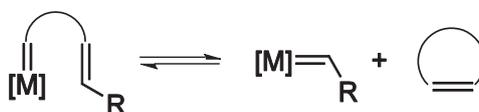
The development of ROMP is also documented in the academic literature [125–128]. The driving force for ROMP is the release of the ring strain enthalpy and, since the number of molecules is considerably reduced by polymerization, a positive ( $-T\Delta S$ ) must be compensated by the enthalpy term in order for the reaction to proceed according to:

$$\Delta G = \Delta H - T\Delta S \quad (1)$$

Table 5 lists  $\Delta H$ -,  $\Delta S$ - and  $\Delta G$ -values for a selection of cyclic olefins. The positive  $\Delta G^0$  confirms that cyclohexene cannot be polymerized by a ROMP at room temperature.

The remaining double bonds in the backbone of the polymer allow backbiting reactions (see Figure 51) to form macrocycles, which are often observed as products from the ROMP of cyclic olefins [131].

**Figure 51.** The formation of macrocycles via back biting during the ROMP of cyclic olefins.

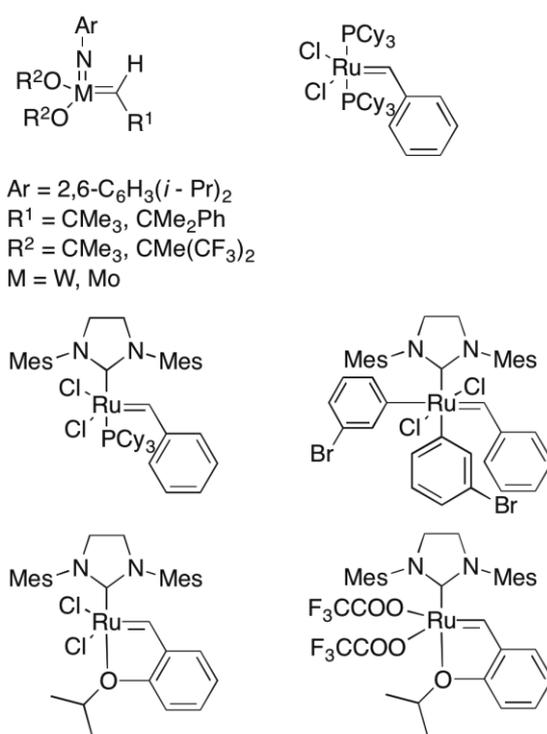


**Table 5.** Thermodynamic parameters for the ROMP of a selection of liquid monomers to amorphous polymers at 25 °C [129,130].

Monomer	Configuration of the double bond in the polymer	$\Delta H^0$ /(kJ/mol)	$\Delta S^0$ /(J/(mol K))	$\Delta G^0$ /(kJ/mol)
Cyclopentene	<i>cis</i>	-15.4	-52	-0.3
	<i>trans</i>	-18	-52	-2.3
Cyclohexene	<i>cis</i>	-1-3	-31	6.2
	<i>trans</i>	1-3	-28	7.3
Cycloheptene	<i>cis</i>	-16	-20	-10.0
	<i>trans</i>	-20	-17	-15.0
Cyclooctene	<i>cis</i>	-20	-2	-19.4
	<i>trans</i>	-22	-2	-21.5
1,5-Cyclooctadiene	<i>cis</i>	-25	-5	-23.5
	<i>trans</i>	-33	-5	-31.5

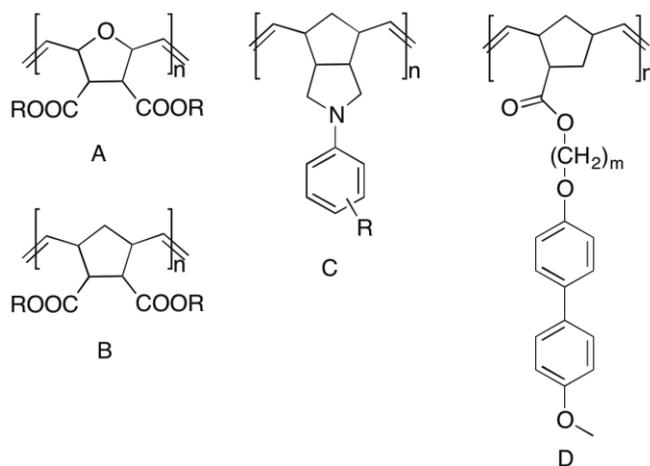
The metathesis of olefins and in particular cyclic olefins can be initiated by homogeneous, heterogeneous and immobilized catalysts. The classical catalysts are the oxides of Group VI transition metals on Lewis acid carriers, which are robust and can be regenerated. Typical examples of heterogeneous catalysts are  $\text{WO}_3/\text{Al}_2\text{O}_3$  and  $\text{MoO}_3/\text{Al}_2\text{O}_3$  [125], as homogeneous catalysts  $\text{WCl}_6/\text{SnBu}_4$  und  $\text{MoCl}_6/\text{SnPh}_4$  are quoted whereby these and a large number of other systems have been mentioned in previous reviews of the subject [125–128]. Only with the development of well-defined complexes based on Molybdenum or Ruthenium metals could a tolerance with respect to e.g., acid, ester and amide functionalities be developed and the possibility for a much wider variety of polymer structures opened up. Schrock, Grubbs and Chauvin were honored with a Nobel Prize in 2005 for their synthetic and mechanistic work in this area [132–134].

A selection of catalysts is shown in Figure 52.

**Figure 52.** A selection of ROMP catalysts [135–140].

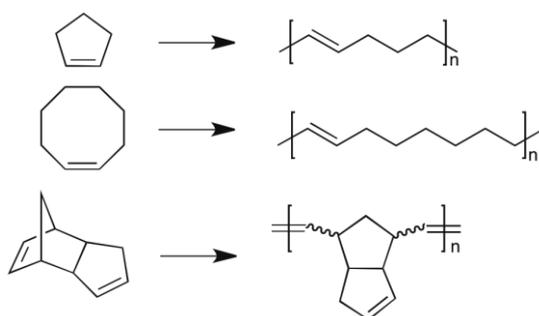
ROMP is employed to produce a variety of interesting polymer structures of which a selection is shown in Figure 53 together with their reported commercial applications.

**Figure 53.** Functional polymers via ROMP: (A) Super absorber, after crosslinking [141]; (B) Ion exchange resin, flocculation aid [141]; (C) High temperature thermoplast [141]; (D) Polymer with liquid crystal side chains ( $m \geq 20$ ) [142].



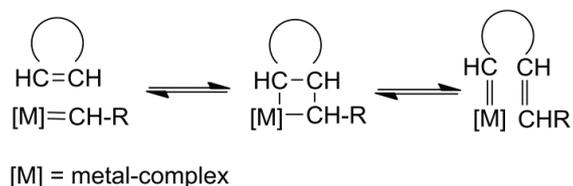
The best known industrial products synthesized via ROMP are: Norsorex<sup>®</sup> (Polynorbornene, Astrotech Advanced Elastomerproducts GmbH) (see Figure 50), Vestenamer<sup>®</sup> (Polycyclooctene) (Evonik Degussa GmbH), polycyclopentene and polycyclopentadiene (Metton<sup>®</sup>) are all well established commercial products (see Figure 54).

**Figure 54.** The structures of Norsorex<sup>®</sup>, Vestenamer<sup>®</sup> and Polycyclopentadiene.



It is now widely accepted that the critical propagation step in ROMP is the formation of a metallocyclobutane intermediate from a coordination of a cycloolefin by the catalytic metal center of the carbene complex followed by a [2+2] cycloaddition. The metallocyclobutane then undergoes a cycloreversion and the metal atom separates from the olefin bond (see Figure 55) [143].

**Figure 55.** The mechanism of ROMP including the metallocyclobutane intermediate.



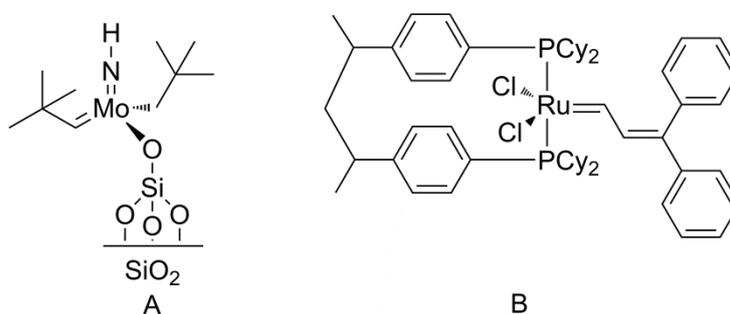
The reactivity of the metal complexes with respect to different functional groups is graphically shown in Figure 56; thus, ruthenium complexes react preferentially with olefins and can, indeed, be used in aqueous media for metathesis reactions whereas the titanium complexes are sensitive to almost all impurities [144].

**Figure 56.** The reactivity/tolerance of metathesis catalysts.

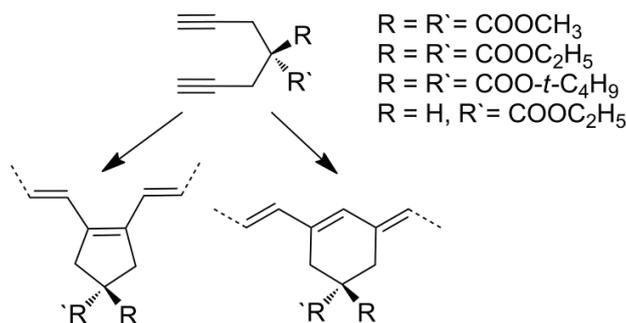
Activity ↑ ↓ Tolerance	Alcohols, water	Alcohols, water	Alcohols, water	<b>Olefins</b>
	Acids	Acids	Acids	Alcohols, water
	Aldehydes	Aldehydes	Aldehydes	Acids
	Ketones	Ketones	<b>Olefins</b>	Aldehydes
	Ester, amides	<b>Olefins</b>	Ketones	Ketones
	<b>Olefins</b>	Ester, amides	Ester, amides	Ester, amides
	Titanium	Tungsten	Molybdenum	Ruthenium

One disadvantage of homogeneous metathesis catalysts is that they cannot be reused; one solution is to immobilize them on either inorganic or organic carrier materials [128] as shown in Figure 57.

**Figure 57.** Metathesis catalysts immobilized on A silica (Schrock Type) and B polystyrene (Grubbs type).



The opposite of ROMP, *i.e.*, a ring “closure” metathesis polymerization occurs during the metathesis of  $\alpha, \omega$ -dialkynes. Thus, controlled backbiting reactions occur leading to interesting new polymers with perfect 5- or 6-membered ring structures which exhibit good electrical conductivity, as shown in Figure 58 [145].

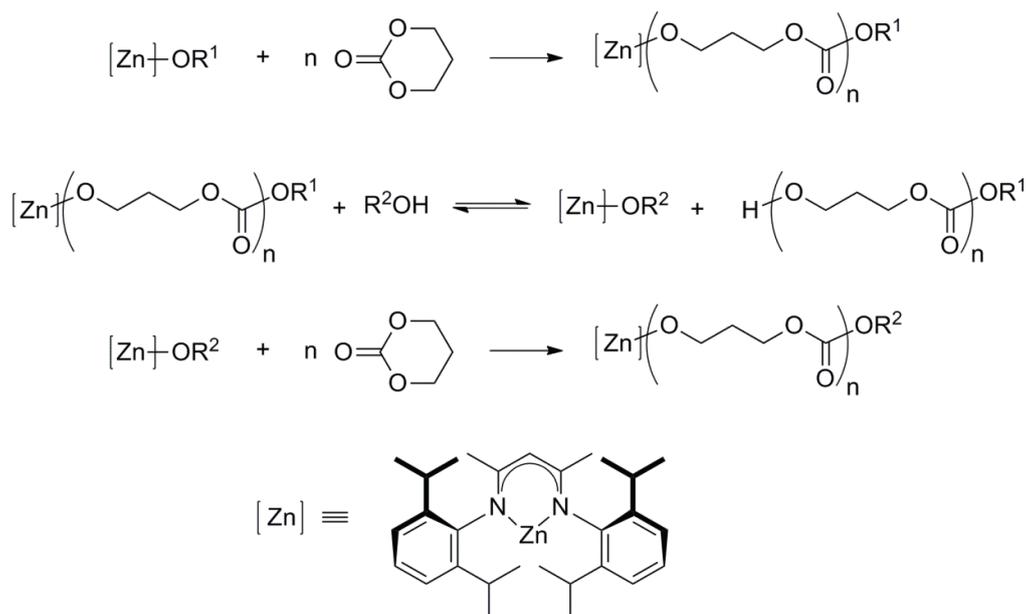
**Figure 58.** The ring-closure metathesis polymerization of  $\alpha, \omega$ -dialkynes.

The good control of polymer structures possible via ROMP has led to many studies concerning the synthesis of polymers with well-defined end groups which have been reviewed in detail recently [146].

## 6. Other Ring-Opening Polymerizations

In this section the living (also sometimes called “Immortal”) polymerization and ring opening that occur via oxidation/reduction processes are briefly described [147,148].

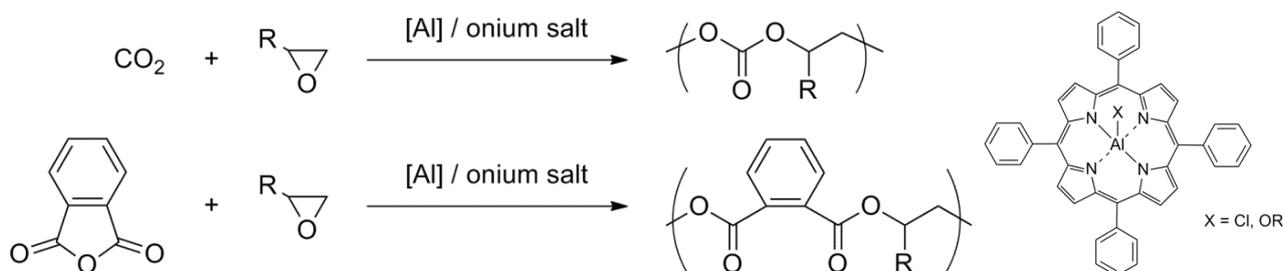
The pioneering work of Inoue [147,149] involving the ROP of oxiranes initiated by aluminium porphyrin/alcohol describes an “immortal” polymerization; a living polymerization during which the growing chains do not “die”. Rapid and reversible chain transfer takes place between the growing chains and alcohol molecules. Thus, only a very small initiator concentration is required. The number of polymer chains is equal to the sum of the number of initiator and transfer molecules. The overall reaction is shown in Figure 59 using the ROP of trimethylene carbonate, initiated by a [Zn]-mediated initiator in the presence of an alcohol ( $\text{R}^2\text{OH}$ ) as an example [150].

**Figure 59.** [Zn] mediated living ring-opening polymerization of trimethylene carbonate.

The initiators based on porphyrin complexes or complexes with related structures based on Al, Zn, Y, Lu, In have been used for the polymerization of e.g., oxiranes, thiiranes, lactones, lactides, cyclic

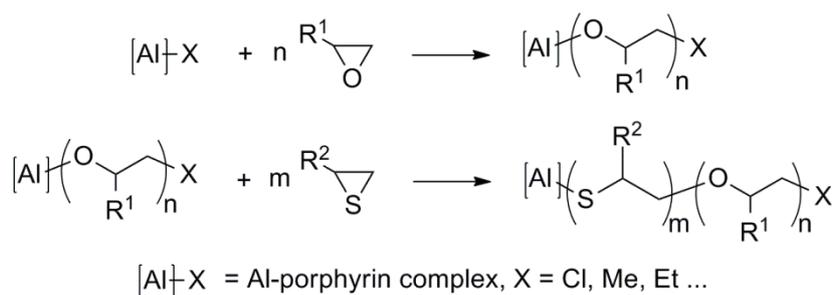
carbonates and others [147,149–156]. Early examples of alternating copolymerization are shown in Figure 60 [147].

**Figure 60.** Alternating copolymers via a living copolymerization of oxirane with CO<sub>2</sub> or phthalic anhydride.



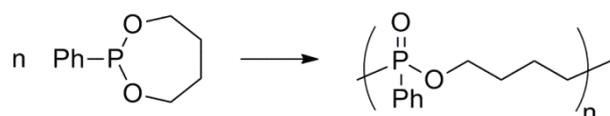
Furthermore, a great variety of block copolymers have been synthesized using this method [147]. One typical example is presented in Figure 61.

**Figure 61.** Synthesis of a block copolymer via a living ring-opening polymerization.



Cyclic phosphonites undergo an electrophilic ring-opening polymerization via an Arbuzov-type reaction to yield a polyphosphonate (Figure 62) [148].

**Figure 62.** Electrophilic ring-opening polymerization of a cyclic phosphonite.

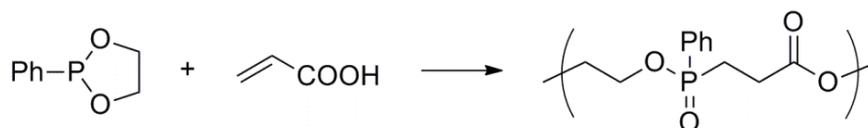


During the polymerization the phosphorus atom of the monomer is oxidized (from +3 to +5) and the carbon of the CH<sub>2</sub>O group is reduced (from −1 to −3) to yield the PCH<sub>2</sub> moiety in the polymer; *i.e.*, an intramolecular oxidation-reduction reaction takes place.

An interesting aspect of this type of ROP is the alternating copolymerization of a cyclic phosphorus (III) compound as reductant with a simple vinyl monomer as oxidant, as depicted in Figure 63 [157].

This copolymerization takes place without any initiator or catalyst and additional details are available in the literature [158].

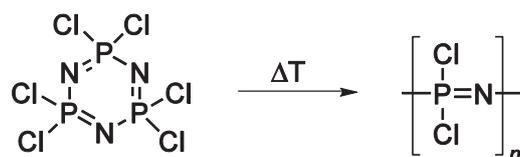
**Figure 63.** Intermolecular reduction-oxidation during the alternating copolymerization of a cyclic phosphorus (III) monomer with acrylic acid.



## 7. Ring-Opening Polymerization of Phosphazenes

An interesting and promising class of polymers, which is still waiting for a real industrial breakthrough, can be obtained by the ring-opening polymerization of phosphazenes. The literature contains reports on more than 300 polymers on this basis [159,160]. The simple polymerization of  $(\text{PNCl}_2)_3$  (Figure 64) is carried out in sealed vessels under an inert atmosphere by heating to *ca.* 250 °C for several hours. A conversion of much greater than 50% is avoided to minimize the formation of insoluble material. The polymerized material is then converted, by reaction with a stoichiometric amount of an alcoholate, an amine or an organometallic reagent, to yield a polymer more stable to hydrolytic decomposition [159,161].

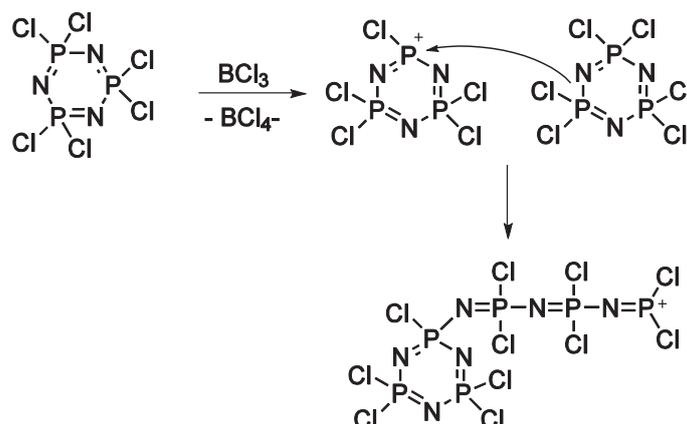
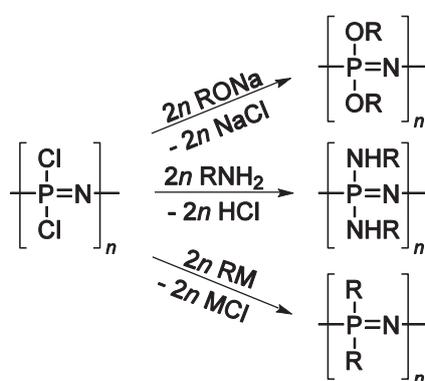
**Figure 64.** The ROP of hexachloro cyclo-triphosphazene at higher temperatures.



This reaction was first reported at the end of the 19th century by Liebig [162] and Stokes [163] and represents the first example of a synthetic rubber. At higher temperatures the cyclic phosphazene eliminates  $\text{Cl}^-$  to yield a cyclic cation which then reacts with the free electron pair on a nitrogen of another monomer ring (see Figure 65); the P–N single bond in the second ring is broken to yield a linear phosphazene with a  $-\text{P}(\text{Cl})_2^+$  terminus. The reaction can be catalyzed by Lewis acids such as  $\text{BCl}_3$ . As the reaction proceeds charge generation along the chain becomes more prevalent and eventually leads to crosslinked insoluble material at conversions much greater than 50%. The poor yields of soluble polymer have proved a major limitation for the commercialization of polyphosphazenes. Thus, alternative, non-ROP, routes have also been investigated [164–167], albeit with, as yet, limited commercial success.

Almost one hundred years after polyphosphazenes were first documented, Allcock's group showed how to convert the base polymer into useful materials (see, e.g., Reference [168]).

Since the base material  $(\text{PNCl}_2)_n$  is unstable in moist air, all the Cl-atoms must be substituted e.g., by alkoxy or amino groups to convert the so-called “inorganic rubber” into a material which is stable under practical conditions and thus makes the material suitable for a number of applications (Figure 66) [169]. Polyphosphazenes with perfluorinated alkoxy side chains have been commercialized under the trade name Eypel F<sup>®</sup> (Ethyl Corp., USA).

**Figure 65.** The cationic polymerization of hexachloro cyclo-triphosphazene.**Figure 66.** Some substitution reactions to yield useful polyphosphazenes.

By changing the side group substitution the flexibility, refractive index, the transparency (especially for UV light) and the flammability can be adjusted and the hydrophobic or hydrophilic nature of the polymer determined [168,170,171]. Phosphazene elastomers having  $-\text{OCH}_2(\text{CF}_2)_n\text{CF}_3$  side groups exhibit excellent oil resistance and  $T_g$  as low as  $-60\text{ }^\circ\text{C}$  without the addition of plasticizers. They are thus very suitable for special automotive and aerospace applications [172–175] and have also been suggested for biostable biomedical devices [176]

Polyphosphazenes with oligo-ethylene oxy side chains have also been considered for use in lithium-ion polymer batteries [177–179] and those with sulfonated aryloxy side groups as membranes for fuel cells [180]. Polyphosphazenes with ethylene oxy side groups can be crosslinked with  $\gamma$ -rays to give hydrogels, which have been investigated as controlled drug release agents [181–185]. Polyphosphazenes with amino acid side chains are biodegradable and can be employed to aid the regeneration of bone tissue *in vivo* [186–189]. Polyphosphazenes with aryloxy side groups have also been studied as fire retardants and thermoplastics.

Numerous researchers have tried to substitute the monomer in order to avoid the polymer analogue reactions (Figure 66) but substitution of  $-\text{Cl}$  in the  $(\text{PNCl}_2)_3$  monomer by  $-\text{CH}_3$ ,  $-\text{OCH}_2\text{CF}_3$ ,  $-\text{OPh}$  or  $-\text{Ph}$  leads to molecules which simply decompose or undergo ring expansion on heating. If one of the  $-\text{PCl}_2$ -groups in the ring is exchanged for  $\text{XCl}$  (see Figure 67) the ring strain can be increased and a ring-opening polymerization occurs at lower temperature but necessity of subsequent substitution of the  $-\text{Cl}$  groups and the crosslinking during polymerization remain as disadvantages [190–192].



We have chosen to treat polyphosphazenes in a separate section because, on the one hand, the mechanism of ring-opening is not understood in detail. On the other hand, the monomer, hexachloro cyclo-triphosphazene, can be polymerized and modified employing a plethora of reagents to yield a very wide variety of different materials for very different applications from plastics to elastomers and from damping to biomedical elements. The challenge remains to develop an economically viable synthesis.

Of course, the polyphosphazene backbone does not rely on fossil fuels but nor do many of the monomers discussed in this review, especially some oxacyclic monomers can be easily obtained from e.g., (potato) starch or sugar sources, so that with the current emphasis on renewable raw materials it can be expected that the interest in ring-opening polymerization will not wane in the near future.

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