Cyclic Monomers: Epoxides, Lactide, Lactones, Lactams, Cyclic Silicon-Containing Monomers, Cyclic Carbonates, and Others

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Abstract Cyclic monomers constitute a broad family of monomers which are able to be polymerized by anionic ring-opening polymerization or related nucleophilic ring-opening mechanism. This chapter presents successively the polymerization of cyclic ethers, cyclic esters, cyclic amides, cyclosiloxanes and other cyclic silicon-based compounds, cyclic carbonates, and other cyclic monomers, i.e., cycloalkanes, cyclic sulfides, cyclic amines, cyclic ureas, depsipeptides, and cyclic phosphorus monomers. The main synthetic strategies are reviewed in terms of monomer reactivity, side reactions, and control of macromolecular architectures. Ring-opening polymerization of cyclic monomers utilizing alkali metal derivatives or other initiating systems in conjunction or not with activating systems is described. Emphasis is also put on the use of organic initiators or catalysts to trigger the metal-free ring-opening polymerization.

Keywords Anionic ring-opening polymerization • Epoxides • Lactones • Lactams • Cyclosiloxanes

1 Introduction

For many years, efforts in polymer science were directed toward the control of polymerization methods, a precise control of the structure, topology, and functionality of polymeric chains enabling the design of macromolecular scaffolds that may find applications in high added value domains. For polymers bearing heteroatoms in their backbone, two pathways are generally possible: step-growth polymerization and ring-opening polymerization (ROP). The main advantage of step-growth polymerization is the easy accessibility of a wide range of monomers of various structures. Nevertheless, it suffers from limitations. Indeed, high conversions are needed to get high molar mass polymers, often not controlled, and high polymerization temperatures are generally required. These drawbacks are overcome by the

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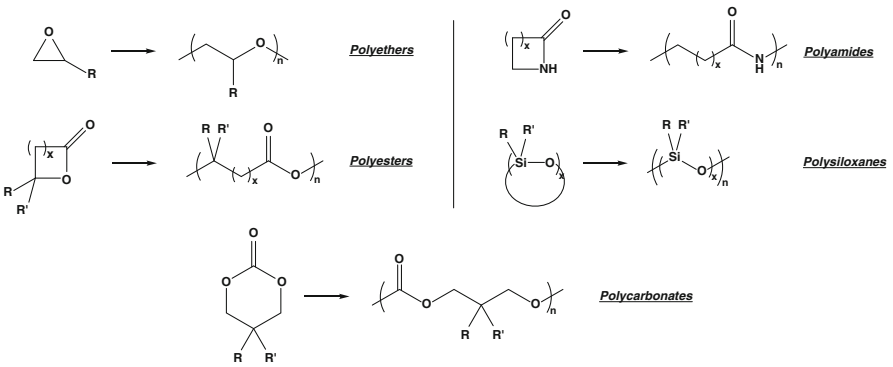


Scheme 1 Ring-opening polymerization of main cyclic monomers

implementation of ROP, which has become a powerful tool for the synthesis of various polymers, mainly polyethers, polyesters, polyamides, polysiloxanes, and polycarbonates (Scheme 1).

The ring strain, coming from distortion of the ring angles and stretching bonds, is generally responsible for conversion of monomer into polymer units. The ROP can be performed according to several mechanisms, namely, anionic, cationic, and coordination-insertion. In this chapter, we will focus on polymerization for which the propagating species is an anion. Few exceptions, where the propagating species are not fully charged, will also be presented. This chapter will be divided into several sub-chapters, each one focusing on one type of cyclic monomer. It will be presented successively the anionic ring-opening polymerization of cyclic ethers, cyclic esters, cyclic amides, cyclic silicon-containing monomers, cyclic carbonates, and other cyclic monomers, i.e., cycloalkanes, cyclic sulfides, cyclic amines, cyclic ureas, depsipeptides and cyclic phosphorus monomers. When well established, the elementary steps involved in the polymerization are given. Recent developments concerning the synthesis of controlled macromolecular architectures are also presented.

2 Cyclic Ethers

2.1 Introduction

The anionic ring-opening polymerization (AROP) of cyclic ethers enables the synthesis of polyethers like poly(ethylene oxide) (PEO) and poly(propylene oxide) (PPO), often referred to as poly(ethylene glycol) and poly(propylene glycol), respectively. The worldwide production of these polymers attains several million tons per year for commodity (precursors for polyurethanes, surfactants, and lubricants) or high-performance (biomedical or cosmetic domains) applications. Nucleophiles can initiate the polymerization leading to alkoxides able to attack a

new monomer enabling the propagation step. Cyclic ethers reactivity and polymerization kinetics are predominantly influenced by their polymerization enthalpy and ring strain but also by electronic and steric factors associated with the nature of the ring substituent as well as reaction conditions like temperature and solvent. An anionic-related mechanism can be considered after preliminary complexation of the monomer by specific additives (an *electrophile*), which strongly facilitate nucleophilic attack and ring-opening. Based on this chemistry, as well as organic synthetic tools, many substituted epoxide monomers are able to be polymerized, opening pathways for well-defined polyether structures and functionalities and allowing the preparation of materials with various properties.

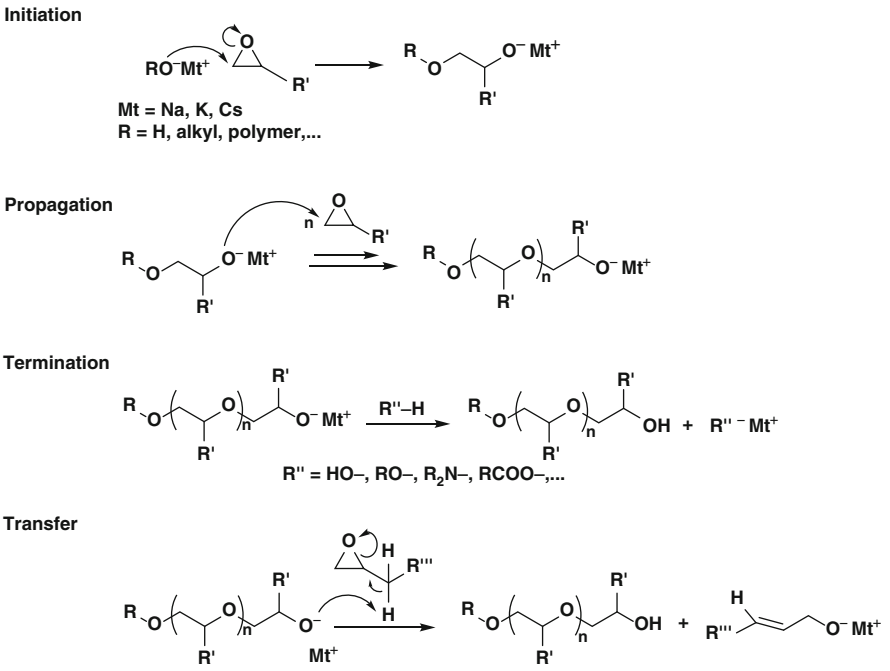
2.2 Conventional Anionic Polymerization of Epoxides

Propagation may proceed without side reaction in anionic polymerization of ethylene oxide [1]. Alkali metal derivatives like hydrides, alkyls, aryls, and amides and mainly alkoxides of sodium, potassium, and cesium represent the most common initiators used for the AROP of epoxides [2, 3]. Lithium alkoxides do not lead to the polymerization of such monomers due to strong aggregation between lithium species after insertion of the first epoxide unit. Polymerizations initiated by alkali metal alkoxides are generally carried out in aprotic and apolar media or in coordinative solvents like dimethylsulfoxide (DMSO) or dimethylformamide (DMF) in order to dissociate active species. The driving force for the ring-opening reaction is the relief of the strain energy of the epoxide ring. High temperatures are usually needed for the AROP of long-chain alkylene oxides.

The different steps of conventional AROP of epoxides are shown in Scheme 2. The initiation step consists of a nucleophilic substitution – S_N2 type – of the alkoxide species leading to the formation of new alkoxide species able to further attack monomer molecules resulting in polyether chains with an atactic structure. The termination step is achieved by addition of an acidic compound with labile hydrogen. Alcohols and water are the most commonly used termination agents in order to obtain hydroxyl end groups. The transfer to monomer is observed with most of the initiating systems when substituted epoxides are polymerized.

2.2.1 Ethylene Oxide

Alkali metal salts of carbanions [4–6] and nitranions [7] are efficient initiators for the polymerization of ethylene oxide (EO). Alkali metal alkoxides were also investigated in detail due to the fact that the structure of these derivatives is similar to the one of propagating species. In aprotic solvents with low to medium polarity, i.e., ethers, alkali metal alkoxides exhibit a strong tendency to aggregate leading to complex reaction kinetics. This is particularly significant for small-sized metals such as lithium or sodium. If the reaction follows a monomer order of 1, the order in

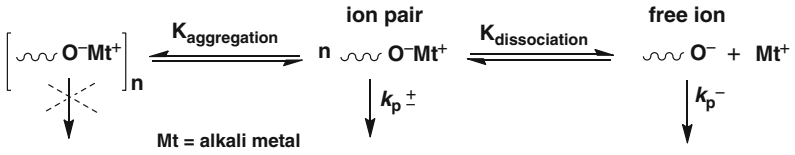


Scheme 2 Anionic ring-opening polymerization (AROP) of epoxides initiated by alkali metal alkoxides

alkoxide propagating species varies according to counterion and solvent. This can be related to the presence of aggregates, ion pairs, and free ions of different intrinsic reactivity (Scheme 3). EO polymerization with alkoxide aggregates is extremely slow and does not even proceed in most cases.

The combination of alkoxide with its parent hydroxy compound was used to limit aggregation and preserve solubility [8–10], allowing a better control of the initiation and propagation, to the detriment of reaction kinetics [11, 12]. This would be referred today as a "degenerative transfer," already reported by Flory in the 1940s.

The use of potassium *tert*-butoxide as initiator was reported to yield living PEO in DMSO with molar masses controlled by the ratio [monomer]/[initiator] [13–15]. With K^+ and Cs^+ salts, EO polymerization in DMSO proceeds almost exclusively by free ions in agreement with a higher dissociation constant in this solvent in line with a high DMSO permittivity ($\varepsilon = 48$ at 20 °C). With Na^+ as counterion, both ion pairs in equilibrium with a small proportion of free ions contribute to the propagation. In tetrahydrofuran (THF) ($\varepsilon = 7.6$ at 25 °C) and in the presence of sodium, potassium, and cesium naphthalene as initiators, a living polymerization takes place, the rate of propagation increasing with the size of the counterion [16, 17]. However, kinetics are complicated due to the strong association of alkoxide end groups.



Scheme 3 Aggregates, ion pairs, and free ions in EO polymerization and their capacity to contribute to propagation

2.2.2 Monosubstituted Epoxides

Although alkali metal derivatives are efficient initiators for AROP of ethylene oxide, they are much less efficient for monosubstituted epoxides, e.g., propylene oxide (PO), glycidyl ethers, etc. Indeed, as alkoxide species are relatively strong bases, the abstraction of monomer substituent proton can take place. This side reaction leads to the formation of polyether chains, initiated by an allyloxy group, limiting the molar masses of polyethers (Scheme 2) [14, 18].

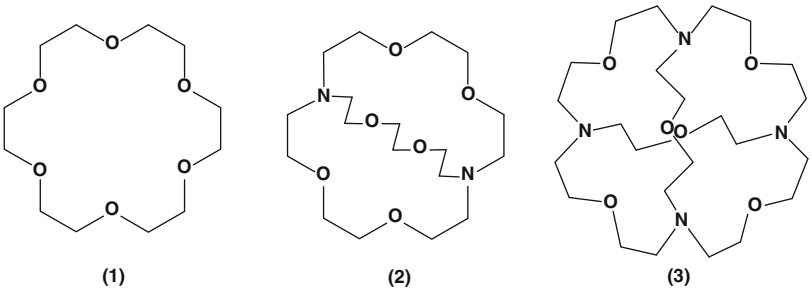
Similarly to ethylene oxide, the size of the counterion and the temperature were shown to influence the polymerization rate of monosubstituted epoxides. Increasing the size of the counterion leads to more dissociated active species and thus to higher polymerization rate, faster polymerizations being observed with cesium counterion. Higher temperatures increase the polymerization rate [18, 19] with the time frame being generally in the magnitude of several hours or days to reach high yields. In the presence of potassium as counterion (*t*-BuOK as initiator), the reactivity of racemic propylene oxide in hexamethylphosphoramide (HMPA) at 40 °C is about four times lower than that of EO on the basis of overall polymerization rates [20]. The reactivity of other monosubstituted epoxides depends on both electronic and steric factors induced by the substituent attached to the epoxide ring [21]. For instance, the reactivity of 2,2-dimethyloxirane (DMO) is ten times lower than that of PO, whereas glycidyl ethers such as *tert*-butyl glycidyl ether (*t*-BuGE) are more readily polymerized than PO [20].

Conventional anionic ring-opening polymerization suffers in general from slow kinetics and, more particularly for substituted epoxides, of transfer reactions. Other systems were therefore developed.

2.3 Systems for Activated Epoxide Polymerization

2.3.1 Alkali Metal Derivatives Associated to Crown Ether

Addition of complexing agents to alkali metal cations, such as crown ethers or cryptands (Scheme 4), was shown to drastically increase ethylene oxide propagation rate in ethereal solvents [8, 22, 23], reducing the aggregation of alkoxide polymer ends and increasing the proportion of free ions. For example, the dissociation constant of $PEO^-\ K^+$ at 20 °C in THF is 1,700 times higher when K^+ is



Scheme 4 Crown ether 18C6 (*1*), cryptand 222 (*2*) and sphere (*3*) used to complex alkali metal cations in ethylene oxide polymerization

complexed by cryptand 222. In this system, the reactivity of free ions is about 60 times higher than that of cryptated ion pairs.

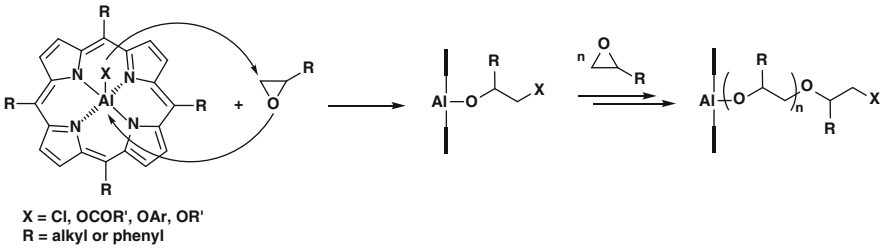
For monosubstituted epoxides, 18-crown-6 was also shown to increase the reactivity, the propagation rate constant being up to 14 times at 25 °C [10, 24–26]. In line with the acidic character of hydrogen on the α-carbon of the monomer, the nature of epoxide substituent plays an important role in the chain transfer process. For instance, the anionic polymerization of long-chain alkylene oxides initiated by potassium and cesium alkoxides is much less subjected to chain transfer processes than alkoxides deriving from PO. However, relatively high temperatures were needed to reach reasonable polymerization times, which caused residual side reactions limiting molar masses. The breakthrough of using the additive 18C6 was associated with a decrease of polymerization temperatures, minimizing transfer reaction to monomer. This is reflected by the production of poly(2-butyloxirane) of higher molar masses at 20 °C (Table 1) [19]. The polymerization temperature of 2-butyloxirane and of higher 2-alkyloxiranes like 2-hexyloxirane and 2-octyloxirane could even be reduced below 0 °C, which almost eliminate completely all side reactions. However, very long reaction times were required, i.e., 4–8 days, and conversion did not go to completion [19]. Alkali metal hydrides were also associated to 18C6 for the AROP of glycidyl butyl ether [21, 27]. Polyethers with molar masses lower than 5,000 g/mol and low dispersity were obtained. For this range of molar masses, polymerization time was considerably reduced, from several days to a few hours, as well as transfer reactions.

2.3.2 Aluminum Systems: From Bulky to Simpler Compounds

In the 1980s, Inoue and coll. used metalloporphyrin as catalyst, in particular aluminum-based porphyrin, for the polymerization of methacrylates [28, 29], lactones [30], and epoxides [31] and, in some extent, oxetane [32] which is usually polymerized by a cationic route. The equimolar combination between diethylaluminum chloride and α, β, γ, δ-tetraphenylporphyrin (TPPAlCl) led to a high catalytic activity in the polymerization of propylene oxide. The covalent nature of the Al-Cl bond suggests a

Table 1 Polymerization conditions and characteristics of poly(2-butyloxirane) synthesized in presence of K or Cs *tert*-butoxide in toluene with or without crown ether 18C6 (molar ratio 18C6/metal = 3)

Counterion	T (°C)	Time (h)	Conv. (%)	$\overline{M_n}$ th. (g/mol)	$\overline{M_n}$ exp. (g/mol)	D
K	80	40	96	14,700	11,200	1.15
Cs	80	18	97	14,800	11,700	1.11
K/18C6	20	19	92	47,000	43,600	1.11
Cs/18C6	20	68	81	39,600	28,000	1.13



Scheme 5 Polymerization mechanism of epoxides initiated by an aluminum porphyrin

polymerization via a coordination mechanism. Synthesized polyethers, by the so-called "immortal" polymerization, reached molar masses up to 70,000 g/mol with a narrow distribution [33]. A monomer molecule is first inserted between the Al-Cl bond of the initiator (Scheme 5). Aluminum porphyrin, due to its nucleophilic character, was used as initiator enabling coordination with epoxide. Under such conditions, transfer reactions were considerably decreased, allowing the synthesis of a series of block copolymers, including poly(PO-*b*-EO), poly(1,2-butene oxide-*b*-PO), poly(PO-*b*-epichlorohydrin), poly(lactones-*b*-PO), poly(lactones-*b*-EO), etc. [34, 35]. Although EO polymerization could be achieved rapidly (half-time reaction is about 30 min at room temperature for [EO]/[TPPAlCl] = 400 in dichloromethane), other epoxides exhibited a lower reactivity. In similar conditions, several hours were required for the polymerization of PO and 1,2-epoxybutane [31] in order to reach complete conversion, whereas for styrene oxide or 1,2-epoxy-2-methylpropane conversions did not exceed 15 % after 8 days of reaction [33].

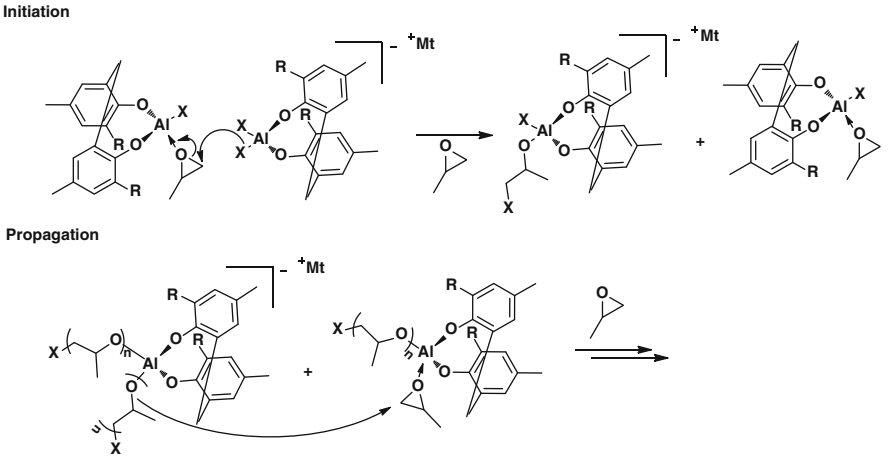
In order to increase polymerization rate of propylene oxide, aluminum porphyrin was used in association with a bulky Lewis acid [36–38]. For instance, methylaluminum bis(2,4,6-tri-*tert*-butylphenolate) (MAlBP) was used to coordinate the epoxide and to activate the monomer substrate toward a nucleophilic attack. As compared to the previous system, the catalytic species and the initiator are independent, i.e., employed as a bi-component initiating/activating system. There is no interaction between these two aluminum derivatives due to their bulkiness. Polymerization rates of propylene oxide and 1,2-butene oxide were strongly enhanced due to the presence of the bulky Lewis acid [36]. Only 0.25 %

of MAlBP, with respect to propylene oxide concentration, was added to increase the polymerization rate by a factor of 460. With a [MAlBP]/[TPPAlCl] ratio equal to 0.5, 3 min was enough for propylene oxide to be polymerized with 86 % conversion, leading to a PPO with a molar mass up to 12,000 g/mol. Without MAlBP, in 7 h, the conversion is around 20 % and molar mass reached 3,300 g/mol. The Lewis acid alone did not initiate the polymerization under similar conditions. The "living" nature of the polymerization could be demonstrated by the successful formation of block copolymers based on propylene oxide and 1,2-butene oxide, though complete conversions could not be obtained.

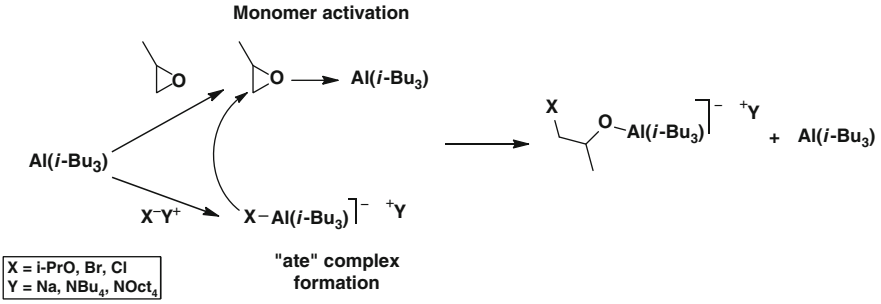
Using relatively similar systems based on quaternary ammonium and quaternary phosphonium halides associated to sterically hindered methyl(diphenoxy)aluminum, poorly reactive four-membered ring oxetane, e.g., 1,3-propylene oxide, was polymerized according to a coordinated-anionic mechanism, as a result of strong monomer activation by complexation with the aluminum derivative [39].

Braune and Okuda used porphyrin-free aluminate complexes for the polymerization of propylene oxide activated by their neutral Lewis acid precursors [40]. The nucleophilic species were easily obtained by reaction of a bulky Lewis acid based on diphenoxyaluminum compounds, with a cesium alkoxide or an ammonium salt. The ring-opening polymerization proceeds under the synergic interaction of a phenolate-aluminum-oxirane complex forming an activated monomer with the corresponding "ate" complex which initiates the reaction (Scheme 6). Ring-opening takes place by transfer of an alkoxy group from the "ate" complex, regenerating an aluminate able to activate a new monomer. The synthesis of poly (propylene oxide)s with molar masses up to 4,000 g/mol was reported following an anionic (or coordinative) mechanism because of exclusive head-to-tail linkages.

Tsvetanov reported in 1985 the polymerization of ethylene oxide initiated by sodium tetrabutylaluminate [41]. PEO were prepared in toluene in the range 15–



Scheme 6 Initiation and propagation steps of propylene oxide polymerization initiated by bulky aluminum complexes



Scheme 7 Nucleophilic attack of sodium alkoxide or ammonium salts/triisobutylaluminum on activated propylene oxide

70 °C with a high kinetic order with respect to the initiator. The polymer chain growth was explained by the presence of aggregates of $NaAlBu_4$, predominantly trimers of the "ate" complex. Interaction between the oxygen atom of EO and the alkali metal, as well as EO and aluminum to a lesser degree, was shown, in line with some activation of the epoxide.

Using epoxide monomers and combinations of a Lewis acid – typically a trialkylaluminum – and alkali metal alkoxides or onium salts [42–47], Carlotti and Deffieux developed efficient synthesis of various polyethers. An excess of Lewis acid with respect to the initiator was required. The formation of an "ate" complex, which was able to ring-open the activated epoxide by the excess of activator, was observed (Scheme 7).

Propylene oxide polymerization, based on a monomer-activated anionic polymerization, occurs at room or lower temperature. Control over the polymerization strongly depends on the nature of the counterion. Sodium and potassium enable the polymerization, whereas lithium does not. In few hours, controlled poly(propylene oxide) chains, up to 20,000 g/mol, were obtained with nevertheless the presence of some residual transfer reactions, i.e., transfer to monomer leading to allyloxy groups in the α-position and transfer to triisobutylaluminum (i-Bu_3Al), which generates initiation by a hydride coming from an isobutyl group. Ammonium salts were more successful as much higher molar masses could be achieved in a controlled manner, especially at −30 °C, yielding polyethers of low dispersity (e.g., $Đ = 1.34$ for $\overline{M_n} = 170{,}000$ g/mol) [45]. The strong decrease of transfer reactions was explained by the decrease of basicity of the active bi-component complex. The exclusive preparation of regioregular polymers (head-to-tail) was indicative of an anionic/coordination type mechanism. Polymerization proceeds at [Al]/[Initiator] ratio higher than unity, indicating that only complexed PO molecules are susceptible to ring-open, thanks to significant electron-withdrawing effect that makes the ring carbon atoms much more electrophilic. Increasing trialkylaluminum concentration, at constant monomer and initiator concentrations, was shown to yield a drastic increase in polymerization rate, whereas the number of PPO chains remained unchanged.

These initiating systems were also applied to the polymerization of a broad variety of epoxides including several alkylene oxides and glycidyl ethers, epichlorohydrin (ECH), etc. Compared to conventional alkali metal initiators, the tetraoctylammonium bromide/i-Bu_3Al-initiating system strongly enhanced the rate of ethylene oxide polymerization while retaining the living character of the reaction [48]. At a ratio [i-Bu_3Al]/[$NOct_4Br$] = 1.5, the synthesis of PEO of 20,000 g/mol was completed within 2 h at room temperature in dichloromethane. By changing the ammonium salt by an alkyllithium, a PEO of 10,000 g/mol was synthesized at low temperature and in nonpolar media, e.g., toluene [49]. The presence of trialkylaluminum used in excess with respect to the lithium initiator permits disaggregation of lithium alkoxide species by forming lithium/aluminate complexes which are able to ring-open the AlR_3-complexed EO molecules. However, ligand exchanges in the lithium/aluminate complex lead to slow deactivation of the propagating species during the polymerization which limits the access to high molar mass PEO.

Monomer-activated anionic polymerization of epichlorohydrin utilizing similar conditions was also described. In contrast to conventional anionic polymerization, aluminate species that ensures propagation in AlR_3/onium systems selectively react with activated ECH ring, keeping the chloromethyl function [50]. Syntheses of poly (glycidyl methyl ether) (PGME) [51], linear poly(2-ethoxyethyl glycidyl ether) (PEEGE), and poly(*tert*-butyl glycidyl ether) (P*t*BuGE) [52] with narrow chain distribution and controlled molar masses were also reported. The amount of Lewis acid required to trigger the reaction and achieve quantitative monomer conversions was shown to increase with the number of oxygen atoms in the monomer.

This anionic living/controlled polymerization, employing onium salt/triisobutylaluminum systems and involving a monomer-activated mechanism, was applied to the synthesis of a series of random and block copolymers. For instance, EO/PO random copolymers with a gradient structure, molar masses up to 70,000 g/mol, and narrow dispersity were prepared [48]. PPO-*co*-PECH [50] and amphiphilic poly (alkylene oxide-*co*-glycidol) were also synthesized via the synthesis of PPOx-*co*-PEEGE and PBO-*co*-P*t*BuGE copolymers [52], followed by the deprotection of hydroxyl groups under acidic conditions. Despite the determining role of the monomer complexation in this polymerization process, the copolymerization ratios remain close to those reported for conventional anionic copolymerization. Different diblock and triblock copolymers of various compositions and lengths were also prepared by sequential monomer addition. Synthesis of PEO-*b*-PPO-*b*-PEO triblock copolymers with $NOct_4Br$/i-Bu_3Al initiating system was first achieved [48]. PPO-*b*-PECH block copolymers with molar masses ranging from 6,000 to 30,000 g/mol and with various PPO and PECH block lengths were also prepared by sequential addition of the two monomers [50]. The re-initiation efficiency was shown to be quantitative, no matter the order of addition of the two monomers. Finally, block copolymerization of EO initiated with lithium derivatives was also lately described [49]. Although it is known that EO polymerization could not proceed properly when lithium alkoxide species are involved [53, 54], it was shown that living polystyryllithium and polyisoprenyllithium chains can play the

role of a macroinitiator for EO polymerization in presence of trialkylaluminum. Block copolymers polystyrene(or polyisoprene)-*b*-poly(ethylene oxide)s were obtained in hydrocarbon within a few hours with a PEO block molar mass up to 10,000 g/mol and a re-initiation efficiency of about 80 %.

2.3.3 Calcium-Based Systems

The association of two metals was also proposed in 1980 to polymerize ethylene oxide [55]. A calcium amide/alkali metal alkoxide initiating system was used at high temperature in order to produce poly(ethylene oxide)s with high molar masses. EO polymerization involves monomer coordination at the catalyst active site via σ bond formation between the monomer heteroatom and the catalyst metal atom. It is followed by a nucleophilic attack of the alkoxide active group [56]. Tsvetanov and coworkers investigated this combination for the synthesis of poly(propylene oxide) and miscellaneous copolyethers [57–61]. The authors explained that calcium derivatives are much weaker than other metals, like aluminum or zinc, in the formation of oxiranes complexes. As a result, Ca-EO complexes are more readily formed in comparison with substituted epoxides where low-rate polymerizations are observed. In addition, the polymerization takes place under heterogeneous condition as the calcium-based initiator is not soluble in the solvents used. As an example, the synthesis of an amphiphilic poly(ethylene oxide)-*b*-poly(alkylglycidyl ether) copolymer with a molar mass up to 10^6 g/mol and a high dispersity (5–8) was achieved in relatively short times (several hours, but not days) at 97 °C [59].

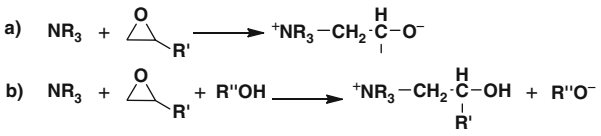
In summary, various systems such as metals associated to crown ethers or metallic activators as well as combinations or organic initiators associated to organometallic compounds were used to polymerize epoxides affording control and fast kinetics. Nowadays, complementary challenges concerns metal-free systems which are able to fulfill all criteria so far discussed.

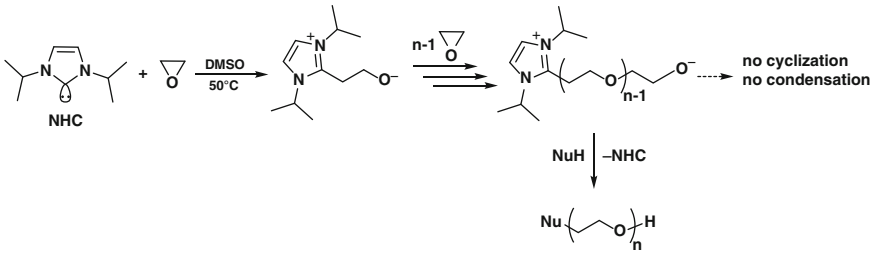
2.4 Toward Organic Initiating Systems

2.4.1 Tertiary Amines

Amines were essentially used for the anionic polymerization of di- and polyepoxides, mainly diglycidyl ether of bisphenol A and its derivatives as well as glycidyl phenyl ether [62]. Reaction with amines leads to slow polymerization rates, to long induction periods, and to the formation of short chains due to transfer reactions. Benzyldimethylamine, pyridine, triethylamine, 4-dimethylaminopyridine (DMAP), and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) are the most common amines used as initiators. Ammonium salts and imidazoles are also employed to open epoxides by anionic polymerization. The main drawback of all these compounds is the limitation in terms of molar masses. Although the initiation mechanism is not well established,

Scheme 8 Possible initiation steps for the epoxide polymerization in the presence of tertiary amines



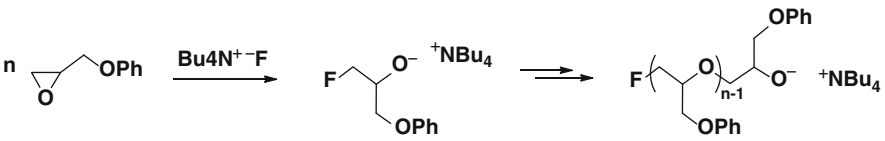


Scheme 9 Proposed mechanism for ethylene oxide polymerization initiated by N-heterocyclic carbenes

two pathways are generally considered (Scheme 8) [63, 64]. The addition of alcohol decreases induction periods and increases polymerization rates but limits molar masses [62]. The alkoxide formed by the second way (Scheme 8b) is more reactive than species resulting from usual initiation step (Scheme 8a). Williams and coll. succeeded to decrease the time of initiating step by using DMAP thanks to its conjugated structure with a negative charge on the nitrogen atom of the cycle and a positive charge on the tertiary amine [64]. The molar masses were about 1,000 g/mol at 80 °C.

2.4.2 *N*-Heterocyclic Carbenes

N-Heterocylic carbenes (NHCs) can be used as ligands of transition metallic complexes [65] but also as organic catalysts for various metal-free reactions [66, 67]. Ring-opening polymerization of some epoxides was triggered by NHCs [68–70]. Taton and coll. showed that 1,3-bis-(diisopropyl)imidazole-2-ylidene is able to initiate ethylene oxide polymerization according to a zwitterionic mechanism (Scheme 9) [68]. NHC plays in this case the role of initiator controlling PEO molar masses and forming zwitterionic imidazolium. It can be released by attack of functionalizing terminators added to the medium. Polymerizations were performed at 50 °C in DMSO and required long times, i.e., several days. Molar masses up to 13,000 g/mol were obtained with narrow distribution and good agreement between theoretical and experimental molar masses, in line with a good control of the polymerization. This approach was less effective for the polymerization of propylene oxide due probably to transfer reactions to monomer. Poly(propylene oxide) oligomers with a relative low dispersity were nevertheless prepared [70].



Scheme 10 Polymerization of glycidyl phenyl ether initiated with tetrabutylammonium fluoride

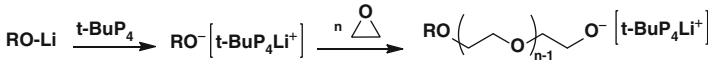
Controlled EO polymerization was found to proceed also with a catalytic amount of NHC, in DMSO at 50 °C, and in presence of a variety of chain regulators, e.g., benzyl alcohol, propargyl alcohol, or trimethylsilyl azide. They possess a nucleophilic part and an electrophilic one (Nu-E). In this case PEO molar masses match the [EO]/[Nu-E] ratio, typically in molar proportions [NHC]/[Nu-E]/[EO] = 0.1/1/100 [69]. Reversible exchanges with Nu-E molecules, involving the formation of active and dormant chains, yield α-Nu-ω-E-poly(ethylene oxide) opening a way for chain-end functionalization.

2.4.3 Ammonium, Phosphonium, and Phosphazene Bases

Ammonium salts were first used by Hemery, Ganachaud and coll. for the AROP of glycidyl phenyl ether (GPE) in miniemulsion [71]. Didodecyldimethylammonium hydroxide was used as an inisurf (initiator-surfactant) exhibiting both surface-active properties and the ability to initiate polymerization. Average molar masses increased with conversion and were dependent on the initiator concentration. A critical polymerization degree of 8 was reached. Using a similar initiator, i.e., tetrabutylammonium fluoride, in solution polymerization, endo achieved the synthesis of poly(glycidyl phenyl ether) oligomers with controlled molar masses up to 4,000 g/mol (Scheme 10) [72] and the synthesis of poly(ethylene oxide-*b*-glycidyl phenyl ether) when the polymerization of glycidyl phenyl ether was performed in the presence of poly(ethylene glycol) monomethyl ether [73].

As already mentioned, the size of the counterion plays a preponderant role in epoxide polymerization, in particular on the kinetics. As a result of their bulky size, some phosphonium and phosphazenium derivatives arising from strong Brönsted phosphazene bases, developed by Schwesinger, revealed potential interesting counterions in order to limit aggregation phenomena [74, 75]. Several of these commercially available bases were used as organic deprotonating agents of –OH (−CH, −SH, −NH, or –COOH) containing initiators, to polymerize epoxides like ethylene oxide [76–84], propylene oxide [85–87], butene oxide [82, 88, 89], styrene oxide [90], as well as ethoxy ethyl glycidyl ether [88, 91, 92] and other protected form of glycidol [93], affording homopolymers, copolymers [94–96], grafted or block copolymers [81, 84, 93, 97–100], and star-shaped structures [89].

Phosphonium and phosphazene bases can be used with an alcohol to form a protonated counterion. The use of t-BuP_4H^+ enables an increase of the polymerization rate of propylene oxide, but transfer reactions still occur. Polymerization



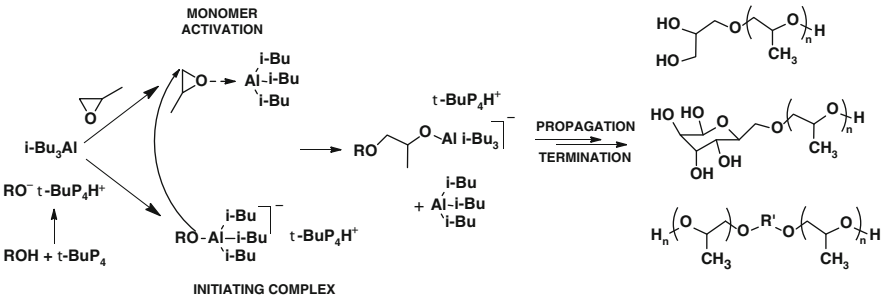
Scheme 11 Ethylene oxide polymerization initiated by lithium alkoxide in the presence of phosphazene base

rates increase when the positive charge is delocalized into the molecule, which is due to better ion separation [80, 81]. Phosphazene bases were also utilized in order to complex lithium alkoxides allowing the (co)polymerization of ethylene oxide and ethoxyethyl glycidyl ether with lithium derivatives (Scheme 11) [76, 79, 88, 91, 92, 101], which is generally not possible because of strong aggregation between lithium alkoxides except when a trialkylaluminum is added [49]. The base behaves as a cryptand for Li^+ ions via polar amino and imino groups located inside the globular molecule, and the outer shell is formed by alkyl substituents. The equilibrium between complexed lithium alkoxide ion pairs and reactive free anions is thus shifted toward the latter species allowing polymerization. Copolymers based on polystyrene and polyethers were prepared without the need of cation exchange. However, the presence of residual transfer reactions and an induction period resulting from the slow disaggregation of the lithium alkoxide ends still complicated the epoxide polymerization [79].

A broad range of polyethers can be synthesized leading to an important class of materials used in many applications. Controlled structures and dimensions as well as easy, inexpensive, and rapid polymerizations remain the major challenges to be addressed. Preparation of functional polyethers used as reactive precursors, by an anionic route, is also of major interest.

2.5 *Functionalization of Polyethers Prepared by Anionic Ring-Opening Polymerization*

Functionalization of polyether chains can occur either to chain ends or along the polymer backbone. In the first case, a functional initiator and/or a termination agent is employed. Further polymerization or other reactions can be conducted from the as-introduced functional groups. The functionalization into the chains is carried out by the use of functional monomers. Hydroxy, amine, epoxide, carbonate, thiol, azide, as well as double and triple bonds are the most commonly used functions in order to obtain a versatile range of functional polymers for many applications. Carlotti and coll. [102], Frey and coll. [103, 104], and Riffle and coll. [105] have reviewed main syntheses, properties, and applications of various functional polyethers. This part will focus on the functions introduced into polyethers prepared by AROP.



Scheme 12 Combination of phosphazene base and *i*-Bu_3Al for the synthesis of polyhydroxy telechelic PPO

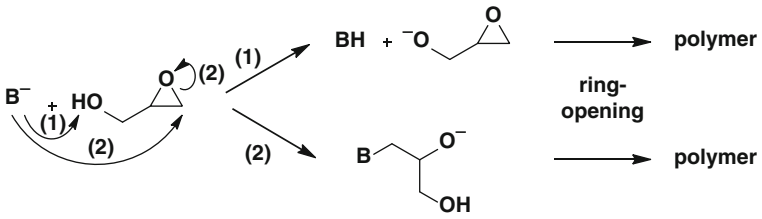
2.5.1 Polyethers with Hydroxyl Functions

Low molar masses polyether polyols are mainly used as precursors of polyurethanes [106]. The majority of hydroxy telechelic polyethers are synthesized by AROP initiated by potassium or cesium hydroxide [18]. Initiation by a hydroxy group followed by termination reaction using water or an alcohol yields α-, ω-dihydroxy polyethers. As shown previously, this approach is efficient for ethylene oxide but much less with monosubstituted epoxides. Branched and star polyethers were synthesized from tri-, tetra-, penta-, and octa-alkoxides of potassium with molar masses close to 5,000 g/mol and a relatively broad dispersity [107–114]. With a similar approach and using hyperbranched polyglycerol initiators, Lutz, Frey and coll. prepared functional multiarm star PEO [9].

Bulkier counterion like phosphazene bases was used as deprotonating agents with dipropylene glycol as initiator showing some decrease of usual transfer reactions [86]. Using the monomer activation methodology [45], di-, tri-, and penta-hydroxy telechelic poly(propylene oxide)s were obtained in very short times (hours) at room temperature in hydrocarbon solvents with molar masses up to 80,000 g/mol with a relatively low dispersity (Scheme 12) [115].

Using an organo-catalysis approach described previously (Scheme 9), Taton and coll. reported that *N*-heterocyclic carbenes (NHC) could lead to α-,ω-dihydroxy poly(ethylene oxide) using water as terminating agent. Hydroxide (OH^-) was shown to behave as a nucleophile that displaces the α-imidazolium moiety from PEO chains, thus releasing the NHC, whereas the terminal alkoxide was transformed into a ω-hydroxy function [69].

Hydroxyl functions can also be introduced after post-modification of other reactive functions introduced via initiation. An amino function can lead to an OH group after reaction with a molecule of ethylene oxide [116]. The use of tetrabutylammonium acetate as initiator proved efficient to introduce acetate-end groups to poly(glycidyl phenyl ether) [117]. Hydroxyl functions were obtained after hydrolysis with an acidic treatment. A narrow molar mass distribution and molar masses up to 4,000 g/mol were thus obtained.



Scheme 13 Initiation mechanisms of glycidol in presence of a base

The introduction of pendant hydroxyl functions is predominantly obtained from anionic polymerization of glycidol and its derivatives. These polymers are very attractive for biological and medical applications [118]. Direct reaction of glycidol with bases such as triethylamine, pyridine, alkali metal hydroxide, and sodium methoxide leads to two distinct initiation steps at room temperature (Scheme 13) [119–123]. The first way corresponds to a basic attack toward the hydrogen atom of the hydroxyl group, and thus an oxyanion bearing an epoxy group is formed. The second way is the attack of the base over the methylene of the epoxide leading to ring-opening. Hyperbranched polyethers with a high functionality in hydroxyl groups were achieved [103, 124–126].

In order to access to well-defined linear polyols derived from glycidol, hydroxyl functions of that monomer had to be protected. Dworak, Tsvetanov and coll. [114, 127–131], and Möller and coll. [132–134] investigated the AROP of ethoxyethyl glycidyl ether using metal alkali alkoxides such as KOH, CsOH, and *t*-BuOK. These systems enabled the synthesis of linear polyols up to 30,000 g/mol. Quantitative conversion was obtained between 17 and 48 h, depending on targeted molar masses, and required high temperatures (up to 120 °C). Due to the initiating systems used, residual transfer reactions were observed, limiting somehow the control over the structures [91]. Linear polyglycidols with molar masses up to 85,000 g/mol, starting from ethoxyethyl glycidyl ether (EEGE), were obtained using $NOct_4Br$/triisobutylaluminum as initiating system at room temperature in a few hours [52]. The formation of an initiating and propagating "ate" complex of weak basicity was proposed to explain the decrease of side reactions. Allyl glycidyl ether or isopropylidene glyceryl glycidyl ether was also used as a protected form of glycidol to obtain polyethers polyols [114, 133, 135, 136].

Taking advantages of the anionic route, various well-defined functional block copolymers were prepared [128, 133, 137–141].

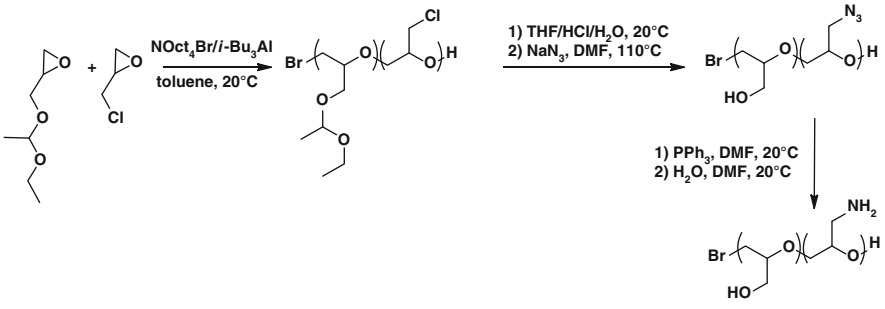
2.5.2 Polyethers with Amine Functions

Jeffamines® represent the most industrially produced polyetheramines. Such polyamino telechelic polyethers cannot be directly obtained by initiation and termination steps. They are synthesized from hydroxytelechelic random copolymers of ethylene oxide and propylene oxide via reaction between hydroxyl

functions and ammoniac gas at 300 °C. Considering the nature of the polymerization, only polyetheramines with low molar masses can be prepared. They are thermoresponsive polymers possessing a lower critical solubility temperature around 30 °C in water. Amino end groups are mainly used as curing agents in epoxy resins [142, 143] and as chain extenders for polyurethane applications [144, 145].

The introduction of amino groups at the head of polyether chains is generally carried out using an initiator bearing a primary amine function and another more reactive function, i.e., an alcohol, which enables the initiation. Aminoalcohols can be thus used to polymerize ethylene oxide by an anionic mechanism [116]. In basic media, both metal alkoxide and amide are formed, and the equilibrium is driven toward the formation of alkoxide by increasing the size of the counterion. Molar masses of α-amino-ω-hydroxy functional polyethers reached 1,000 g/mol. Transfer and termination reactions occur due to the hydrogen of amino groups. Protection of the primary amino group by a tertiary one was considered to overcome those limitations [96, 100, 116, 135]. Molar masses increased up to 6,000 g/mol and required long times, i.e., 150 h [146]. Schlaad used α-methylbenzyl cyanide as a CH-acidic compound to obtain α-cyano, ω-hydroxy poly(ethylene oxide) with controlled molar masses up to 2,500 g/mol with narrow distributions [78]. The cyanide function was then reduced in $–NH_2$ group by $LiAlH_4$.

Polyethers bearing primary amino groups are also generated by using epoxide monomers with protected amines such as *N*,*N*-dibenzyl amino glycidol or *N*,*N*-diallylglycidylamine prepared from epichlorohydrin and *N*,*N*-dibenzylamine or *N*,*N*-diallylamine, respectively [147, 148]. The synthesis of copolymers with EO was next performed using cesium alkoxide as initiator giving controlled copolyethers with molar masses up to 10,000 g/mol. Pendant amine functions can also be introduced from chlorine atoms. Statistical or block copolyethers, made by $NOct_4Br$/i-Bu_3Al systems and having both hydroxy and amine pendant groups, were brought, respectively, by ethoxyethyl glycidyl ether (protected glycidol) and epichlorohydrin monomers (Scheme 14) [149]. Chlorine atoms were subsequently transformed into azido groups using sodium azide. Consequent reaction with



Scheme 14 Synthesis of poly(glycidol-co-glycidyl amine) from protected glycidol and epichlorohydrin units

triphenylphosphine enables quantitative formation of amino groups. Such type of copolymers was proposed to enable selective electrophilic reactions due to the difference of reactivity between –OH and $–NH_2$ functions.

2.5.3 Polyethers with Alcene Functions

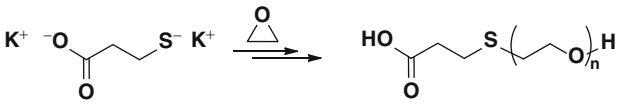
Double bonds are known to be stable toward anionic ring-opening polymerization conditions but can be further easily modified into various functions which make them attractive. They can be introduced via initiation with an alcohol bearing such a function [96, 150–152]. Allyl alcohol and 10-undecen-1-ol can be deprotonated, for instance, by naphthalene potassium or by sodium hydride, respectively. However, during polymerization, double bonds can be isomerized into propenyl group to form $CH_3CH=CHO^-$ as initiating species. To avoid this side reaction, polymerization has to occur between 15 and 20 °C, rather than at high temperatures [151]. As one example, thiol-ene reactions were applied to PEO oligomers initiated by 10-undecen-1-ol [152]. The synthesis of α,ω-diallyl PEO was achieved by reaction between α,ω-dihydroxy PEO, deprotonated with diphenylmethyl potassium, and allyl bromide. Hydrogels were obtained by their post-reaction with octafunctional silsesquioxanes via hydrosilylation [153, 154].

Monomers bearing allyl functions, like allyl glycidyl ether (AGE), can be directly used to synthesize polyethers with pendant double bonds through AROP with alkali metal alkoxides as initiators [21, 133, 155]. Generally, molar masses lower than 10,000 g/mol and long polymerization times are required. Ammonium salts/trialkylaluminum systems [156] allowed controlled and high molar mass structures in a few hours. With potassium alkoxide/naphthalenide initiators, Lynd and Hawker could also obtain molar masses up to 100,000 g/mol with low dispersity within 20–144 h [157]. Similarly, ethoxy vinyl glycidyl ether (EVGE) was shown to be selectively polymerized and copolymerized with ethylene oxide to give functional polyethers able to be post-modified [158].

2.5.4 Polyethers with Azide Functions

Most of the PEO azidation routes reported in the literature involve the chemical modification of previously formed hydroxyl-terminated PEO [159–162]. Kataoka achieved the synthesis of azido-terminated heterobifunctional poly(ethylene oxide) s in a multistep process, involving ring-opening polymerization of ethylene oxide initiated by allyl alcohol and subsequent transformation of R-allyloxy and ω-hydroxy PEO end groups by a series of chemical reactions [163]. The azide group was introduced by mesylation of the hydroxyl terminus, followed by its subsequent substitution with sodium azide [164, 165].

The monomer-activated approach allowed the direct synthesis of a broad series of heterofunctional polyethers bearing an azido head group, and a hydroxy-terminated chain end, starting from tetrabutylammonium azide in the presence of



Scheme 15 Thiolate-initiated polymerization of ethylene oxide

triisobutylaluminum [166]. Poly(alkylene oxide)s, protected polyglycidol, and polyepichlorohydrin were obtained in this way with a high functionalization efficiency. Reduction reactions can lead to amine functionalization, or Huisgen's coupling reaction with alkyne moieties can be applied [167].

2.5.5 Polyethers with Other Functions

Carboxylic acid groups were, for instance, introduced from the initiation step. The use of dipotassium-3-mercaptopropionate synthesized from 3-mercaptopropionic acid and two equivalents of potassium naphthalide allowed the direct synthesis of α-carboxy, ω-hydroxy poly(ethylene oxide) up to 25,000 g/mol with narrow distribution [168]. Only the thiolate was shown to react; the carboxylate did not participate in the polymerization (Scheme 15), but the usual way to introduce such a function is post-modification of chain ends [152, 169–171].

Aldehyde functions in α-position can also be introduced by using an initiator bearing a protecting group, i.e., 4-(diethoxymethyl)benzyl alcohol [172].

As a last example, polyethers with pendant methacrylate functions were achieved by selective ring-opening polymerization of glycidyl methacrylate using a monomer-activated anionic approach affording cross-linkable low Tg polymers [173].

The method based on chemical modification of previously and anionically formed polyethers is the most common way to get various functionalized and reactive structures. In many cases a simple chemistry can be used which makes this way very attractive. But, in the other cases, the interest is much more limited particularly for an industrial application. The recent advances in the control of the anionic polymerization of epoxide offer nowadays direct routes to prepare reactive and new polymers. The research and development of novel technologies will certainly contribute to an increasing use of such recent methods.

3 Cyclic Esters

3.1 Introduction

The biodegradability and biocompatibility of aliphatic polyesters render them very attractive for a wide range of applications as environmental friendly thermoplastics and biomaterials [174]. Moreover, many of them could be obtained from renewable resources, which is one of the great challenges for polymer chemists. Three

different polymerization mechanisms can be implemented to synthesize aliphatic polyesters: the step-growth polymerization through esterification reaction of hydroxyl acids or diacids/diols, the ring-opening polymerization (ROP) of cyclic ketene acetals, and the ROP of cyclic esters. The step-growth polymerization is highly used as its main advantage is the easy availability of a very wide range of acid and alcohol precursors. Nevertheless, this polymerization suffers from severe limitations: extremely high conversion has to be reached to get high molar masses, high temperatures are generally needed, control of the molar masses is very difficult, and dispersity is quite large. The ROP of cyclic ketene acetals could proceed through cationic and radical processes [175]. Even if this polymerization is known for long, its development remains limited due to many drawbacks: there is competition between direct vinyl polymerization and indirect ring-opening of the cycle depending on the ring size, substituents, and temperature; monomers are not readily accessible; and branching reactions could occur. All these limitations can be overcome by implementing the ROP of cyclic esters either by ionic (cationic or anionic) or coordination-insertion mechanisms. Indeed, this technique allows living and/or controlled polymerization with fast initiation and high molar masses with low dispersity. Availability of the monomers occupies an intermediate position between step-growth polymerization and ROP of ketene acetals. The question of polymerizability of cyclic esters arises since the polymerization rate is highly dependent on the ring size and the substituents. Moreover, in the case of anionic mechanism, the active species varies with the ring size. Many recent reviews could give other details than those presented in this subchapter [175–183].

3.2 *Thermodynamics of Cyclic Esters Ring-Opening Polymerization*

The ability of a cyclic ester to be polymerized by the ring-opening mechanism has to be allowed both thermodynamically and kinetically. Indeed, the monomer-polymer equilibrium has to be shifted to the polymer formation, and the polymerization time has to be reasonable. ROP of cyclic esters could be sometimes limited by the presence of a relatively high concentration of the unreacted monomer when at the equilibrium. This is typically the case for γ-butyrolactone which is hardly polymerizable. The driving force for the polymerization of the majority of cyclic esters is their ring strain. As a consequence, large-ring lactones are more difficult to polymerize than small ones.

3.3 *Lactide*

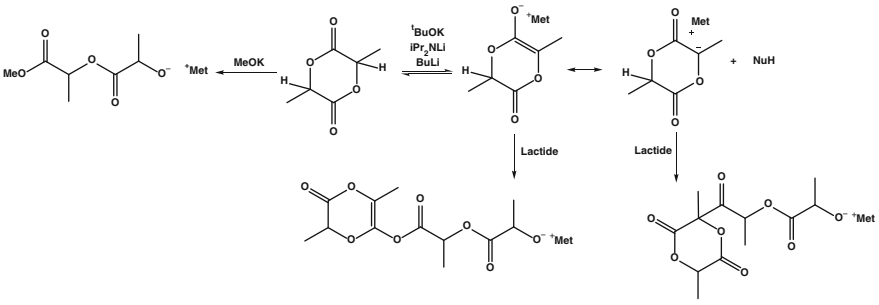
The AROP of lactide was not as extensively studied as its coordination-insertion polymerization, this latter being most investigating because it could enable

stereoselective polymerization [179, 182, 184–186]. Nevertheless, several types of initiators were able to perform polymerization of lactide.

3.3.1 Initiators with Alkali Metals

Studies concerning the AROP of lactide with alkali metals initiators were essentially conducted in the 1990s [187–202]. It was shown that strong bases were needed as carboxylates and phenolates were not able to initiate the polymerization [192]. On the contrary, potassium *tert*-butoxide and butyllithium allowed the polymerization of lactide with yields below 80 % and with the presence of racemization, transesterification reactions, and macrocyclics formation whatever the polymerization conditions [192]. Moreover, it was demonstrated that the initiation did not proceed through a nucleophilic attack of the strong base but through a proton abstraction from lactide to give an enolate which was the actual initiator of the polymerization (Scheme 16). After the nucleophilic attack of the enolate onto a lactide molecule yielding acyl cleavage, the active species responsible of the propagation was an alkoxide. Better results were obtained with primary and secondary lithium and potassium alkoxides as in this case the initiation proceeded mainly through the nucleophilic attack, but still uncontrolled molar masses were achieved (Scheme 16) [194, 201]. With potassium methoxide as the initiator, polymerizations were completed in less than 2 h in THF at room temperature allowing a good control of the molar masses with dispersities around 1.3 and low extent of racemization [188–190].

The addition of a crown ether onto potassium *tert*-butoxide or naphthalenide potassium revealed beneficial for the dispersity that dropped below 1.2 and for the reduction of racemization reactions but detrimental for the polymerization rate that slowed down dramatically [191, 196, 197]. Finally, it was demonstrated that the AROP of *rac*-lactide initiated by lithium *tert*-butoxide could yield to the synthesis of disyndiotactic polylactide (PLA), provided that yield remained quite low (below 35 %) [199, 200].



Scheme 16 Mechanism of AROP of lactide

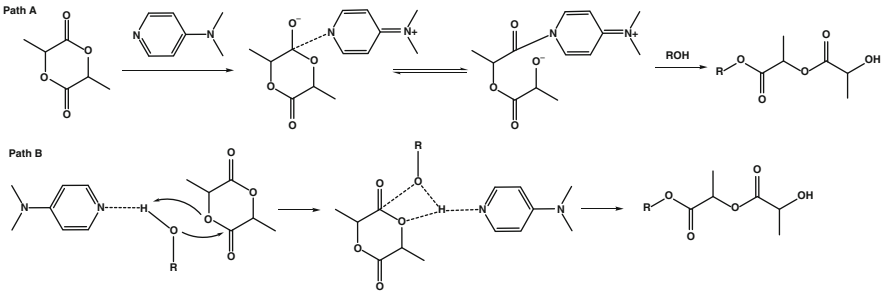
In spite of some side reactions, many studies described the synthesis of block copolymers with at least one PLA block via AROP of lactide. For example, poly (ethylene oxide)-*b*-polylactide synthesis was highly investigated as these copolymers could be used in the biomedical field. They were either synthesized through the sequential AROP of ethylene oxide and lactide [203–212] or by the AROP of lactide using commercial poly(ethylene oxide)s [213–217]. Starting from a difunctional (macro)initiator, tri- [218, 219] and penta-blocks [220] copolymers were also produced. The sequential polymerization allowed also the synthesis of poly(ethylene oxide)-*b*-polyglycidol-*b*-polylactide copolymer [221]. Finally, the synthesis of polysaccharides-*g*-polylactide was described [222, 223].

3.3.2 Organocatalyzed Polymerization

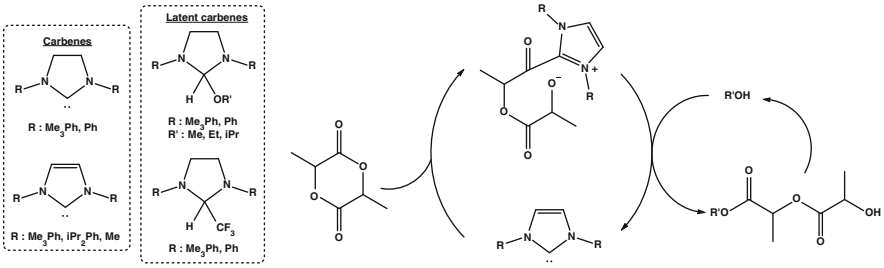
Since 2001 and the description of the first nucleophilic organocatalyzed ROP of lactide [224], this field was highly investigated [225–228], with the use of imidazole [229], amines [224, 230], amidines [231], phosphines [232], phosphazene [233, 234], or *N*-heterocyclic carbenes (NHC) [235–250].

Tertiary amines and phosphines are among the simplest metal-free catalysts. The controlled ROP of lactide was thus performed in the presence of 4-dimethylaminopyridine (DMAP) or 4-pyrrolidinopyridine (PPY) in dichloromethane at 35 °C or in the melt at 135 and 185 °C yielding PLA with controlled molar masses and low dispersities [224]. The polymerization was proposed to proceed through a monomer-activated mechanism with a nucleophilic attack of the amine onto the lactide monomer resulting in a zwitterionic species that was attacked by the initiating or propagating alcohol chain end (Path A, Scheme 17). Nevertheless, computational calculation suggested that the propagation occurred preferentially through an alcohol-activated mechanism (Path B, Scheme 17).

Phosphazenes were described to also induce such an alcohol-activated mechanism to produce polylactides with predictable molar masses, low dispersities, and high chain-end fidelity [233, 234]. By analogy with cyclic ethers, one can ask about the mechanism implying the deprotonation of an alcohol by a phosphazene base and propagation through a phosphazenium alkoxide. With phosphines, polymerizations



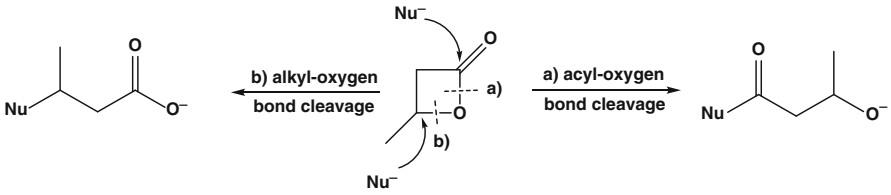
Scheme 17 ROP of lactide with tertiary amines



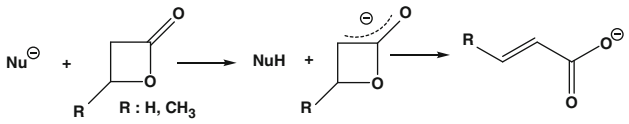
Scheme 18 Representative carbenes and mechanism of AROP of lactide

had to be conducted in bulk at high temperature to proceed with at least one equivalent of phosphine compared to initiator in order to control the polymerization [232]. A monomer-activated ROP mechanism comparable to that of tertiary amine was proposed for these catalysts. In the absence of any alcohol, it was shown that imidazoles [229] and amidines [231] were able to polymerize lactide in bulk at high temperature or in solution at room temperature, respectively. In both cases, it was shown that the catalyst was capable of nucleophilic attack onto lactide and that cyclic polylactides were almost exclusively obtained.

NHCs were also investigated as organocatalysts for lactide ROP. They proved to be active, with complete monomer conversion in a few hours at room temperature to afford PLAs with high and controlled molar masses and low dispersities [237, 242]. The mechanism is supposed to be an activated monomer mechanism (Scheme 18). NHCs can be obtained from ionic liquids, with the advantage that the use of a biphasic system (THF/ionic liquid) allowed an easy polymer and catalyst recovery [240, 242]. NHCs can also be produced in situ from thermally activated NHC adducts, but in this case, lactide racemization occurred [247]. Alcohol adducts of NHCs proved to act as single-component catalyst/initiators with various alcohols as initiators. Some of them are stable solids and readily release the alcohol and the carbene in solution at room temperature [248], whereas for some others, polymerization could only take place at 90 °C [236, 238]. In the absence of an alcohol, NHCs promoted the polymerization of lactide, and the propagating species was demonstrated to be a zwitterion [241, 245]. Under these conditions, exclusively cyclic PLAs with rather low dispersities and a good degree of control were obtained at room temperature. The presence of both even and odd numbers of lactate units deduced from Maldi-Tof analyses indicated the presence of transesterification reactions. Very recently, carbene carboxylates were able to perform the polymerization of lactide [235]. Finally, the use of bulky NHCs allowed the synthesis of highly isotactic and heterotactic polylactides from *rac*-lactide and *meso*-lactide, respectively, at low temperatures [244]. In aprotic conditions (absence of exogenous alcohol), it was shown that sparteine was able to perform the zwitterionic ROP of L-lactide from both nitrogen atom to end up with macrocyclic polylactide [251].



Scheme 19 AROP of four-membered lactones



Scheme 20 Side reaction occurring during β-lactones polymerization

Finally, the ROP of *O*-carboxyanhydride catalyzed by NHCs yielded to the formation of polylactide with controlled molar masses and chain ends when the polymerization was performed at room temperature in THF [252]. Star-shaped structures were also successfully obtained.

3.4 β-Lactones

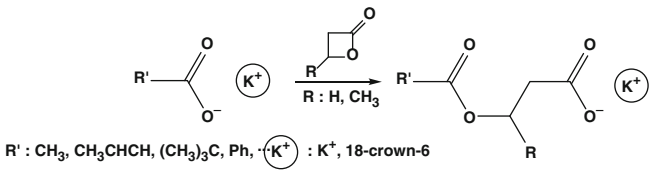
As polymer chemists would like to be able to synthesize polyesters that would resemble polyhydroxyalkanoates (PHA) that are natural polyesters produced by many bacteria [253], AROP of *β*-lactones was by far the most studied ROP of cyclic esters [188, 189, 193, 254–261]. Besides, *β*-lactones behave differently than other larger lactones due to their high polarity and high internal strain. Their polymerization can occur through the nucleophilic attack onto the carbonyl carbon or onto the carbon adjacent to the endocyclic oxygen atom (Scheme 19).

Another important difference from other lactones is the easy α-proton abstraction as a side reaction that would produce acrylate or crotonate ions that are also able to initiate the polymerization (Scheme 20). As a consequence, the control over the molar masses and chain-end fidelity could be problematic.

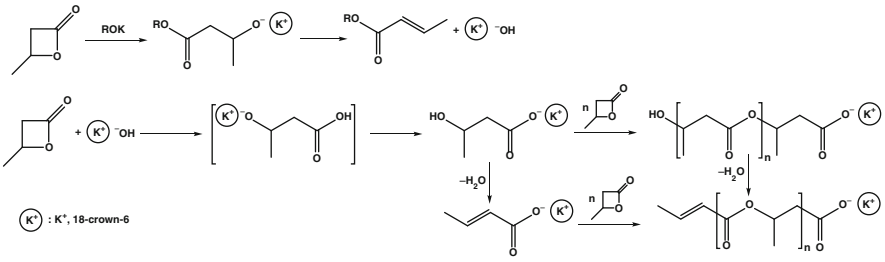
3.4.1 *β*-Propio- or *β*-Butyrolactone

Alkali Metal-Based Initiators

From the 1960s, the AROP of *β*-propiolactone (PL) was shown to be easily initiated by weak bases like alkali metal carboxylates but also by stronger bases such as alkali metal alkoxides. On the contrary, *β*-butyrolactone (BL) was shown to be



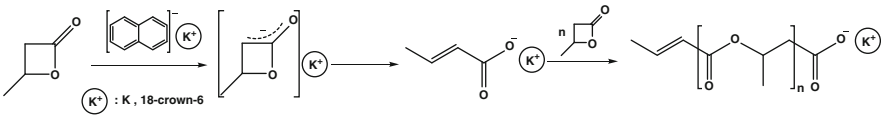
Scheme 21 AROP of β-lactones initiated by alkali metal carboxylates



Scheme 22 AROP of β-butyrolactone initiated by metal alkoxides

polymerized by such bases only if they are activated by the addition of macrocyclic ligands (crown ethers or cryptands) [262]. When carboxylates salts were employed as initiating species, the polymerization of PL was not living as transfer reactions to the monomer occurred leading to side initiation by acrylate ions (Scheme 20). It was shown independently in 1976 by Penczek [263] and Boileau [264] that the introduction of crown ethers or cryptand could enable the living polymerization of PL (Scheme 21). Since then, many carboxylate salts were utilized as initiators [262, 265–275]. Polymerizations were generally performed in THF at room temperature with long reaction times (generally more than 100 h for BL).

When the polymerization of *β*-lactones was initiated by strong bases such as alkali metal alkoxides, active species involved in the propagation were highly debated in the literature [259, 274, 276–283]. Penczek and coll. suggested that, when polymerization of PL was initiated by potassium methoxide in DMF at room temperature, both acyl-oxygen and alkyl-oxygen bond could occur yielding alkoxide or carboxylate propagating species, as indicated in Scheme 19 [274, 276]. Nevertheless, as alkyl-oxygen bond cleavage is preferred, after few monomers addition, the only propagating species are carboxylates. Later, as double bonds were observed as chain ends, some other authors showed that initiation occurred through a nucleophilic attack at the carbonyl carbon atom of a monomer by the alkoxide anion of the initiator, cleaving the acyl-oxygen bond to yield the corresponding potassium alkoxide of the *β*-hydroxycarboxylic acid esters, followed by the formation of an unsaturated ester due to KOH elimination (Scheme 22) [259, 278–281]. Finally, KOH acts as the actual initiator of the polymerization, and block copolymers were obtained with this type of initiator [284].

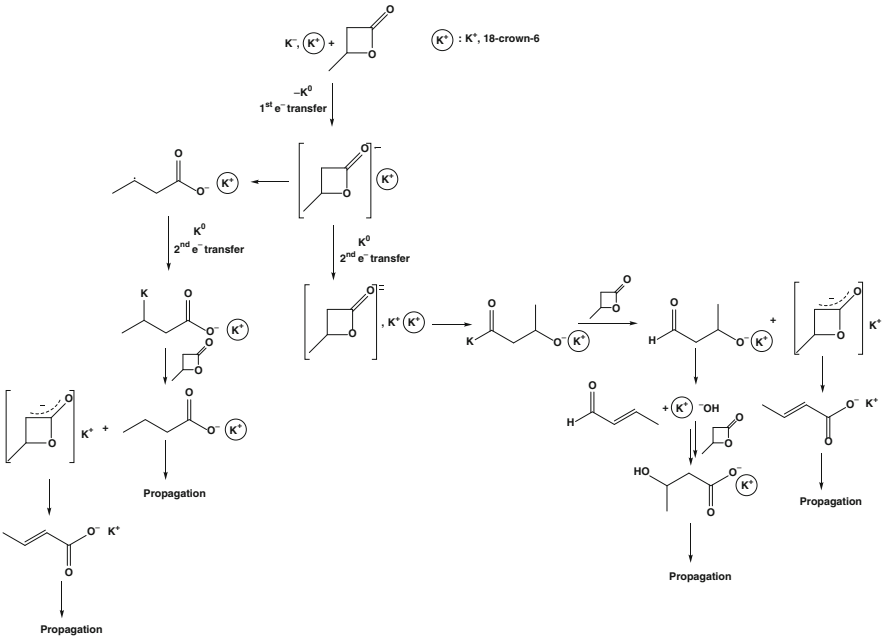


Scheme 23 AROP of β-butyrolactone initiated by naphthalenide potassium

In few examples, naphthalenide potassium was used as the initiator for the polymerization of *β*-lactones (BL, PL) in THF at 20 °C [262, 285, 286]. The initiation only occurred in the presence of a crown ether (18C6) or a cryptand ([222]), but even in this case, polymerization rate was very slow as more than 100 h or 10 h were needed to rich a conversion higher than 90 % for BL and PL, respectively, yielding polyesters with molar masses up to 10,000 g/mol with dispersities around 1.3. Concerning the mechanism involved with this type of initiator, as indicated on Scheme 23, it was demonstrated first the α-deprotonation of β-lactones followed by the ring-opening of the monomer yielding potassium crotonate for BL (or acrylate for PL) which is the actual initiator. Again, the active species are carboxylates. It is thus possible to produce macromonomer of BL or PL with a good control as the molar masses are in good agreement with the theoretical ones, and each chain bears a double bond at one chain end coming from the initiation step. In the same vein, very similar results were obtained with potassium hydride as the initiator in the same conditions [287].

Finally, potassium solutions (obtained from 18C6 THF solution in the presence of a potassium mirror) revealed also powerful initiators for the polymerization of *β*-lactones [285, 288–293]. When polymerizations were performed in THF at 20 °C, the polymerization rate was quite high (at least higher than with other anionic initiators) as PPL with 12,000 g/mol was obtained in 3 h. Very high molar mass PPL could also be obtained. For BL again, polymerization rate was much slower yielding atactic PBL with molar masses up to 6,000 g/mol in more than 100 h. As the polymerization is living, block copolymers of BL and PL were also achieved [291]. Again, concerning the mechanism and more specifically the initiation step, controversy can be found in the literature. The last suggested mechanism is depicted in Scheme 24. The initiation proceeds through a $2e^-$ transfer in two steps. After the first e^- transfer, an anion radical is formed, and after the second e^- transfer, the resulting dianion lactone is decomposed with the heterolytic cleavage of the acyl-oxygen bond. This compound deprotonates the monomer giving potassium enolate and potassium *β*-alkoxide aldehyde, this latter being unstable, it decomposes into crotonaldehyde and potassium hydroxide. Both potassium enolate and potassium hydroxide are able to generate initiators as indicated on Scheme 24. As a side reaction, the *β*-lactone anion radical can undergo a homolytic alkyl-oxygen bond cleavage yielding finally potassium butyrate that can also initiate the polymerization.

Few studies investigated the tacticity of PBL through anionic polymerization. Starting from racemic butyrolactone, mainly atactic PBL were obtained, whatever the initiating system [262, 270, 281, 287, 293, 294]. Nevertheless, it was also

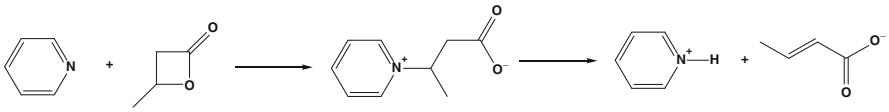


Scheme 24 AROP of β-butyrolactone initiated by potassium solution[288]

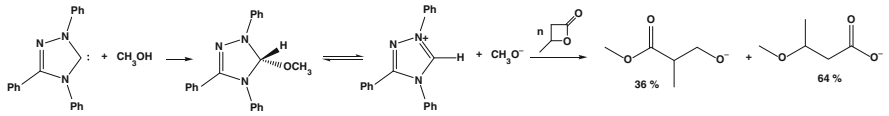
demonstrated that reducing polymerization temperature or adding tartrate esters could induce the synthesis of partially syndiotactic PBL (up to 60–65 %) starting from racemic butyrolactone [295, 296]. Finally, isotactic PBL were also synthesized efficiently using R-butyrolactone [295] (around 80–85 %) or S-butyrolactone [270, 273] (up to 95 %).

Organic Initiators

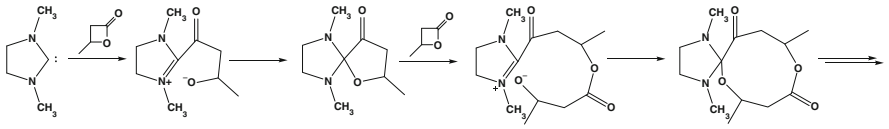
Organic bases, like phosphines, pyridines, tertiary amines, and betains, were among the first to be used for the initiation of β-lactones [259, 297–302]. It was first suggested that the initiation step involved the formation of betain species that are the actual initiator with active species being carboxylates. The propagation would then proceed via alkyl-oxygen bond cleavage yielding macrozwitterions [297, 298, 300]. Nevertheless, this was inconsistent with the respective nucleophilicity/basicity ratio of the engaged initiators, at least for amines. It was thus demonstrated that after the betain formation, the protonated base was released yielding acrylate or crotonate ions that were the actual initiators (Scheme 25) [299]. Eventually, PPL or PBL can be produced with unsaturated chain ends. In the case of phosphine, both phosphonium and unsaturated chain end were detected indicating the concomitance of both types of initiation [299]. These side reactions proved to be a limiting factor in the control over molar mass and molar mass distribution.



Scheme 25 Polymerization of β-butyrolactone initiated by organic bases



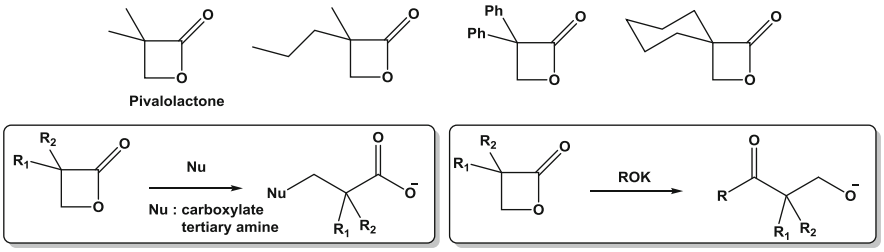
Scheme 26 AROP of β-butyrolactone initiated by triazole carbene



Scheme 27 Zwitterionic polymerization of β-butyrolactone initiated by a saturated carbene

More recently, other organic (co-)initiators, like carbenes [235, 236, 303], guanidine [304], amidine [304], and phosphazenes [304, 305], revealed powerful for the polymerization of β-lactones. Polymerizations initiated by a carboxylic acid/phosphazene base led to atactic PBL with good control over the molar masses, the polymerization rate being dependent on the basicity of the phosphazene used. With triazole carbenes, it was demonstrated that the polymerization of BL in toluene at 80 °C with methanol as the initiator was controlled for DP up to 200 with good chain-end fidelity (few crotonate chain end detected) in the presence of tert-butanol as the co-solvent [236, 303]. Concerning the initiation mechanism, it was shown that the initiator was deprotonated by the carbene, and it was thus an alkoxide that was the actual initiator (Scheme 26). Moreover, the propagation proceeded both via alkyl-oxygen or acyl-oxygen bond cleavage, yielding concomitantly alkoxides and carboxylates as active species. Nevertheless, the acyl bond cleavage being less favored, after a couple of monomer additions, carboxylates were the only active species.

Besides, with some other carbenes, the polymerization mechanism revealed different, yielding only cyclic polymers with a good control of the molar masses [306]. As spirocycles were formed all along the polymerization, it was proposed that 1,3-dimesitylimidazol-2-ylidene was able to perform a nucleophilic attack onto the carbon of the carbonyl group of BL yielding a zwitterion that ring-closed after each monomer addition (Scheme 27).



Scheme 28 Examples of α,α-disubstituted-β-propiolactones and propagating species depending on the initiating system

3.4.2 Other β-Lactones

α,α-Disubstituted-β-Propiolactones

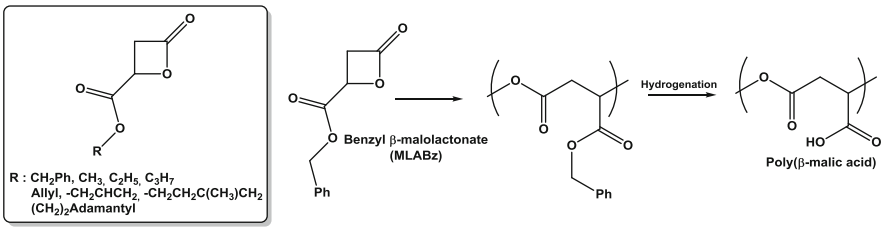
The AROP of α,α-disubstituted-β-propiolactones (Scheme 28) was highly investigated, pivalolactone (α,α-dimethyl-β-propiolactone, PVL) being the most studied monomer [307–316]. Due to the absence of proton in α position compared to other β-lactones, the polymerization of α,α-disubstituted-β-propiolactones could be easily controlled, especially the chain ends, as the side reactions yielding crotonate or acrylate groups (Scheme 20) could not occur with these monomers.

In most of the studies, potassium or ammonium carboxylates were used as the initiating species, the propagating species being carboxylates in this case. When tertiary amines were the initiating species, again carboxylates were the propagating species [316]. On the contrary, when the initiator was a metal alkoxide, the propagation proceeded through an alkoxide, and the formation of macrocyclic structures was noticed [311, 312].

β-Substituted-β-Lactones

The AROP of β-substituted-β-lactones was also highly studied (Scheme 29) [317–345]. More specifically, researchers were interested in the monomers that could be precursors for the synthesis of poly(β-malic acid), which is a water-soluble, biodegradable, and biocompatible polymer that exhibits biological properties (proteinase inhibitor, for instance). Whereas this polymer is available from natural and/or bacterial resources, many studies deal with its chemical synthesis, especially since the first description of the synthesis of β-malolactonate in 1979 [346]. The racemic or the optically active versions of benzyl-β-malolactonate were the most studied monomers. Optically active polymers could be obtained (no racemization) with an inversion of the configuration [320].

Several types of initiators were able to polymerize β-substituted-β-lactones. With triethylamine, only low molar masses were obtained with poor control [337]. Great enhancement was achieved when tetraalkylammonium benzoate was



Scheme 29 Examples of β-substituted-β-lactones investigated in the literature

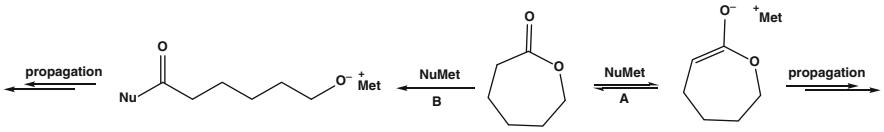
employed as the initiator. Polymerizations were generally performed in bulk at temperature ranging from 30 to 70 °C, but like for BL and PL, transfer reactions occurred through proton abstraction, preventing a good control over the molar masses and the chain-end fidelity [317, 318, 330, 340]. Transfer reactions were shown to be highly reduced when polymerizations were performed in THF at 0 °C, at low reactant concentration [330], or when monomers were highly purified [327]. Another possibility to suppress transfer reactions is to start from an α,1;α-disubstituted-β-substituted-β-lactones instead of β-substituted-β-lactones; as for pivalolactone, proton abstraction is no more possible in this case [319, 336, 343]. More recently, carbenes [236], phosphazenes [336, 344, 345], amidines [344, 345], and guanidine [344, 345] were described as efficient initiators for the polymerization of β-substituted-β-lactones. Nevertheless, the transfer reactions were still present. Despite the presence of transfer reactions, the synthesis of macromolecular architecture was possible since it was described the synthesis of block copolymers with the first block constituted of β-substituted-β-lactones and the second block constituted of another β-substituted-β-lactones [328], butyrolactone [317], lactide [334, 335], or caprolactone (CL) [330, 331, 334], these two latter being polymerized through organometallic catalyzed ROP. The synthesis of random copolymers was also performed [317, 322, 323, 326, 329, 332, 343], as well as the synthesis of graft copolymers [329, 332].

3.5 Larger-Ring Lactones

3.5.1 ε-Caprolactone and δ-Valerolactone

Polymerization Initiated with Alkali Metal Compounds

The AROP of other lactones was by far less investigated than that of β-lactones. The polymerization of CL could be initiated by metal alkoxides [264, 274, 279, 347–356], cyclopentadienyl sodium [357], phenyllithium [358], carbazole potassium [359], lithium diisopropyl amide [360], or sodium hydride [361]. Depending on the initiator, the initiation proceeded via monomer deprotonation (Path A, Scheme 30) or via nucleophilic attack, the monomer being opened at the acyl-oxygen bond and



Scheme 30 Initiation step in the AROP of ε-caprolactone

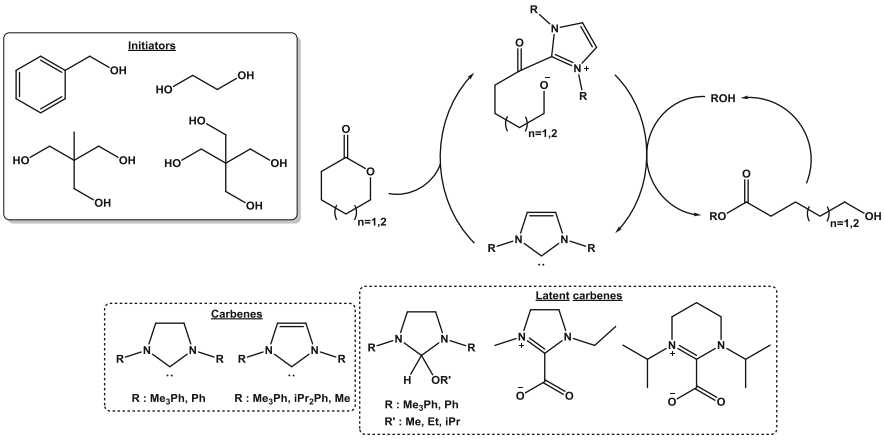
the growing species being an alkoxide (Path B, Scheme 30). For example, using cyclopentadienyl sodium as the initiator, no cyclopentadienyl groups were present on the polymeric chain ends, and the polymerization is said to proceed through deprotonation of the monomer [357].

The main drawback of this method is the occurrence of significant intramolecular transesterification reactions, also called "back-biting," which were very dependent on the polymerization conditions and the initiator and resulted in the formation of generally low molar mass polymers and in cyclic polymers. For instance, it was demonstrated that with *tert*-butoxide potassium as the initiator, high dilution favored the formation of cyclics (less than 6–7 CL units) to the detriment of polymer formation [351, 352]. With cyclopentadienyl sodium as the initiator, in bulk and in nonpolar solvents, molar masses up to 130,000 g/mol were obtained, whereas in polar solvents, only oligomers were produced [357]. When the polymerization of CL was initiated with lithium diisopropylamide, medium molar mass polymers were obtained [360]. The polymerization of CL initiated by phenyl lithium in bulk at 170 °C led to high molar mass polymers (50–70,000 g/mol) [358]. Polymerizations performed in supercritical carbon dioxide exhibited low yields probably because of the occurrence of side reactions between the anionic species and carbon dioxide [350]. It was also demonstrated that alkali graphitides allowed the synthesis of very high molar mass polylactones with nevertheless the presence of a low molar mass fraction [362–368].

In spite of many possible side reactions and like for the other cyclic esters, the possible synthesis of poly(δ-valerolactone)-*b*-polylactide [188, 189, 369], poly (ethylene oxide)-*b*-poly(ε-caprolactone) [370], and polyglycidol-*b*-poly(-ε-caprolactone) [371] was described in the literature.

Organocatalyzed Polymerization

Few organocatalysts were shown to be able to perform the polymerization of lactones compared to lactide. Indeed, most of the studies employed carbenes [237, 242, 372–379], with few examples using phosphazenes [234, 380] or TBD [381]. With $tBuP_1$ or BEMP, in the presence of alcohols, only δ-valerolactone (δ-VL) was polymerized with high conversion in 2–4 days, whereas for ε-caprolactone only 15 % conversion was obtained after 10 days. On the contrary, with $tBuP_2$, CL was polymerized in few hours to yield PCL with controlled molar masses. NHCs were shown to polymerize both δ-valerolactone and ε-caprolactone giving access not only to linear but also to cyclic aliphatic polyesters. While the



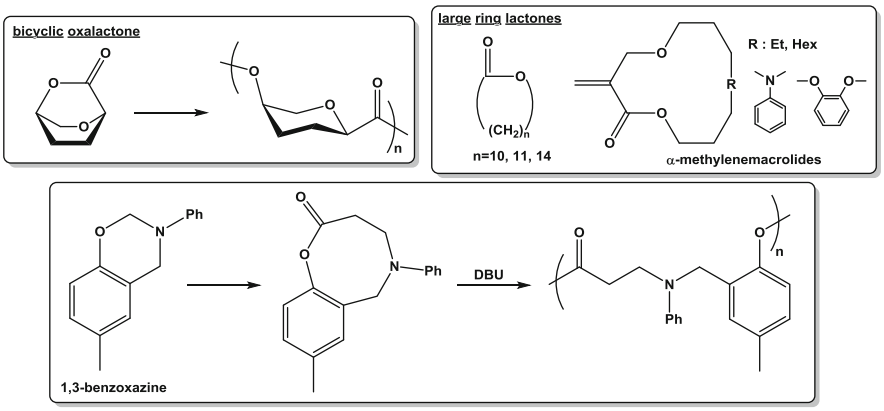
Scheme 31 Examples of initiators and carbenes employed for lactone ROP

NHCs were generally highly active in the polymerization of lactide, less efficiency was observed toward the ROP of CL. The mechanism is supposed to be an activated monomer mechanism, and several NHCs, either in their "bare" or masked form, were shown to perform the polymerization of lactones (Scheme 31).

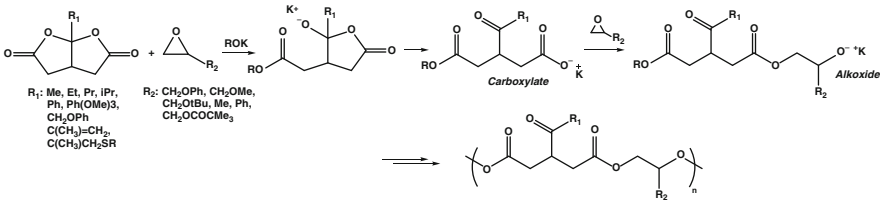
The ROP of CL was generally performed at room temperature in THF solution (0.5–2.0 M), in the presence of monofunctional initiators or multihydroxylated initiators such as ethylene glycol, 1,1,1-tris(hydroxymethyl)propane, pentaerythritol, or a six-arm poly(propylene glycol) (Scheme 31), yielding well-defined linear or star polycaprolactone (PCL). Catalytic activity was sensitive to steric and electronic properties of the carbene, as more electron-rich and less bulky substituted carbenes were more active for the synthesis of well-defined PCL [242, 374]. A so-called "abnormal" NHC, in which the carbene center is no longer located between the two nitrogen atoms but between a nitrogen and a carbon atom, was reported to exhibit a high catalytic activity in the ROP of CL [376]. Again, like for lactide ROP, in the absence of alcohol, the polymerization was shown to be zwitterionic, and it was thus synthesized cyclic polycaprolactones at room temperature with relatively high dispersity (between 1.4 and 2.1) for a wide range of molar masses (41,000–114,000 g/mol) [372, 377, 378]. Copolymerization of CL and δ-VL led to the formation of cyclic copolyesters with a gradient microstructure due to the difference in the reactivity ratios between the two monomers, which is usually not observed with metal-based alkoxides [375].

3.5.2 Other Lactones

Some other lactones were shown to be polymerizable through AROP. For instance, bicyclic oxalactone (Scheme 32) could be polymerized with butyllithium to afford polymers of moderate molar mass and high dispersity [382]. The polymerization of



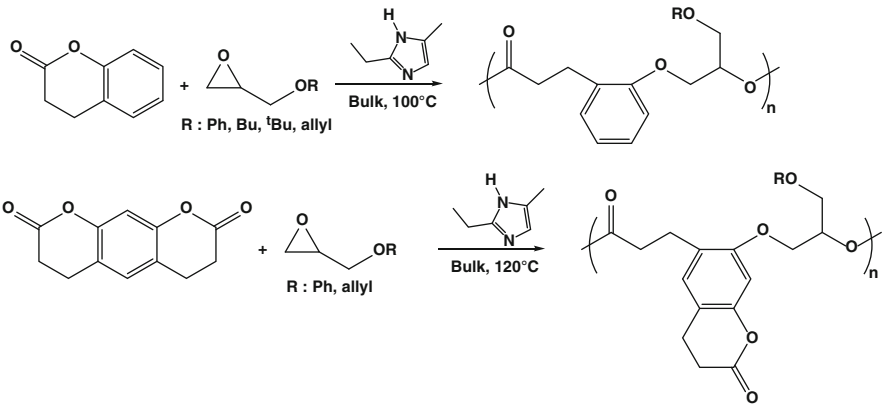
Scheme 32 Other lactones polymerized by AROP



Scheme 33 Bis(γ-lactones) and epoxides for the synthesis of alternated copolymers

large-ring lactones (undecanolide, λ-lauryllactone, and pentadecanolide) was also performed in bulk at high temperature or in solution at moderate temperature in the presence of metal alkoxides [383, 384]. The presence of back-biting reactions leading to the formation of macrocycles was still detected. α-Methylenemacrolides were successfully polymerized with butyllithium at low temperature [385]. PEG-containing macrolactones were also successfully polymerized using thiols and $tBuP_4$ [386]. More recently, 8-membered lactones obtained from 1,3-benzoxazine were polymerized in bulk at high temperature in the presence of 1,8-diazabicyclo [5.4.0]undec-7-ene (DBU) yielding low molar mass polymers with high dispersity due to intensive back-biting reactions [387].

5-Membered γ-butyrolactones do not generally afford polymers because the rate of ring closure is faster than that of ring-opening, and therefore only insufficient formation of the corresponding polyesters was achieved. On the contrary, Endo et coll. showed that copolymerizations of bis(γ-lactones) with epoxides led to the synthesis of alternated copolymers (Scheme 33) [388–398]. This was possible due to the presence of an isomerizable structure onto the monomer that prevents backward ring closure. Concerning the mechanism, the bislactone reacts with alkoxide-type propagating chain end exclusively, to undergo double ring-opening reaction. The formed acyclic carboxylate is thermodynamically stable and thus does not undergo backward ring closure. At the same time, the nucleophilicity of



Scheme 34 6-Membered lactones and epoxides for the synthesis of alternated copolymers

the carboxylate is not high enough to react with the bislactone but is reactive with epoxide to regenerate an alkoxide. Moreover, as the formation of the copolyester synthesis was accompanied by low volume shrinkage during polymerization, such polymers are useful for network formation when bisepoxides were used. It was also shown that phosphines could replace alkali metal alkoxide to perform a zwitterionic polymerization.

The AROP of 3,4-dihydrocoumarin (DHCM, an aromatic lactone, Scheme 34) was also studied with an imidazole as the initiator in bulk at high temperatures (100–120 °C) [399–405]. Whereas DHCM is a 6-membered ring like δ-valerolactone, its homopolymerization was not possible. On the contrary, it was shown that DHCM was easily copolymerized with an epoxide to yield alternated copolymers. When the bislactone was copolymerized with epoxides, only one of the two lactones participated in the copolymerization yielding only linear polymers. Networks were only obtained by post-reaction of the remaining lactone with a diamine, for example.

4 Cyclic Amides (Lactams)

4.1 Introduction

Polyamides are well-known polymers that are present in markets such as fibers, engineering plastics, and specialties, due to specific and various properties depending on their structures. Ring-opening polymerization of lactams (cyclic amides) initiated by water, referred to hydrolytic polymerization (i.e., reactions between the amine chain-end group and the lactam and/or carboxylic group of its hydrolyzed derivative), is carried out for industrial polymerization of ε-caprolactam (ε-CL) to form polyamide 6 (PA6, Nylon 6), though nylon 6–6, 4–6, and 6–10 are

synthesized by stepwise reactions of a diacid monomer with a diamine monomer. Cationic initiation is also possible, but not useful because of the low conversion and molar mass of the resulting polyamides [406]. Anionic initiation following an activated monomer mechanism is mainly used for polymerization in molds in order to prepare polyamides (PA6, 10, 12) directly from the corresponding lactams [407]. Polymerization mechanism of lactams, their polymerizability, and the properties of the resulting polymers were largely investigated. Reviews published by Reimschuessel [408, 409], Šebenda [410], Sekiguchi [406], Hashimoto [411], Roda [412], and Russo and Casazza [413] can precise this presented overview.

The anionic route is the fastest method for producing polyamides due to the low activation energy needed. This fast kinetic makes nowadays this route of high interest for industrial processes producing lightweight composite materials for automotive and wind energy. The anionic polymerization of lactams may be accomplished in solution or in the bulk either below or above the melting point of the polymer for the latter.

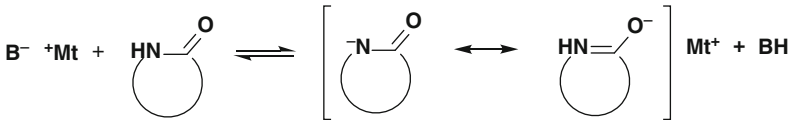
4.2 Mechanism of the Anionic Polymerization of Lactams

The mechanism differs from the anionic polymerization of most of the unsaturated and heterocyclic monomers because the growth center is not an anionically activated end group but is represented by an N-acyllated neutral chain. The anionic polymerization of lactams is initiated, under anhydrous conditions, by formation of the lactamate anion. Strong bases are able to deprotonate lactams and produce N anion of lactam effective for initiating the polymerization.

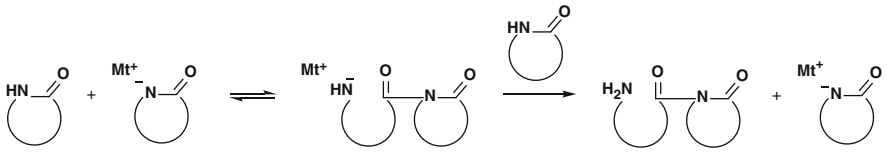
4.2.1 Initiating and Activating Systems

The anionically activated species is the monomer in the form of lactamate anion which is a very strong nucleophile (Scheme 35). The negative charge is delocalized on the amide group due to resonance stabilization by conjugation with the carbonyl group.

The lactamate anion is acylated by a lactam monomer, although the acylating ability of the latter is poor, with the amide group being stabilized by resonance. The lactamate anion reacts with the monomer by a ring-opening transamidation reaction forming *N*-acyl lactam structures carrying primary amine anions. Assuming a free ion mechanism [414], the imide anion is formed, in the first slow step, by nucleophilic attack of the lactamate on the carbonyl of the lactam molecule (Scheme 36). As it is not stabilized by resonance, rapid proton exchange undergoes with lactam monomer, yielding imide dimer (*N*-acyl lactam) and regenerating the lactamate. Result of these two combined reactions is the disproportionation between two amide groups (present in lactam monomer and in lactamate anion) to give amine



Scheme 35 Structures of the anionically activated monomer



Scheme 36 Nucleophilic attack of lactamate to a lactam

and acyl lactam moieties (in the *N*-acyl lactam species) and the reaction rate dependent on factors like the nature of counterion and reaction medium, lactam ring size, substituents, and structure of the resulting linear monomeric unit. N-substituted lactams are observed to react with lactamate anion with a rate significantly higher than that of the initial reaction, depending on the size and the electrophilicity of the substituent, and are generally used as activators in the activated anionic polymerization. The use of high reaction temperatures (>250 °C) is required in the absence of activator, and only the more reactive lactams, such as ε-caprolactam, undergo polymerization in the presence of a strong base in a non-activated method.

The initiators, which are the monomers carrying the anionic charge able to attack the chain end, are prepared by reaction of a lactam with strong bases such as mainly metal alkoxide, metal halide, alkali metal, and Grignard reagent [406, 414, 415] but also pentamethylene guanidine [406], quaternary ammonium salts [416], phosphazene [417], bicyclic "superbase" protophosphatranes [418, 419], or carbenes [420, 421]. The association of a strong base (NaH, LiH, BuLi) with a reducing agent such metal dialkyl/dialkoxy aluminum hydrides [422–424] or metal dialkyl boron hydride [423] can also be used as precursors of lactamates. In this case, the nucleophilic species obtained, i.e., the activated monomer, is a metal salt of 2-(dialkyoxyaluminoxy)-1-azacycloheptan.

As usual in anionic polymerization, the nature and concentration of the initiator play a crucial role. The rate is directly related to the concentration of active species and in particular to the dissociation constant yielding free ions. It is known that the concentration of free lactam anion increases with temperature, starting to be predominant above 150 °C, alkali metal lactamates being considered completely dissociated at higher temperatures [425, 426]. The rate of polymerization becomes here independent of the nature of the cation. In general, the activity of alkali metals follows the order of electropositivity, except with Li and despite its highest ionization energy: $Na^+ < Li^+ < K^+ < Cs^+ = R_4N^+$. Lactamates of transition metals (e.g., Cr^{3+}) and other metals (e.g., Al^{3+}), exhibiting high electronegativity values and

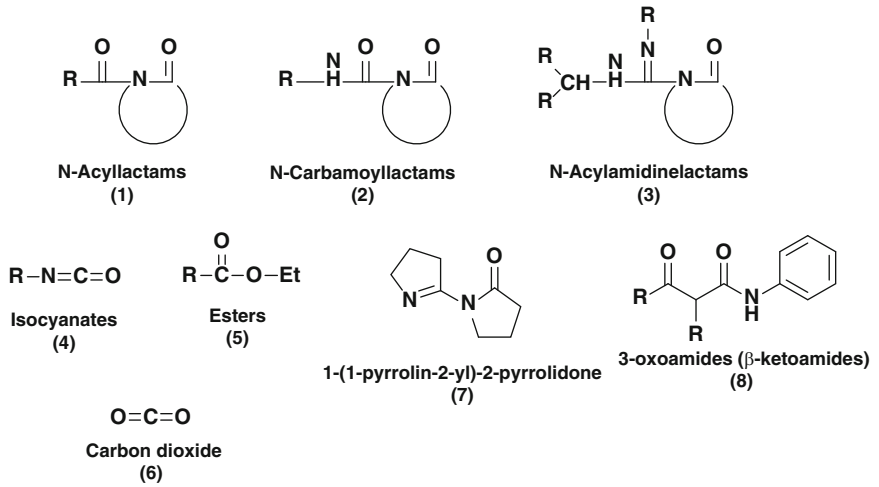
having very low dissociation constants, hardly dissociate even at high temperatures. In the molten monomer medium, without solvating or complexing species, the lactamate dissociation depends on both the lactam properties (i.e., acidity, dielectric permittivity, donor-acceptor capability, substituents) and the electropositivity of the metal. For example, higher lactam permittivity, such as in ω-laurolactam as compared to ε-caprolactam, makes easier the salt dissociation [427].

An induction period and slow kinetics are observed with non-activated anionic polymerization of lactams, whereas opposite behaviors are obtained when an activator is added. The induction period is absent, and the AROP can be performed at much lower temperatures (130–180 °C for ε-CL) [410]. Poorly reactive lactams, such as 2-pyrrolidone and 2-piperidone, can be polymerized by initial reaction of monomers with an acylating agent. In this activated mechanism, the slow self-initiation step is strongly minimized to the detriment of a fast acylation reaction and propagation step. The interest to work with milder conditions for shorter times allows to strongly reducing side reactions, yielding more regular macromolecular chains. These observations are nevertheless dependent on structure and concentration of the activators. Many substances can be used such as N-substituted lactams (*N*-acyllactam (1) [428, 429] and carbamoyllactam (2) [430–434] with electronegative substituent (R) increasing the acylating ability of the cyclic acyl group), compounds capable of producing *N*-substituted lactams, under the conditions of the anionic polymerization (e.g., isocyanate (4), acid halides or esters (5), carbon dioxide (6)) [428, 435–437] and derivatives from side reactions (C-, N-, O-acylation) in low ring strain lactam monomers such as oxoamides type (8), *N*-acylamidine (3), and others (7) (Scheme 37).

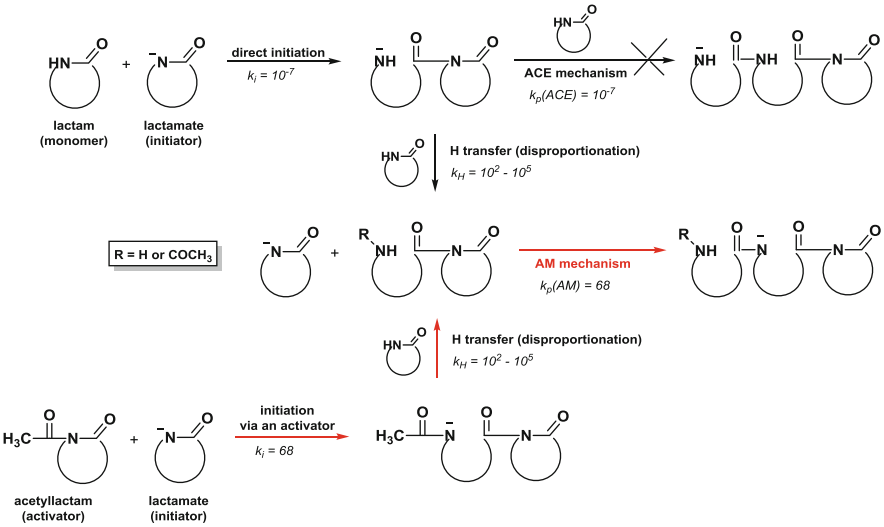
4.2.2 Propagation Reaction

The slow formation of an *N*-acyllactam by reaction between monomer and lactamate ion ($k_i = 10^{-7}$ L·mol^{-1}·s^{-1} for sodium ε-caprolactamate at 160–190°C) [438] is followed by an extremely fast neutralization reaction, i.e., monomer deprotonation. For pyrrolidone at 35 °C and laurolactam at 160 °C, the rate constant of proton exchange (k_H) is 10^5 L·mol^{-1}.s^{-1} [439] and 10^2 L·mol^{-1}·s^{-1} [440], respectively, which prevent the process of ring-opening of lactam via an active chain-end (ACE) mechanism (i.e., $k_{p(ACE)} \sim k_i \sim 10^{-7}$ L·mol^{-1}·s^{-1}) (Scheme 38). The nucleophilic attack of the lactamate anion on the carbonyl group of the monomer is much slower than that of the carbonyl group in an N-acyllactam-type chain end ($10^{-1} < k_{p(AM)} < 10^3$ L·mol^{-1}·s^{-1}, $k_{p(AM)} = 68$ L·mol^{-1}·s^{-1} in the case of ε-caprolactam) [441], which refers to the process of ring-opening polymerization of lactam via activated monomer (AM) mechanism (Scheme 38).

The propagation step is therefore composed of a nucleophilic attack to the acyllactam-type growing chain end ($k_p < 10^3$ L·mol^{-1}·s^{-1}) and a subsequent very fast proton transfer from the monomer to the amidate ($k_H \sim 10^2$–10^5 L·mol^{-1}·s^{-1}) (Scheme 39). The neutral *N*-acyl lactam acts as the growth center at the chain end as the exocyclic carbonyl group in the *N*-acyl lactam increases the electron deficiency



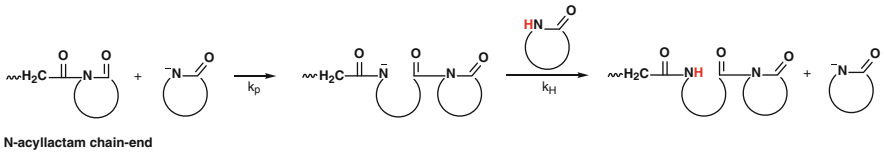
Scheme 37 Main activators in anionic lactam ring-opening polymerization



Scheme 38 Formation of active species in anionic ring-opening polymerization of ε-caprolactam: activated monomer (AM) mechanism vs. active chain-end (ACE) mechanism

of the amide group and, thus, the acylating ability. The polymerization rate is first order with respect to lactamate (L^-) and *N*-acyllactam (Act) concentrations and zero order with respect to lactam monomer (L) concentration [438] and can be written as follows .

$$-\frac{d[L]}{dt} = k_p[\mathrm{Act}][L^-]$$

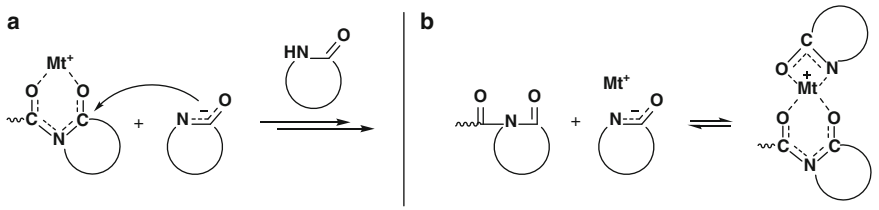


Scheme 39 Propagation step in anionic ring-opening polymerization of lactams via activated monomer mechanism

In the activated polymerization, the number average molar mass is determined by the concentration of the activator as compared to monomer concentration. Experimental values are generally higher than the theoretical ones. This is mainly due to the lowering of the number of growth centers due to the side reactions and to the cross-linking between polymer chains, for example, by Claisen-type condensation reactions, which are more and more relevant as the medium basicity and the polymerization temperature increase [442]. Such a polymerization is thus not living because of these side reactions. When the polymerization is run at temperatures below the melting point of the polyamide, side reactions are largely reduced, and, even at equimolar concentrations of initiator and activator, the polymerization proceeds essentially by the reaction of lactam anions with a constant number of growth centers, resulting in a narrower molar mass distribution ($D < 2$) [443] and the formation of high molar masses [434, 444]. In the non-activated polymerization where the growth centers are both formed at the very beginning and in the final stage, the molar mass distribution is expected to be broader than the ones observed with the use of an activator.

The structure of the activators, in particular the nature of the exocyclic acyl group in *N*-acyl lactam, was shown to play a crucial role on the polymerization rates [445]. "Very fast" activators, like of *N*-carbamoyl lactams in appropriate concentration, allowed to drastically reducing the polymerization time (less than a minute) [434, 446] to get high polymer yield, with the advantage to enable a decrease of polymerization temperature down to 140 °C, minimizing side reactions.

Concerning the mechanism, lactamolytic mechanism proposed by Sekiguchi [447–449] (Scheme 40a) assumes transfer of the alkali metal cation from the activated monomer species to the imide group at the end of the growing chain and its coordination to the carbonyls of the imide. A conductivity increase was attributed to a higher concentration of free ions. The reaction proceeds via formation of an alkoxide-type anion by nucleophilic attack of the lactam anion on the endocyclic carbonyl, proton exchange with monomer, and rearrangement with ring-opening. Alternatively, Frunze et al. [450, 451] proposed the participation of ion pairs of lactam salts in the propagation step and suggested an ion-coordination mechanism. According to this mechanism, complex between the lactamate and the two carbonyl groups of the growing center is formed (Scheme 40b). As already mentioned, side reactions are observed whatever the assumed mechanisms. In any case, free ions play a decisive role at high temperatures and in media of high



Scheme 40 Lactamolytic (**a**) and ion-coordinative (**b**) mechanisms

permittivity, while at low temperatures and in low polar media, the involvement of ion pairs is more expected.

4.2.3 Side Reactions

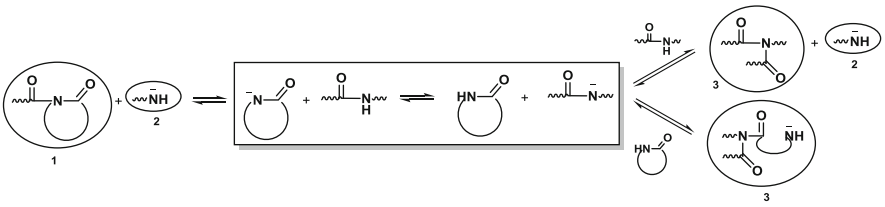
Species involved in anionic polymerization are generally highly reactive, leading to a series of side reactions, in particular at high temperatures for long polymerization times. Reversible and irreversible side reactions can occur, consuming both the growth centers and the monomer anions. The strongly basic conditions in AROP of lactams promote mainly polymer branching and β-keto compounds, yielding to side products and chain irregularities. UV spectrometry was shown to be a powerful tool for monitoring the occurrence of such side reactions [414, 442, 452].

Formation of Acyllactams, Amines, and Imides

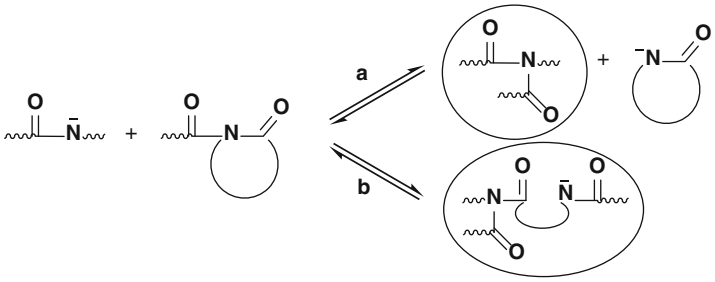
The polymer amide groups may be involved in disproportionation reactions, forming acyl lactams and amine end groups (Scheme 41). The presence of amide N anions along the polymeric chain, derived from equilibrium reactions with lactam anions in strongly basic medium, may also produce imide groups and polymer branching (Scheme 41). Transacylation reactions between polymer amide anions and acyl lactams (N-acylations) (Scheme 42) may cause depolymerization or incorporation of a lactam unit when the exocyclic (Scheme 42a) or the endocyclic carbonyl groups (Scheme 42b) are involved. The nature of the counterion affects not only the degree of dissociation of the corresponding lactamates but also the whole polymerization rate [453].

Formation of β-Ketoimides and β-Ketoamides

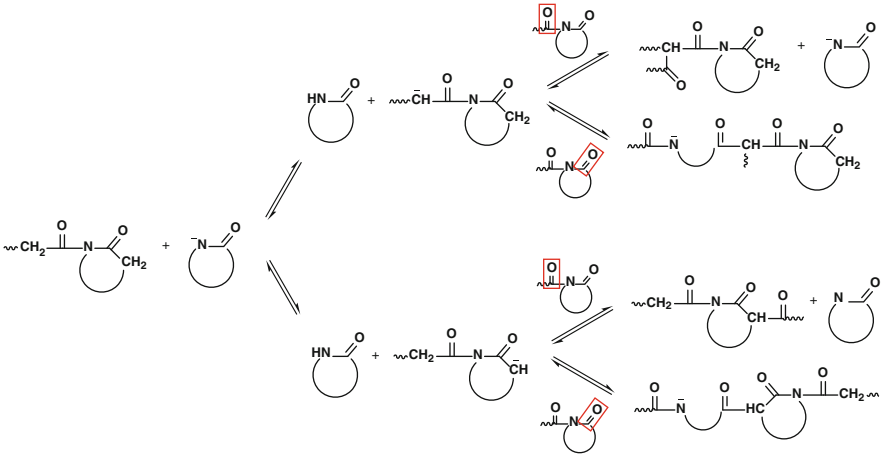
The acidity of the hydrogen atoms in α position of the carbonyl of the imide group in the *N*-acyl lactam chain end is comparable to that of hydrogen in an amide group. As a consequence, in the presence of lactamate, deprotonation may occur, leading to the formation of two distinct carbanions (Scheme 43). The Claisen-type condensation reactions on exo- and endocarbonyls then happen, giving four different



Scheme 41 Formation of acyllactam (*1*), amine (*2*), and imide (*3*) groups during AROP of lactams

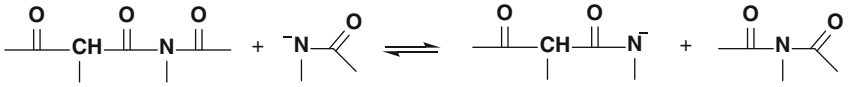


Scheme 42 Formation of imide groups by N-acylation

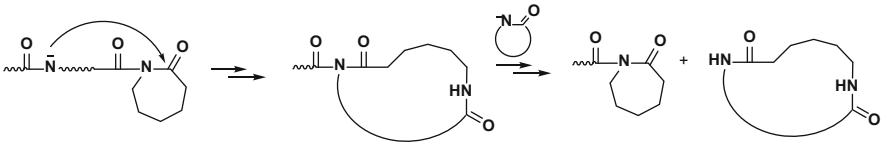


Scheme 43 Formation of carbanions followed by β-ketoimides during AROP of lactams

β-ketoimide structures. The concentration of these carbanions is generally low meaning that C-acylations and, only in some specific cases, O-acylations are competitive reactions with regard to the propagation step [454]. One can also consider the formation of carbanion in the α-position of the carbonyl of a branched structure. Reactivities are related to the lactam size and their substituents, the nature of the activator, the initial ratio of initiator and activator concentrations, the



Scheme 44 Formation of a β-ketoamide from acylation of β-ketoimide



Scheme 45 Formation of cyclic oligomers by intramolecular reactions

permittivity of the reaction medium, and the reaction temperature as well as the nature of the counterion [454–456].

Neutral β-ketoimides are strong acylating agents and may be involved in reactions, acting as growth centers and leading to either linear or branched chains. β-Ketoimides may be converted to β-ketoamides (2-oxoamides) by nucleophilic attack of the N anion on the carbonyl of the imide group (Scheme 44). These keto derivatives decrease the concentration of active species and thus influence kinetics. They are also very reactive under basic conditions or at high temperatures and responsible for complex secondary reactions, i.e., formation of water, carbon dioxide, amines, and heterocyclic structures which are able to act as branching and cross-linking points [454]. The thermal or base-catalyzed decomposition of β-ketoamides can afford ketones and isocyanates. The latter reactive functions can also reform *N*-acyl lactams capable to react in the expected polymerization way. Formation of water can contribute to the deactivation of lactamate and to the hydrolysis of *N*-acyl lactams, β-keto compounds, and imide branching points leading to carboxylates, amine groups, ketones, carbon dioxide, or carbonates [410].

Formation of Cyclic Oligomers

The formation of cyclic oligomers was particularly investigated by Russo and coll. for ε-caprolactam [452, 457], their amount depending on the polymerization temperature (e.g., 3.5 % at 280 °C). The main reaction leading to cyclic oligomers is a back-biting reaction which is an intramolecular reaction of the neutral end groups with amidic groups inside the chain (Scheme 45). The counterion involved in the polymerization also directly influences the occurrence of such a side reaction [458]. With magnesium salts of ε-CL, cyclization reactions are strongly reduced both below and above the melting temperature of the polymer as compared to sodium systems, due probably to coordination between magnesium-based compounds and polyamides end groups. Cyclic structures can have a negative influence on processing or applications as they are able to modify the crystalline structure in the solid phase [459, 460].

4.3 Anionic (Co)polymerization of ε-Caprolactam and ω-Laurolactam

4.3.1 Homopolymerization of ε-Caprolactam and ω-Laurolactam

The polymerization of ε-caprolactam, a 7-membered ring, is usually conducted in bulk conditions, above the melting temperature of the monomer (80 °C) in the presence of initiator and activator. Initially liquid, the mixture turns turbid and then solidifies in the course of the polymerization which can be as fast as few tens of seconds for "very fast" systems. The beginning of solidification is considered as the moment at which the growing chains attain a critical length that enables their crystallization, forming spherulites insoluble in the monomer.

As discussed previously, playing with the structure and concentration of both activator and initiator allows tuning the polymerization rate of ε-CL. The initial polymerization temperature and isothermal, nonisothermal, or adiabatic conditions are also considered as tools to modify the time of reaction. "Very fast", "fast," or "slow" processes affect the structure and properties of the resultant anionic polyamide 6. For a very fast bulk polymerization of ε-CL at 155 °C, conditions close to adiabatic ones are obtained due to high rate and poor heat exchange with the surroundings. A temperature increase of 50 °C is observed with a resultant polymer with high molar mass, low residual monomer content, and low cyclic oligomers [408, 434]. To decrease even more side reactions, quasi-isothermal conditions near 150–160 °C were proposed [433].

Similar polymerization systems and conditions were employed for the synthesis of polyamide 12 obtained by ring-opening of ω-laurolactam (ω-LL), a 13-membered ring. The polymer gained attention for its low level of absorbed moisture, easily removable during heating and melting of the monomer at 150 °C. Moreover, it possesses an excellent ductility, good electrical properties, and significant chemical resistance. However, due to the long methylene sequences between the amide linkages, it has a lower melting point (172 °C) compared to PA6 (210 °C). To get a low content of residual monomer due to favorable monomer-polymer equilibrium, temperatures above 150 °C are generally required [444, 461]. Some specific polymerization systems, based on alicyclic carbodiimide as activator and sodium caprolactamate as initiator, were also developed to allow, for instance, a long-term storage of the initiating species, an efficient control of the polymerization rate, and an accurate tailoring of polyamide molar masses [462]. As for ε-CL, initiation and activation influence also polymerization kinetics and thermodynamics but also the degree of crystallinity [463].

As discussed in the previous paragraph, the AROP of lactams suffers from numerous (ir)reversible side reactions, depending on the experimental conditions. The usual kinetic law depending on activator and initiator concentration ($R_p = -d[M]/dt = k_p \cdot f\ [\text{Activator}]\ [\text{Initiator}]_0$) appears not efficient to get right values but might be sufficient to compare polymerization systems. The autocatalytic model of Malkin, based on a phenomenological approach, seems the most successful to

follow activated polymerization in bulk [464]. It describes the nonisothermal kinetics of both ε-caprolactam and ω-laurolactam, monitoring the temperature rise inside the reactor:

$$-\frac{\mathrm{d}[\lambda]}{\mathrm{d}t} = k\frac{[A]^2}{[M]_0}(1-\lambda)\left(1+\frac{\mathrm{b}\lambda}{[A]}\right)\exp\left(-\frac{Ea}{RT}\right)$$

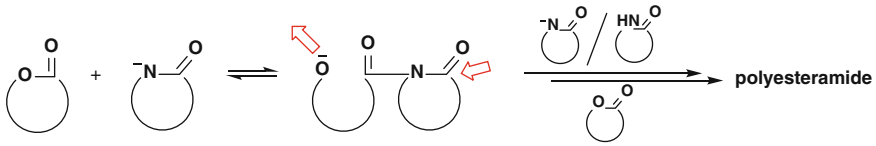
with λ the conversion, $[A]$ the activator concentration, $[M]_0$ the initial monomer concentration, k the reaction rate constant, Ea the activation energy, and b the autocatalytic term characterizing the intensity of the self-acceleration effect during chain growth. Both k and b depend on the chosen activator. The rate constant can be evaluated for low conversions where polymerization and crystallization are not overlapped.

4.3.2 Copolymerization of ε-Caprolactam and ω-Laurolactam

Anionic polymerization is well known and used for the synthesis of copolymers, in particular blocks, due to its living character. Despite the nonliving character of lactam polymerization, copolymers based on polyamide can be synthesized and offer interesting and specific properties. ω-Laurolactam is in general used as co-monomer of ε-caprolactam in order to extend the range of PA6 properties [429], in particular by increasing the notched Izod impact strength at low temperature, and the decrease of water absorption [465]. Roda and coworkers showed the influence of the initiator toward the copolymer structures and therefore properties [461, 466]. As compared to ε-caprolactam magnesium bromide, sodium caprolactamate exhibits higher polymerization activity especially in copolymerization with high content of ω-LL at high polymerization temperatures. The copolymers have only one melting endotherm in the whole range of monomer feed and one single crystalline form, when two melting endotherms (140 °C and 210 °C) and two types (α and β) of crystalline forms are observed from 30 to 70 mol% of ε-CL with the magnesium-based initiator. This is explained by a copolymer microstructure composed of PA6 blocks linked to sequences of ε-CL/ω-LL random copolymer. PA6 is preferentially formed at the beginning of the polymerization, due to the much higher reactivity of ε-CL as compared to ω-laurolactam. Random copolymers are then formed from the remaining ε-CL and slowly reacting with ω-LL. In the case of sodium caprolactamate which is a strong base as compared to the magnesium derivative, transamidation reactions cause full randomization of the sequences.

4.3.3 Copolymerization of Lactams and Lactones

Interesting degradable polyamides could be obtained through the synthesis of polyesteramides by copolymerizing lactams and lactones even if different anionic ring-opening mechanisms are involved in their homopolymers formation



Scheme 46 Parallel initiation of lactams and lactones in the presence of lactamate

[412]. Some lactones were shown to act both as activator of lactam polymerization and as co-monomer for the synthesis of a polyester block [436, 467–469]. The initiation step corresponds to the acylation reaction between a lactamate and the reactive lactone (Scheme 46). The oxyanion formed is then able to initiate the rapid ring-opening polymerization of some cyclic esters such as ε-caprolactone or δ-valerolactone by usual chain growth mechanism (active chain end).

Playing with ε-caprolactam and ε-caprolactone ratios as well as experimental conditions, various random or multiblock copolymers were prepared. Fast transacylation reactions between ester and amide groups in the copolymer chains were proposed to be responsible for the observed copolymer randomness. Using reactive processing like a twin-screw extruder, diblock or triblock copolymers were prepared from various lactams and lactones using suitable sequential monomer feeding and specific temperature profiles [470–472]. The block lengths can be adjusted by controlling the feed rate. The use of poly(ε-caprolactone) (PCL) was also proposed as additive to the polymerization of ε-CL with ε-caprolactam magnesium bromide as initiator, with or without activator. PCL was shown to act as an activator, and random copolymers were prepared [473].

4.3.4 Polyamide-Based Copolymers with Non-polyamide Blocks

The use of macroactivators obtained from appropriately terminated prepolymers is the main route leading to lactam-based block copolymers. In general, hydroxy telechelic polymers are reacted with diisocyanates and then blocked with ε-CL. Combination of properties is the driving force of reacting various non-polyamide blocks as activators of anionic lactam polymerization. The toughness improvement of PA6 being a key issue, soft polymers such as polybutadiene [474–477], polyethers [478–483], and polysiloxanes [480, 484, 485] were particularly used. Following a similar approach, Styrene-Butadiene Rubber was also introduced into PA6 with the aim to tune the mechanical properties [486]. Graft copolymers were also designed for compatibilization purpose. Polypropylene or polystyrene grafted with polyamide-6 chains was easily obtained [430, 487–490].

4.3.5 Industrial Processes Using AROP of ε-Caprolactam and ω-Laurolactam

Ring-opening polymerization of ε-caprolactam initiated by water, i.e., the hydrolytic mechanism, is carried out for industrial cast nylon-6. Nowadays, due to fast kinetics of the "activated" anionic ring-opening polymerizations, this approach is more and more envisaged for the preparation of PA6 and PA6-co-PA12 in newly developed industrial applications using mainly powdered materials and molding or extrusion approaches.

Powdered Polyamides

As compared to techniques industrially utilized so far, i.e., low-temperature grinding and polymer dissolution/precipitation, AROP yielding PA6 and PA6-co-PA12 offers some advantages such as a much higher particle porosity, a total absence of irregular edges and sintered zones, and a controlled and narrow particle size. Dispersion [491–496], suspension [497], and miniemulsion [498] polymerizations are generally proposed. More recently, the use of phase inversion in PA6/PS blends allowed the preparation of microspheres with controlled diameters [499]. Fast polymerization systems have to be selected for such processes. The suspension method has the advantage to be the faster but suffers from difficult and expensive purification. Such materials are of great interest for cosmetic formulations, coating and graphic art applications, protein or enzyme immobilization techniques, rotational molding and sintering processes, chromatography applications, as well as filtration devices in food and beverage industry.

Molding and Extrusion

Reaction injection molding (RIM), resin transfer molding (RTM), rotational molding, and reactive extrusion are the main processes used with an in situ activated anionic polymerization of ε-CL [500, 501]. Due to its high crystallinity and high molar mass, anionic PA6 exhibits, for instance, better thermomechanical properties or lower water uptake as compared to the extruded or molded PA6. The short polymerization times in the order of minutes, as compared to hours for hydrolytic polymerization, the very low cyclic oligomer content, and the much lower initial polymerization temperature (130–170 °C vs. 230–280 °C) are the main advantages of this activated AROP.

Soft polymers bearing terminal *N*-acyl lactam groups are used in RIM processes as activators of ε-CL polymerization yielding PA6 with good impact strength. Usual initiators such as sodium ε-caprolactamate or magnesium bromide ε-caprolactamate are efficient in that process [502]. RTM enables the injection of the melted monomeric reactants of low viscosity into a mold filled with reinforcing

materials like fibers. Reactive extrusion processes regain also attention for the easy preparation of nanocomposites and nanoblends [501, 503–506]. Single- or multiwalled carbon nanotubes and nanosilica are also shown to be dispersed in PA6 modifying its initial properties [507, 508]. Nevertheless, it has to be mentioned that anhydrous conditions are required and may sometimes be considered as a limitation. Deactivation of the anionic groups is known to occur when some clays are used as reinforcing agents.

4.4 Anionic Polymerization of Other Lactams

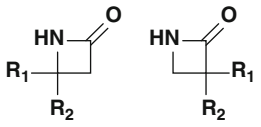
β-Lactams, 2-pyrrolidone, and 2-piperidone are the three main unsubstituted lactams available and studied by AROP. They are, respectively, yielding polyamide-3, polyamide-4, and polyamide-5. It has to be noticed that *N*-substituted polyamide-1 as well as polyamide-2 (polypeptide) is not obtained from lactams but from oxadiazolinones and *N*-carboxyanhydride, respectively.

4.4.1 β-Lactams

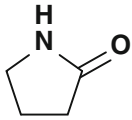
Living anionic polymerization can be reached as substituted β-lactams (or -β-propiolactams) (Scheme 47) are highly reactive, due to high ring strain, enabling thus the use of low polymerization temperatures and times. The review of Hashimoto published in 2000 describes in detail the specificities of the ring-opening polymerization of such monomers [411].

Šebenda et al. showed first that the activated anionic polymerization of a bulky β-lactam, i.e., 3-butyl-3-methyl-2-azetidinone, has a living character giving a monodisperse polyamide of molar mass very close to the theoretical value [509, 510]. Other substituted monomers were also polymerized in a controlled manner in homogeneous solution, using aprotic and apolar solvents like *N*,*N*-dimethylacetamide, DMF, or DMSO in the presence of lithium salts [511–513]. Depolymerization and transamidation both at the acyl lactam chain end and on the polyamide chain are known to occur, therefore broadening the molar mass distribution [411]. Stopping the reaction before complete conversion minimizes the transamidation, enabling the preparation of block and graft copolymers or other structures taking advantage of the living character of the polymerization. The possibilities to play with substituents offer nowadays PA3 materials with amphiphilic character and possibly bioactivity, for instance [514].

Scheme 47 Structures of β-lactams



Scheme 48 Structure of 2-pyrrolidone



4.4.2 2-Pyrrolidone

The particularity of the polymerization of 2-pyrrolidone (Scheme 48), leading to polyamide-4, can be found in a rather low ceiling temperature (70 °C) limiting the reaction temperature to 50 °C [515]. In bulk conditions, economically more interesting than in solution, polymerization rate decreases with time, and partial conversion is obtained due to a phase separation, nucleation, and crystallization with occlusion of the growth centers in this solid phase [516–518]. Despite some potential industrial interests in textile for its good mechanical properties and hydrophilic behavior similar to cotton, synthesis difficulties are one main reason for its non-development.

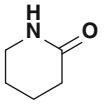
Similar to ε-caprolactam polymerization, CO_2 was also proposed as activator to successfully prepare PA4 with an improved thermal stability [435, 519]. But depolymerization still remains a major drawback. Using quaternary ammonium salts of 2-pyrrolidone as initiator, instead of sodium or potassium ones, and *N*-acetyl-2-pyrrolidone as activator, yields up to 80 % could be obtained after 24 h at 30 °C [416]. It is assumed that bulky counterion allows the breaking of hydrogen bonds between polymer chains and creates local irregularities of the crystalline structure, enabling the contact between lactamates and reactive chain ends. Suspension polymerization can also be used [520], and whatever the process used, polyamide-4 was obtained free of structural irregularities thanks to the low polymerization temperature and limited conversions. Block copolymers containing PA4 segments could be obtained using the macroactivator approach [521]. The synthesis of PA4 with a terminal azide function [522] or with ε-CL as co-monomer above the ceiling temperature of 2-pyrrolidone was also performed [523, 524].

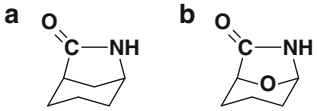
4.4.3 2-Piperidone

The ring-opening polymerization of 2-piperidone, also called 2-piperidinone or δ-valerolactam, is kinetically slow due to its stable 6-membered ring [406] (Scheme 49). Moreover, crystallization and side reactions contribute also to the slowness of the reaction. The use of activators is mandatory, and relatively high molar masses of PA5, with a melting temperature of 283 °C, were obtained with quaternary ammonium salts of monomers used as initiators [516, 525].

The use of bicyclic lactams is proposed as an alternative, the ring strain being favorable to a faster AROP.

Scheme 49 Structure of 2-piperidone





Scheme 50 Structures of a bicyclic lactam, i.e., 6-azabicyclo[3.2.1]octan-7-one (**a**) and of a bicyclic oxalactam, i.e., 8-oxa-6-azabicyclo[3.2.1]octan-7-one (**b**)

4.4.4 Bicyclic Lactams

The key point in the AROP of bicyclic lactams is indeed the ring strain, coming, for instance, from the repulsion of hydrogen atoms, and its release. At first, Hall reported in the 1960s the polymerization of a bicyclic lactam, i.e., the 6-azabicyclo[3.2.1]octan-7-one (Scheme 50a), in the presence of sodium hydride [526, 527]. Hashimoto proposed a detailed review in 2000 relative to bicyclic and heterobicyclic lactams [411]. High temperatures are generally required limiting the livingness of such polymerizations. For the case of bicyclic oxalactams (Scheme 50b), the polymerization could be run at 25 °C in DMSO due to a high kinetic polymerizability related to the high strain of internal bond angles [528, 529]. A living character was observed till 60 % of conversion.

5 Cyclosiloxanes and Other Cyclic Silicon-Based Compounds

5.1 Introduction

Cyclic silicon-containing monomers associated, or not, with oxygen, nitrogen, and carbon represent the main reactants toward the synthesis of silicon-based polymers by anionic polymerization. Their ring-opening leads to polysiloxanes and polycarbosiloxanes, polysilanes and polycarbosilanes, polysilazanes, and a few other silicon-containing polymers. The possibility to vary the molecular structure, of both the main chain and the side groups, enables the modulation of unique physicochemical properties which make them attractive in academic field as well as for industrial applications in some cases. Ring-opening polymerization (ROP) of cyclic oligomers allows in general a better precision in terms of chain lengths and molecular weight distributions than the polycondensation of functional precursors. Both cationic and anionic mechanisms can undergo polymerization of certain monomers, but a stringent control of the reaction conditions is required in order

to avoid the formation of by-products, such as short oligomers and rings [530]. Recent reviews [531–534] may add complementary information to this chapter focusing on silicon-containing polymers obtained by anionic polymerization. ROP of strained rings exploits the release of ring strain as the thermodynamic driving force [535]. It proceeds either by kinetic or thermodynamic control, which has noticeable consequences for the product distribution. Under kinetic control, the selective cleavage of the precursors and chain propagation occur almost exclusively, providing high molar mass polymers and barely any by-products. Under thermodynamic reaction control, equilibrium mixtures are obtained which generally consist of low molar mass polymers and high amounts of smaller oligomers and ring species.

5.2 *Cyclosiloxanes*

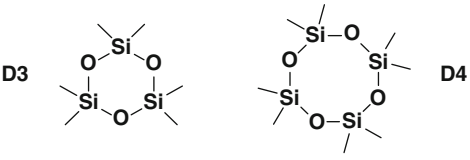
5.2.1 Polymerization Generalities

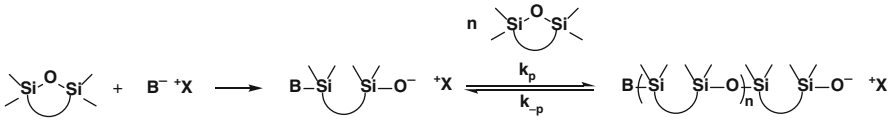
Anionic ring-opening polymerization (AROP) of cyclosiloxanes involves the cleavage of the Si-O bond in the monomer ring and the subsequent regeneration of this bond in a polymer chain. Among the various siloxane monomers, the two most important are hexamethylcyclotrisiloxane (D3) and octamethylcyclotetrasiloxane (D4) (Scheme 51).

Other cyclosiloxanes derived from these monomers are also available by substitution of methyl with various organic groups, such as vinyl, phenyl, fluoroalkyls, etc. Three-dimensional structures, i.e., silsesquioxanes or multicyclic siloxanes, are also available and attractive precursors. Cyclic organosiloxanes are usually prepared by hydrolytic polycondensation of dichlorodialkylsilane (R_2SiCl_2) or a mixture of α,ω-dichlorooligosiloxanes ($Cl(R_2SiO)_{n-1}R_2SiCl$) [536, 537]. Other routes are also proposed in the literature [538–540].

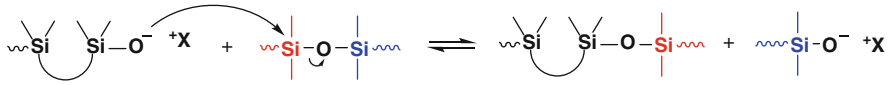
Initiation step requires strong bases (inorganic, organic, or organometallic), able to ring-open cyclosiloxanes and form silanolate anion, the active propagating species (Scheme 52). Alkali metals, ammonium, and phosphonium salts are the most used derivatives [533, 541]. The propagation is reversible leading to a backbiting reaction with the formation of cyclic structures of various ring sizes. Chain redistribution also occurs due to the nucleophilic attack of a silanolate to another growing polymer chain (Scheme 53). To get nonequilibrium AROP of

Scheme 51 Structure of hexamethylcyclotrisiloxane (D3) and octamethylcyclotetrasiloxane (D4)





Scheme 52 Initiation and propagation/back-biting of cyclosiloxanes by AROP



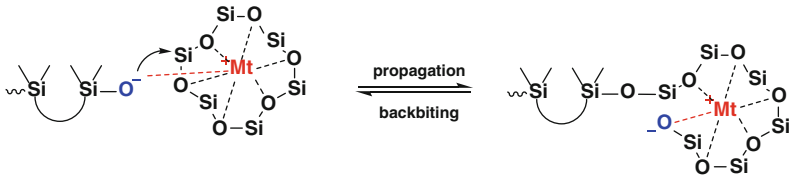
Scheme 53 Chain redistribution in AROP of cyclosiloxanes

cyclosiloxanes in order to minimize those re-equilibration reactions occurring during the final stage of the reaction, the polymerization must be quenched soon after a high monomer conversion is obtained [542].

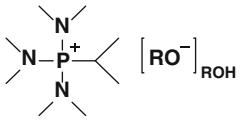
Polymerization kinetic is dependent on monomer and initiator concentrations as well as experimental conditions. Ion pairs are the main active centers involved in the determination of the polymerization rate [533]. Free silanolate anions are not present in sufficient concentration to play a role, in contrary to aggregated species which are in equilibrium with ion pairs [533, 543, 544]. Fractional order in silanolate is introduced in the kinetic law of AROP of cyclosiloxanes due to the existence of less reactive or inactive aggregates.

The aggregation phenomenon can be minimized when bulky cations or additives are used. The polymerization of D3 initiated by trimethylammonium salts shows a first-order kinetic [545]. The rate of polymerization is directly related to the size of the counterion and increases in the series: $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+ \sim {}^+NR_4 \sim {}^+PR_4$ [546]. Hexamethylphosphorous triamide, dimethylsulfoxide, dimethylformamide, *N*-methylpyrrolidone or cryptands, and crown ethers were shown to act as deaggregating agents [547–553]. Ring strain affects also the polymerization rate constants with the following order: D3 > > D4 > D5 > D6. Cyclotrisiloxanes show a remarkable high reactivity thanks to its ring strain and planar conformation [554]. Nevertheless, unexpected enhanced reactivity was observed with unstrained cyclodimethylsiloxanes in the order D4 < D5 < D6 < D7 < D8 when alkali metal were used in bulk or nonpolar solvents [533, 555, 556]. Multidentate interactions of siloxane units of the monomer with the counterion can explain this observation (Scheme 54). Lithium derivatives such as silazane lithium salts ($(RMe_2Si)_2NLi$), in the presence of promoters such as DMSO, were shown to initiate the AROP of D4 at elevated temperatures in high yields. The resulting polymers exhibited relatively narrow distribution which broaden gradually with time [557]. Propagation in this system is faster than the redistribution reactions, which lead to equilibration.

Organic initiators were more recently proposed for the AROP of cyclosiloxanes. Phosphazene bases, i.e., *t*-BuP_4, acts as a deprotonating agent of a proton donor



Scheme 54 Multidentate interactions of D6 with alkali metal in bulk



Scheme 55 Deprotonated alcohols by phosphorus ylides for the initiation of AROP of cyclosiloxanes

molecule such as an alcohol, leading to the formation in that case of an alkoxide of phosphazenium. Its bulkiness and stabilized positive charge, thanks to the resonance effect, enable an instantaneous polymerization of D4 [101, 558]. Similarly to the chemistry developed with cyclic ether monomers, the combination of lithium and phosphazene bases is also very efficient for the polymerization of cyclic siloxanes [559]. Within the same family, the direct use of amino-substituted oligophosphazenium hydroxides (P_5OH) enables to get polydimethylsiloxane in toluene with a first order both in monomer and base, and a faster rate than lithium cryptate systems [549, 560, 561]. Alcohols deprotonated by phosphorus ylides [562] were also proposed as initiators of D4 with the particularity to be thermolabile, facilitating its removal from the final polymer (Scheme 55). N-heterocyclic carbenes expressed also some interests thanks to the presence of alcohols as co-initiator and regulator of chain length [563].

Although polysiloxanes are not ordinarily considered stereoregular, some polymers enriched in stereoregularity are made from the cis-isomers of unsymmetrically substituted strained cyclosiloxanes. The monomers insert randomly at the reactive chain ends with equal probabilities of forming meso or racemic siloxane links while preserving the stereoconfiguration of the original monomer [564]. An advantage of stereoregularity was shown on the mechanical properties of a silicone elastomer [565].

5.2.2 AROP in Solid State and Emulsion

These two processes can be used both in anionic and cationic ROP of cyclosiloxanes. The discussion will focus on the parameters and consequences of the anionic route.

A simple approach based on crushed potassium hydroxide or potassium silanolates added onto a cyclosiloxane gives high molar mass polymers with high dispersity and high yields [566–569]. Polymerization proceeds inward from the surface of the monomer crystals, producing a highly crystalline material. The highly ordered crystalline state of hydroxycyclosiloxanes provides a possibility of solid-state synthesis of stereoregular polysiloxanes.

Polymerization in emulsion is also proposed to conduct anionic polymerization of cyclosiloxanes [532]. The synthesis of poly(dimethylsiloxane) from D4 in aqueous emulsion using an emulsifying agent acting also as initiator (benzyldimethyldodecylammonium hydroxide) gives controlled molar mass, a low dispersity and high yields [570, 571]. The amount of cyclics formed (essentially D4–D7) is lower than that observed in bulk. Polymerization proceeds by a combination of the addition and condensation mechanism involving redistribution reactions. The first stage of the anionic polymerization process occurs at the siloxane-water interface or in the siloxane phase close to the surface. Once the chains reach a critical degree of polymerization corresponding to their loss of surface tension activity, they penetrate into the particles where side reactions such as redistribution and condensation occur. The rate is strongly dependent on the size of the surface, which is function of the concentration of emulsifier. Polycondensation is responsible for a rapid increase in molar mass observed at high monomer conversions. Another α,ω-dihydroxy-terminated polysiloxane of low molar mass, issued from the polymerization of 2,4,6-trimethyl-2,4,6-tris(3,3,3-trifluoropropyl)cyclotrisiloxane with an anionic miniemulsion process, was also obtained [572]. The kinetic study showed that polymerization occurs in two stages. During the first stage, which corresponds to the nonequilibrium AROP, the maximum yield is close to 100 %, and the dispersity remains narrow (1.3). The second stage involves condensation and back-biting reactions leading to an increase of both molar masses, up to 60,000/mol, and dispersity (2.0). This approach was developed for other homopolymers [573] and copolymers [574].

5.2.3 Copolymerization and Functionalization

Anionic ring-opening polymerization offers possibilities in the controlled synthesis of functionalized polysiloxane polymers and copolymers. Functionalized initiators and terminators are currently used in nonequilibrium polymerization to introduce functional groups to one or both ends [548, 575–581]. The AROP allows the synthesis of block copolymers [550, 582–588], graft copolymers [589, 590], star polymers [544, 548, 591, 592], and polymeric networks [577, 581]. Alternating copolysiloxanes were also prepared by a regioselective polymerization of cyclosiloxanes containing different siloxane units. It depends strongly on the nature of counterion [593, 594]. Simultaneous polymerization of a mixture of cyclosiloxanes gives polymers with a composition depending on Mayo-Lewis reactivity ratios only when the propagation reactions are irreversible. Gradient copolysiloxanes can be obtained starting from cyclotrisiloxane monomers

[595]. Equilibrium copolymerization of cyclotetrasiloxanes leads to random structures [596, 597]. As usual, copolymers aim at broadening the scope of properties and applications. For instance, the introduction of methylphenyl or diphenylsiloxane units to PDMS helps to improve thermal, oxidation, or radiation stability, whereas fluoroalkyl groups enhance their resistance to fuel and oils.

5.3 *Other Cyclic Organosilicon Monomers*

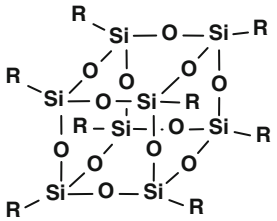
5.3.1 Silsesquioxanes, Cyclic Carbosiloxanes, and Cyclic Silaethers

These three monomers are very similar to the cyclosiloxanes family as they can be polymerized anionically by breaking a siloxane bond.

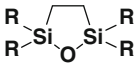
Silsesquioxanes, of empirical formula $RSiO_{3/2}$, represent a wide class of more or less ordered three-dimensional structures (Scheme 56). They are intermediate structures between siloxanes (O/Si = 1) and silica (O/Si = 2). They are usually generated by hydrolytic condensation of trialkoxy- or trichlorosilanes. Numbers of reviews may give additional and detailed information about this compound and its properties and applications [598–601]. As an example, the anionic ring-opening copolymerization of D4 with polyhedral oligomeric silsesquioxanes (POSS) derivatives leads to cross-linked polysiloxanes exhibiting good thermal stability [602, 603].

Poly(carbosiloxane)s are obtained from high ring strain cyclic monomers, i.e., 1-oxa-2,5-disilacyclopentanes, having both carbosilane and silyloxy linkages (Scheme 57). Lithium or sodium silanolates were shown to initiate the polymerization in the presence of a polar solvating agent such as THF or dioxane to avoid aggregation of active centers [543, 604–606]. Strongly basic N-heterocyclic carbenes and guanidine derivatives in the presence of alcohols or other hydrogen bond donors were shown to allow the synthesis of poly(carbosiloxane)s with controlled molar masses [607] and also to cyclic poly(carbosiloxane)s in the

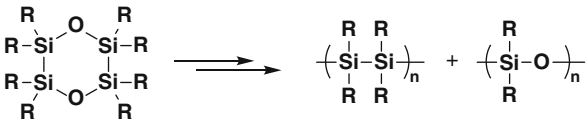
Scheme 56 Structure of an octaalkyl polyhedral oligomeric silsesquioxane



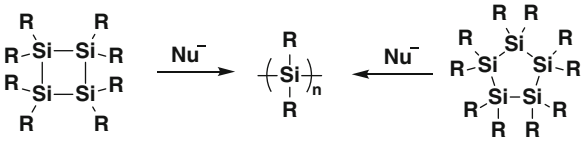
Scheme 57 Structure of cyclic carboxysiloxanes



Scheme 58 AROP of cyclic silaethers at equilibrium



Scheme 59 AROP of cyclosilanes



absence of alcohol [608]. Monomers bearing a chiral center could be synthesized and led to optically active polymers by AROP [609, 610].

The anionic polymerization of cyclic silaethers, or oxysilylenes, enables the cleavage of both the Si–Si and Si-O bonds, and lead to a polysilaether with an irregular structure and, at equilibrium, a mixture of polysiloxanes and polysilanes by rearrangement (Scheme 58) [611–613]. A silyl anion, as compared to a silanolate one, is a nucleophile able to initiate the polymerization of an ethylenic monomer. It was used for instance to change an alkoxide into a carbanion active center [613].

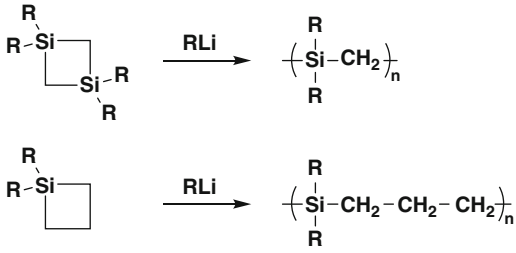
5.3.2 Cyclosilanes

Strained cyclosilanes were shown to ring-open anionically yielding high molar masses polysilanes (Scheme 59). Initiators such as butyllithium, silylpotassium, or lithium silyl cuprates were used with cyclotetrasilane [614–617] bearing methyl and/or phenyl groups. Diblock polystyrene-polysilane copolymers exhibiting a phase separation could be prepared using polystyryllithium to initiate the ROP of 1,2,3,4-tetramethyl-1,2,3,4-tetraphenylcyclotetrasilane in the presence of 12-crown-4 to enhance the polymerization [618]. Tetrabutylammonium fluoride and silyl potassium appeared efficient initiators for nonamethyl(phenyl)cyclopentasilane [619]. The strong affinity of fluoride anion to Si atom promoted the generation of silyl anion without any additives. The potassium initiator required the use of hexamethylphosphoramide or crown ethers promoters capable to solvate the potassium cation in order to enhance the reactivity of the silyl anion. Low temperature was needed (−78 °C) to reach high polymer yield (80 %), as well as quenching to prevent the back-biting reaction when temperature increases. Such a polymer is a kinetic product and cyclic oligosilanes are thermodynamically more stable.

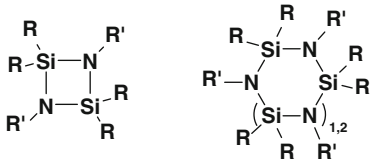
5.3.3 Cyclocarbosilanes

Polycarbosilanes are attractive materials as they contain only Si-C bonds in the backbone making them of interest as silicon carbide precursors used for the

Scheme 60 AROP of silacyclobutanes



Scheme 61 Structures of cyclosilazanes

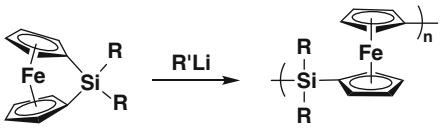


preparation of ceramic fibers. The anionic route offers an attractive way to ring-open strained silacyclobutane monomers using organolithium as initiators (Scheme 60) [620–625]. The polymerization yields high molar mass poly (silanediylmethylene)s with a strictly alternating SiR_2/CH_2 backbone structure. Depending on substituents in the ring and on the initiator, polymerizations may proceed in a controlled and living manner [626, 627]. Optically active polymers [628] as well as block copolymers based on silacyclobutane [629, 630] were also described. As cyclic silaethers, silacyclobutane may be used to transform a weak nucleophilic center into a more nucleophilic one. This makes possible the copolymerization of heterocyclics with vinylic monomers [631].

5.3.4 Cyclosilazanes

Despite the high reactivity with water, oxygen, etc., of Si-N bonds present in polysilazanes, obtained by ROP of cyclosilazanes (Scheme 61), these materials gained interest as precursors of Si-N and Si-CN ceramics through pyrolysis. Organolithium and organosodium are the typical initiators used in AROP leading to high molar masses in a living manner [632, 633]. The polymerization is kinetically controlled by the ring strain and by the steric hindrance around the nitrogen atom and/or the electronic effects of the R substituent on the Si-N bond [634, 635]. As a possible example, a pendant double bond could be introduced into a polystyrene-polysilazane block copolymer using 1,1,3,*N*,*N*'-pentamethyl-3-vinylcyclodisilazane as co-monomer added to living polystyryllithium [636]. Such a copolymer enabled the formation of cross-linked micelles and ceramic nanoparticles after pyrolysis.

Scheme 62 AROP of ferrocenylsilanes



5.3.5 Ferrocenylsilanes

Polyferrocenylsilanes (PFS) and polyferrocenylsilane block copolymers, where iron and silicon are present in the main chain, are obtained from AROP of strained ferrocenylsilanes. The first report of living carbanionic ROP appeared in 1994, and this process permitted the synthesis of PFS with predictable molar masses and narrow dispersity [637]. The mechanism is based on a Cp-Si bond cleavage in the presence of lithium-based initiators (Scheme 62). Reviews published by Rider and Manners [638] and Bellas and Rehahn [639] propose details in their preparation as well as other polymerization routes or self-assembly toward nanostructured materials.

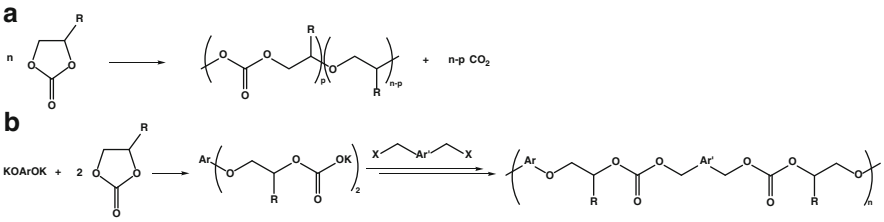
6 Cyclic Carbonates

6.1 Introduction

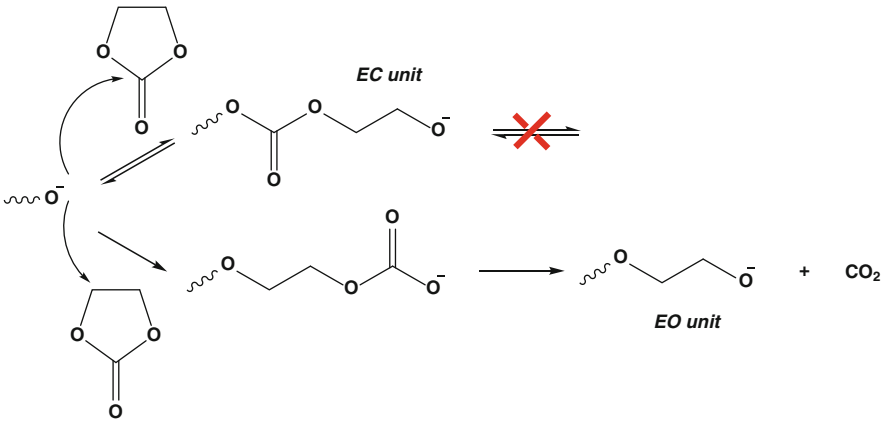
The polymerization of aliphatic or aromatic cyclic carbonates was highly investigated and recently reviewed [640–644]. Indeed, due to transparency, good heat resistance (up to 130 °C), high toughness, and excellent dimensional stability, polycarbonates (PC) are used in a broad range of applications like elastomers, sealants, foams, coatings, adhesives, etc. Aliphatic polycarbonates and copolycarbonates are also valuable biomaterials thanks to their biocompatibility and biodegradability.

6.2 5-Membered Cyclic Carbonates

The polymerization of 5-membered cyclic carbonates follows a peculiar behavior as their ceiling temperatures are below 25 °C. As a consequence, no ROP should be possible to yield poly(alkylene carbonate). Nevertheless, they can be polymerized at high temperatures (above 150 °C) resulting in poly(ether-carbonate)s (path A, Scheme 63), the repeating units being a mixture of alkylene carbonate (content generally lower than 50 mol%) and the corresponding alkylene oxide units coming from decarboxylation reactions during the polymerization with organometallics [645, 646], metal alkoxide [647–651], or organic initiating systems [96, 652]. Rokicki developed also the synthesis of poly(ether-carbonate)s through the



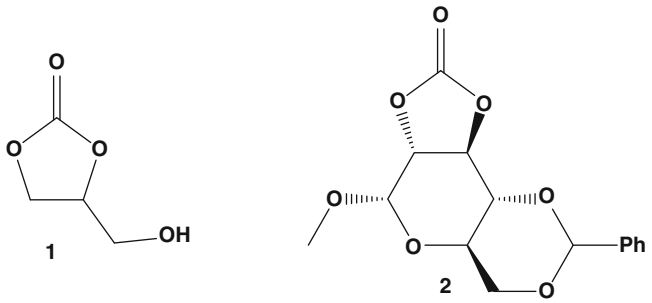
Scheme 63 Poly(ether-carbonate)s obtained from AROP of 5-membered cyclic carbonates



Scheme 64 Mechanism of the AROP of ethylene carbonate

combination of AROP of 5-membered cyclic carbonates initiated by bisphenolates leading to reactive difunctional species and their coupling reactions with dihalo compounds (path B, Scheme 63) [653, 654].

Detailed mechanistic studies of the polymerization of ethylene carbonate (EC) with KOH as the initiator performed at 150–200 °C in bulk suggested that, in the early stage of the polymerization, a major polymer structure comprises one EC unit per two ethylene oxide (EO) units (the content of EC units, even in the earliest stage of the reaction, was not higher than 32 mol-%). For longer reaction times, the content of EO units increases, through hydrolysis of the carbonate units [650]. Polymerization proceeded thus in two stages: during the first stage, EC conversion took place with an increase of molar masses, while in the second stage, when EC was completely consumed, a decrease of both the number of EC units and molar mass was noticed, indicating the occurrence of chain cleavage and decarboxylation reactions. During propagation, the alkoxide propagating species can attack the carbon atom of the carbonyl group. In this case, the reaction is reversible, but the new alkoxide is not able to attack again on the carbon atom of the carbonyl group of another EC monomer as it would yield an EC-EC sequence which is thermodynamically not possible. An alkoxide species can also attack the carbon atom of a methylene group, followed by decarboxylation and irreversible formation of an ethylene oxide unit (Scheme 64). The most probable EC



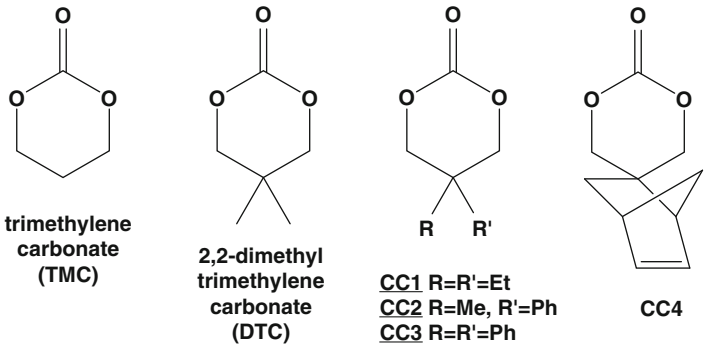
Scheme 65 Other 5-membered cyclic carbonates anionically polymerized

polymerization mechanism should thus be a combination of methylene and carbonyl carbon attack. Finally, after total monomer consumption, elimination reactions were detected, yielding vinyl end groups. Similar results were observed with other initiating systems for the AROP of EC. With butyllithium, the resulting polymers contained only 10 mol-% of carbonated units [645], and with potassium methoxide [647] and phosphazene [96], 28 and 20–25 mol-% of EC units were conserved, respectively. The AROP of propylenecarbonate yielded also poly(propylene carbonate-*co*-propylene oxide) copolymers whatever the initiating system [648, 649, 652].

Rokicki took advantage of these side decarboxylation reactions in order to produce hyperbranched aliphatic polyether through the AROP of glycerol carbonate (1, Scheme 65) conducted at 170 °C using trimethylolpropane/potassium methanolate as the initiating system [651]. Attempts to polymerize aromatic five-membered cyclic carbonate with *sec*-BuLi and potassium dihydronaphthalide revealed unsuccessful [655]. In contrast to other five-membered cyclic carbonates, five-membered cyclic carbonates obtained from methyl 4,6-*O*-benzylidene-glucopyranoside (2, Scheme 65) can be polymerized at relatively low temperatures (<60 °C) with alkali metal alkoxides or organic initiator, without elimination of carbon dioxide, to produce polycarbonates consisting exclusively of carbonate repeating units [656–658]. Such a behavior was suggested to be due to the ring strain which may result from the connection of two hydroxyl groups in E (trans) position by the carbonate linkage.

6.3 6-Membered Cyclic Carbonates

In contrast to thermodynamically unfavorable 5-membered cyclic carbonates, 6-membered cyclic carbonates easily polymerize with anionic initiators to afford PCs without ether sequences and generally high molar masses [659–663]. The AROP of trimethylene carbonate (TMC) was first reported in the 1930s using K_2CO_3 [664, 665]. Since then, many other initiators were able to polymerize

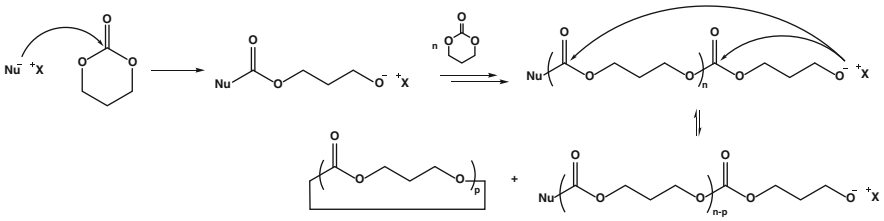


Scheme 66 Examples of 6-membered cyclic carbonates polymerized anionically

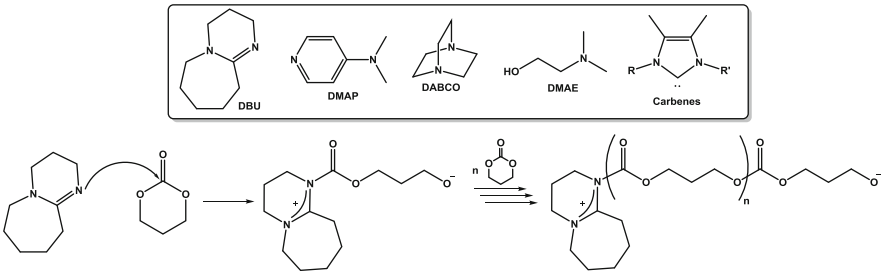
6-membered cyclic carbonates (Scheme 66), like butyllithium [666–672], alkali metal alkoxides [667, 672–676], naphthalene potassium [667], sodium hydride [673], and pure organic nucleophiles [379, 673, 677–688].

An important feature of AROP of 6-membered cyclic carbonates is its equilibrium character. Indeed, polymerization did not go to completion with the presence of residual monomer. Nevertheless, this drawback could be taken as an advantage as it allows polycarbonates recycling. It was shown that the monomer substitution had a strong effect on the equilibrium monomer concentration. For example, the AROP of TMC, 2,2-dimethyl trimethylene carbonate (DTC) and CC1–3 (Scheme 66) in THF solution using potassium *tert*-butoxide as the initiator exhibited an increasing monomer concentration at equilibrium, with an increasing bulkiness of the substituents, CC3 monomer being almost not polymerized [671, 675]. It was assessed that the decrease in polymerizability of the 6-membered cyclic carbonates with increasing bulkiness of the substituents was due to the conformational distortion of the polymer backbone, rather than in the change of conformation of the monomer caused by the substituents [641]. Several other parameters may also influence the polymerization rate. For example, the polymerization of DTC in toluene with lithium as a counterion was slower than that with potassium one due to the covalent character of the lithium-oxygen bond compared with the potassium-oxygen bond leading to a lower nucleophilicity of the lithium alkoxide. In the case of monomer CC4, the back-biting reaction was restricted due to the stiffness of the polymeric chain [670].

The AROP of 6-membered cyclic carbonates presents transesterification reactions, besides initiation and propagation reactions (Scheme 67). The initiation reaction comprises the nucleophilic attack of the initiator on the carbonyl carbon atom, followed by an acyl-oxygen cleavage and formation of the active species, an alkoxide. Peculiar initiation behaviors were also observed. When the ROP was initiated by naphthalene potassium, this latter did not act as an electron-transfer reagent (e.g., like for styrene polymerization) but as a nucleophile, naphthalene being incorporated in the polymeric chain [667]. Intramolecular nucleophilic attacks on carbonyl carbon atom (back-biting) lead to cyclic oligomers, while



Scheme 67 Initiation, propagation, and transesterification reactions occurring in AROP of 6-membered cyclic carbonates

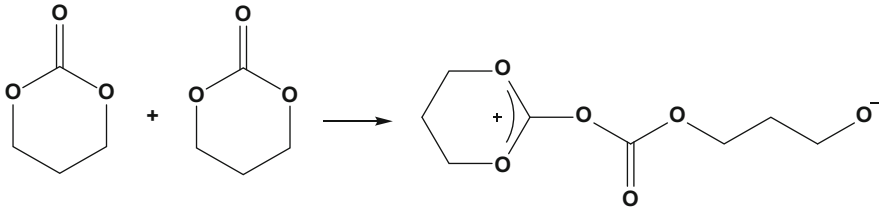


Scheme 68 Examples of organic initiators for the AROP of 6-membered cyclic carbonates and polymerization mechanism

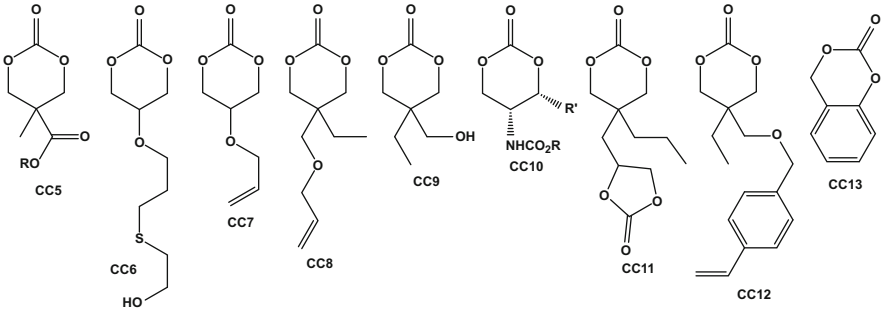
intermolecular transesterification leads to a change of the macromolecule length. As a consequence, the control of the polymerization was poor, and bimodal distribution of molar masses was generally observed.

Instead of using metallic initiators, it is possible to use organic ones. Murayama et al. were the first to show that tertiary amines such as 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), 1,4-diazabicyclo[2.2.2]octane (DABCO), and 4-dimethylaminopyridine (DMAP) (Scheme 68) were able to achieve the AROP of a 6-membered cyclic carbonate (CC4, Scheme 66) in bulk at 120 °C, whereas no polymer was obtained with triethylamine, aniline, *N*,*N*-dimethylaniline, or pyridine [679]. It was suggested a zwitterionic polymerization mechanism, which was confirmed by mass spectrum analysis of the products. Tapered copolymers were also obtained when monomer CC4 was simultaneously polymerized with glycidyl naphthyl ether.

The ROP of TMC was also performed with *N*-heterocyclic carbenes, guanidine, and amidine bases in bulk at 65 °C with a good control, yielding well-defined polycarbonates with molar masses up to 50,000 g/mol, dispersity index below 1.08, and high end-group fidelity [680]. Similarly, the tertiary amine 2-(dimethylamino) ethanol (DMAE) was used as an efficient initiator/catalyst for the ROP of TMC in bulk at 50 °C leading to α,ω-heterotelechelic PTMC [682]. In this case, the mechanism could be either an activated monomer or an activated chain-end one. Phosphazenes revealed also efficient deprotonating agents of alcohols for the



Scheme 69 Spontaneous ROP of TMC



Scheme 70 Examples of functional 6-membered cyclic carbonates anionically polymerized

polymerization of TMC [688, 689]. Recently, several carbenes were used for the controlled polymerization of DTC [379, 685].

Some examples of initiator-free polymerization of cyclic carbonates were also described in the literature, assuming an anionic mechanism [690–693]. TMC can undergo spontaneous polymerization in bulk above 100 °C, with the formation of a zwitterion intermediate with a well-stabilized trialkoxycarbenium ion and on alkoxide (Scheme 69), whereas DTC cannot [691]. Initiator-free polymerizations were also observed for the thermal ROP of 5-benzyloxy-trimethylene carbonate (BTMC) in bulk at 150 °C or the microwave-assisted ROP of TMC. Molar masses were generally high.

In spite of some side reactions, the AROP of functional cyclic carbonates remains the preferable way to prepare functional polycarbonates. Several pathways permit functional monomer synthesis: from 2,2-bis(hydroxymethyl)propionic acid, glycerol, or alkyl malonates [640, 641, 643]. A number of functionalized PCs and copolycarbonates can be obtained by direct polymerization of cyclic monomers bearing functional groups. Functional side-chain groups introduced into PCs are carboxylic group and their derivatives, hydroxyl, allyl, acrylate, methacrylate, styrene, and stilbene derivatives, and even five-membered cyclic carbonates (Scheme 70).

Polycarbonates with carboxylic side groups could be synthesized through the ROP of CC5-type monomers (Scheme 70) with DBU [684] or *sec*-butyllithium [694] at room temperature in solution. With *sec*-butyllithium, bimodal distribution

of the molar masses was observed, whereas the polymers exhibited low dispersity with DBU. Aliphatic amines with different chain lengths were easily conjugated onto the polymer backbone in order to form nanoparticles [684].

6-Membered cyclic carbonate bearing free hydroxyl group attached to the ring via aliphatic spacer (CC6, Scheme 70) was polymerized with DBU in bulk or in solution at temperatures ranging from 60 to 110 °C to yield hyperbranched polycarbonates composed of carbonate and glycerol units [683]. The linear equivalent of poly(CC6) was obtained through the polymerization of CC7 followed by free radical addition of mercaptoethanol to the pendent allyl groups. Attempts to polymerize CC8 with *sec*-butyllithium in solution resulted in a mixture of polymers, cyclic oligomers, and unreacted monomer [668, 669]. The hydroxyl function of monomer CC9 was first protected by reaction with trimethylsilyl chloride and benzyl chloroformate of phenyl isocyanate and then polymerized with lithium alkoxide in solution at low temperature to yield bimodal distributions or even cross-linking [674]. After deprotection, polycarbonates with one hydroxyl group per repeating units were obtained. Amino acid functionalized polycarbonates were also synthesized through the ROP of CC10-type monomers with alkali metal alkoxides or *n*-butyllithium in solution at low temperature followed by deprotection [672]. Monomodal distributions were obtained, and the configuration of the monomer was inverted during the polymerization.

Bifunctional cyclic carbonate consisting of both 5- and 6-membered rings (CC11, Scheme 70) was polymerized with DBU at 60 °C in solution to afford a polycarbonate with remaining 5-membered cyclic carbonate group in the side-chain, as this latter did not polymerize in these conditions [677]. At such elevated temperature, conversion stopped around 50 % due to the equilibrium nature of the polymerization.

Styrene side groups were also introduced onto polycarbonates through the polymerization of monomer CC12 (Scheme 70) with potassium *tert*-butoxide as the initiator in THF at 0 °C [676]. Subsequent radical cross-linking of styrenic groups and anionic de-cross-linking of the carbonate units was performed. Aromatic cyclic carbonate CC13 (Scheme 70) was polymerized by *sec*-butyllithium or dihydronaphthalene potassium, but it was evidenced the presence of decarboxylation reactions to a great extent [655].

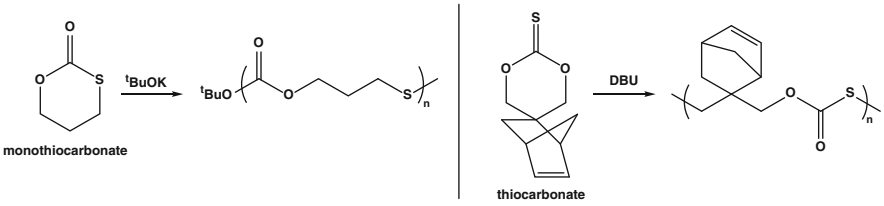
Macroinitiators such as polymeric Li, Na, and K alkoxides can also be used for the initiation of the 6-membered cyclic carbonate polymerization. Thus, living vinyl polymers [695], hydroxyl group-terminated polymers of poly(tetrahydrofuran) (PTHF) [696, 697], poly(ethylene oxide) (PEO) [697–699] and poly(dimethylsiloxane) (PDMS) [697, 700] were transformed to alkoxides by treatment with *sec*-BuLi or K-naphthalene and used as initiators for AROP of DTC allowing the synthesis of di- and triblocks copolymers. The polymerization initiated by PTHF alkoxides with different counterions was slower than that initiated by PEO alkoxides, because of the lower solvation ability of PTHF. It was also shown that the polymerization rate was highly dependent on the counterion, potassium alkoxides being more reactive than lithium alkoxides. Besides, higher molar mass PDMS macroinitiators exhibited lower polymerization rate. In the same vein, living poly

(methyl methacrylate) (PMMA) prepared by Group Transfer Polymerization (GTP) was used as a macroinitiator for the ROP of DTC after transformation of the silyl ketene acetal into an alkoxide [701]. PMMA-*b*-PDTC block copolymers were thus obtained.

The simultaneous or sequential polymerization of DTC with several cyclic esters or other cyclic carbonates (CC4, CC5, and CC8, Scheme 70), initiated with butyllithium, potassium dihydronaphthalene, or organic initiators, was performed in solution or in bulk [379, 668–670, 694, 702–704]. With ε-caprolactone (CL), tapered copolymers were obtained as DTC was more reactive than CL. Triblock copolymers with tapered DTC/CL outer blocks could also be obtained using macroinitiators (PEO or PTHF based) [699]. With pivalolactone, only block copolymers were synthesized; DTC was first reacted by alkoxide active species, followed by the reaction of pivalolactone through carboxylate active species. With the other cyclic carbonates, statistical or block copolymers were obtained from simultaneous or sequential polymerization, respectively.

6-Membered cyclic carbonates were also copolymerized with oxiranes [678, 705] and anhydride [706]. DTC was copolymerized with glycidyl phenyl ether (GPE) with DBU in bulk at 90 °C. An acceleration of GPE polymerization was observed, and quantitative yields were obtained. PGPE-*b*-PTMC copolymers were also successfully synthesized through the sequential polymerization of GPE and TMC with tetrabutylammonium fluoride. Attempts to copolymerize TMC and adipic anhydride with *sec*-butyllithium in several conditions revealed unfruitful as mixture of homopolymers were detected [706].

It was demonstrated that cyclic monothiocarbonate [707] and thiocarbonate [708, 709] (Scheme 71) could be polymerized by AROP. For the cyclic monothiocarbonate, potassium *tert*-butoxide revealed a good initiator yielding a polymer that precipitates during the course of the polymerization. It was shown that the propagating species was not an alkoxide but a thiolate as the monomer ring-opens exclusively through the carbonyl sulfur bond cleavage. Thiocarbonate was polymerized by n-butyllithium or potassium alkoxides in solution at room temperature or by DBU in bulk or in solution at 120 °C. Polymerization was pretty slow and proceeded with an isomerization of the thiocarbonate group.



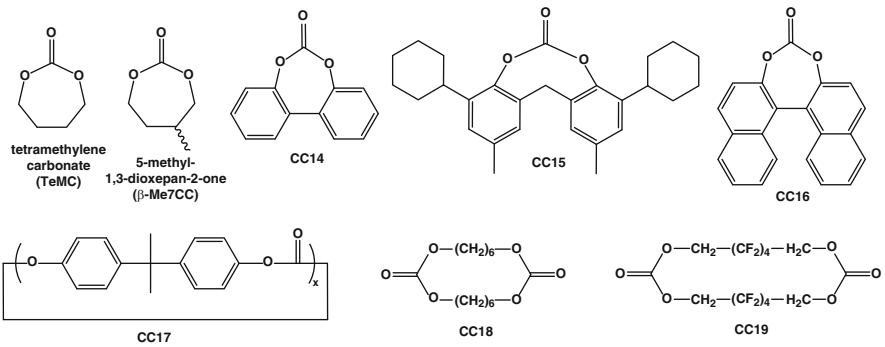
Scheme 71 Cyclic monothiocarbonate and thiocarbonate polymerized by AROP

6.4 *Larger-Ring Cyclic Carbonates*

The ROP of 7-membered cyclic carbonate (tetramethylene carbonate, TeMC, Scheme 72) is generally faster than that of the six-membered one due to relatively high ring strain. However, the polymerization of 7-membered cyclic carbonates was scarcely investigated because of the difficulty to synthesize the monomers. Indeed, TeMC is thermally unstable and difficult to isolate and purify. The polymerization of TeMC initiated with *sec*-butyllithium was carried out in THF to yield the corresponding polycarbonate in a relatively high yield in a short time [710]. Like for 6-membered cyclic carbonates, an important residual monomer concentration was observed with the formation of cyclic oligomers via back-biting reaction, which is characteristic for equilibrium polymerizations. However, the relative polymerization rate of TeMC is about 35 times faster than that of TMC.

Another 7-membered cyclic carbonate (β-Me7CC, Scheme 72) was polymerized in bulk at elevated temperature only (100 °C) with organic compounds (DMAP, phosphazene) with very good yields [711]. No regioselectivity was observed during ring-opening of the monomer.

The ROP of large-ring aromatic cyclic carbonates was also studied. It was shown that the polymerization of monomer CC14 with alkoxide or alkyllithium [712] or CC15 with *sec*-butyllithium or dihydronaphthalene lithium [713] failed, but CC15 was easily polymerized by dihydronaphthalene potassium or potassium *tert*-butoxide. Monomer CC16 was easily polymerized with potassium *tert*-butoxide in THF at room temperature to afford the corresponding polycarbonate in high yield [714]. Cyclic oligomeric carbonates of bisphenol A (CC17, Scheme 72) were polymerized by potassium dihydronaphthalene in THF [713] or in bulk at 250 °C [715]. The polymerization and copolymerization of cyclo bis(hexamethylene carbonate) and its fluorinated analog (CC18 and CC19, Scheme 72) were also successfully performed using *sec*-butyllithium in toluene [716].



Scheme 72 7-Membered cyclic carbonates and larger-ring cyclic carbonates polymerized by AROP

7 Cycloalkanes, Cyclic Sulfides and Amines, Cyclic Ureas, Depsipeptides, and Cyclic Phosphorous Monomers

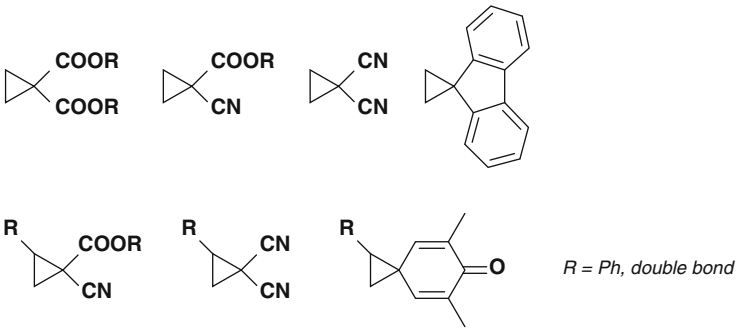
7.1 Introduction

The successful synthesis of polymers and copolymers issued from cyclic ethers, esters, lactams, carbonates, or siloxanes through anionic ring-opening polymerization triggered researches in cyclic monomers containing, or not, other heteroatoms or combination of several heteroatoms. New properties were expected for novel uses.

7.2 Cycloalkanes

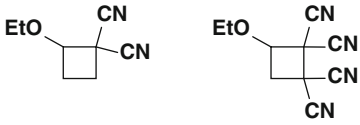
Cycloalkanes are expected to polymerize by breaking a carbon-carbon single bond of a monomer ring. Such a bond does not generally react with free radicals and rarely participate in reactions with electrophiles and nucleophiles [717]. In addition, as the two atoms making the bond are identical, no polarization is introduced into the monomer, making ionic reactions with nucleophiles or electrophiles difficult. Reactivity can only be expected when monomer substituents are introduced on at least one of the two carbons, thereby increasing the bond polarity and introducing some zwitterionic nature into the bond, or when the overlap of atomic orbitals in the carbon-carbon bond is disturbed by geometric parameters, particularly observed with highly strained polycyclic systems [717, 718]. Cycloalkanes polymerized by anionic ring-opening polymerization are composed of functionalized cyclopropanes, cyclobutanes, and polycyclic molecules with high intrinsic polymerizabilities (e.g., bicycloalkanes and propellanes). Detailed reviews may give additional information in anionic polymerization as well as other polymerization methods used [719–723].

The AROP of cyclopropanes activated by various substituents (Scheme 73) was effective using mainly alkali metal derivatives as initiators. Two electron-withdrawing substituents on the same carbon are often needed for the polymerization to be efficient but still drastically less reactive than the corresponding vinyl monomers [724]. Sodium thiophenolate is shown to initiate the polymerization of cyclopropane-1,1-dicarboxylates with a living character in some cases [725–728]. Phosphazenium thiophenol or bisthiols were also proposed for the successful AROP of di-n-propyl cyclopropane-1,1-dicarboxylate [729, 730]. Well-defined monofunctional or difunctional polymers with a low dispersity were obtained through a living process in THF between 30 and 60 °C or in toluene between 30 and 100 °C. A much higher reactivity is noticed as compared to the alkali metal thiophenolate initiator used in DMSO at higher temperature. The polymerization of cyclopropanes bearing cyano [724, 731] or fluorine [732] groups initiated with sodium thiophenolate or fluorenyl lithium, respectively, was also observed. Sodium

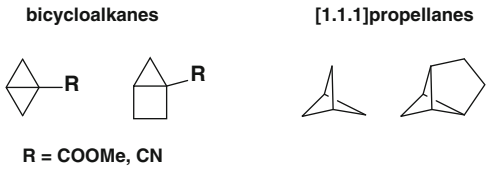


Scheme 73 Structure of cyclopropanes polymerized by AROP

Scheme 74 Structure of cyclobutanes polymerized by AROP



Scheme 75 Structure of polycyclic alkanes polymerized by AROP



cyanide was particularly effective as anionic initiator of various trisubstituted cyclopropanes in DMF [733–737].

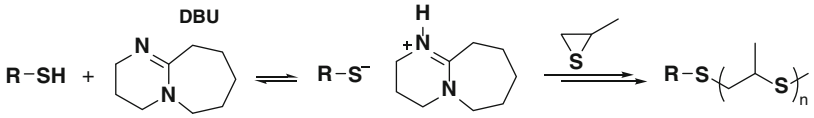
Cyclobutanes exhibit a much lower tendency to anionically ring-open as compared to cyclopropanes and as also observed for heterocyclic rings. Reasonable evidences for an AROP were only reported in highly activated monomers. The polymerizations of cyclobutanes substituted by nitrile groups on one or two carbons, and further substituted by an ether group on a neighboring carbon, are the most efficient (Scheme 74) [738, 739].

Activated bicyclobutanes [740–745] or other bicycloalkanes [746] and [1.1.1] propellanes [747–749] were observed to give oligomers or polymers using conventional anionic initiators, i.e., alkyllithium (Scheme 75).

7.3 Cyclic Sulfides and Amines

The anionic route is proposed, in addition to cationic and coordinative ones [750], as an efficient approach for the polymerization of cyclic sulfides (Scheme 76), in particular for thiirane (ethylene sulfide) and various substituted thiiranes. Thiolates

Scheme 76 Structure of cyclic sulfides polymerized by AROP



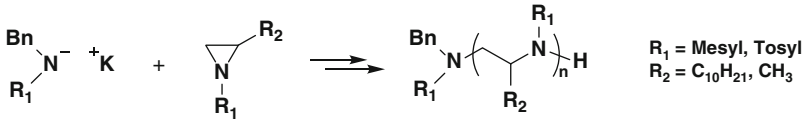
Scheme 77 Anionic polymerization of methylthiirane initiated by thiolates

are commonly used to attack the monomer, proceeding exclusively at the methylene carbon and leading to pure head-to-tail structures [751–753]. Naphthylsodium was found to act as a bifunctional initiator and to give a living character to the polymerization. The initiation reaction was proposed to consist of a desulfurization process producing ion radicals that combine to form dithiolates [754]. In a similar way to epoxide polymerization, Inoue experimented with success (*N*-methyl-5,10,15,20-tetraphenylporphinato)zinc propanethiolate as initiator of propylene sulfide (or methylthiirane MT) [755].

Organic initiators were also proposed. Tertiary amines such as 1,4-diazabicyclo [2.2.2]octane (DABCO) enable the polymerization of ethylene sulfide to high molar mass polymers through a zwitterionic mechanism [756]. In contrast, MT was only slowly polymerized by polyamines to give low molar mass materials. Nicol et al. described the living polymerization of MT initiated by various mono- and dithiolates [757]. The deprotonation of the thiols was carried out by addition of a strict stoichiometric amount of a bulky strong organic base such as 1,8-diazabicyclo [5,4,0]undec7-ene (DBU) (Scheme 77).

Advantages of thiols are based on low p*K*a values ranging from 7 to 11 in water, excluding substantially deactivation due to protonation in environments with pH $\geq$10. That allows a living character of the polymerization at not excessively basic pH and under non-anhydrous conditions, which is different from the structurally similar epoxide polymerization. It is possible to polymerize hydroxyl-containing monomers such as hydroxymethyl thiirane in a living manner [758] or to work in emulsion in water with restrictions, such as limited conversions producing polymers with molar masses lower than predicted ones due to physical reasons and not chemical [759]. On the other hand, the use of thiols is often complicated by the presence of disulfide impurities coming from oxidation of the initiating thiol, which results in transfer reactions [760]. Protected thiols which are deprotected right before polymerization may be proposed. Examples are the use of thioester, which is transformed into thiolate by the addition of sodium methanolate [761, 762] and the ring-opening of cyclic dithiocarbonates by an amine [763].

Thanks to the livingness of the polymerization of thiiranes, di- and triblock copolymers were prepared, marrying mainly polythiirane or poly(methylthiirane) (PMT) with polystyrene and derivatives, poly(methyl methacrylate), polyethers, and polydienes [762, 764–770]. A macromonomer approach was also helpful to



Scheme 78 AROP of sulfonylaziridines

obtain comb-like polymers with polythiirane main chains and various side chains [771–774]. The synthesis of star-shaped PMT by polymerization with tri- and tetrathiol initiators was also investigated [761–763, 775, 776].

The AROP of the four-membered rings family of cyclic sulfides (Scheme 76) is much more limited. Thiethane and 3,3-dimethylthietane were polymerized to high molar mass polymers by initiation with naphthylsodium or butyllithium [777–780]. The polymerizations were shown to occur with carbanions as active species instead of thiolates. The sulfur atom is attacked due to severe bond angle distortions forced upon the atom by the geometry of the molecule.

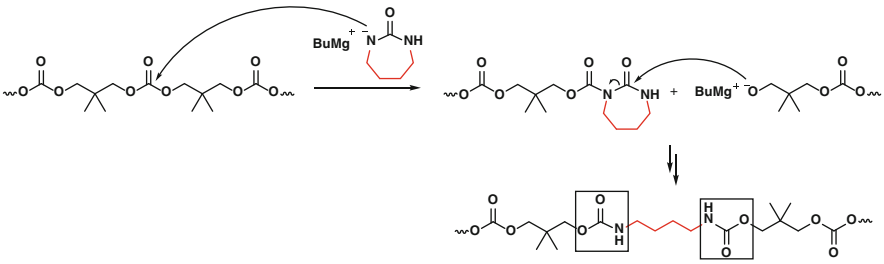
The conversion of cyclic amines into linear polyamines is much more limited by AROP, despite potential utilities, e.g., ion exchange chromatography or biomedicine [781, 782]. The polymerization of sulfonylaziridines was only effective in the presence of amide initiator, generated by the deprotonation of a primary sulfonamide (*N*-benzyl methanesulfonamide) by potassium bis(trimethylsilyl)amide (KHMDS), leading to polymers with a low dispersity (Scheme 78) [783].

7.4 Cyclic Ureas and Depsipeptides

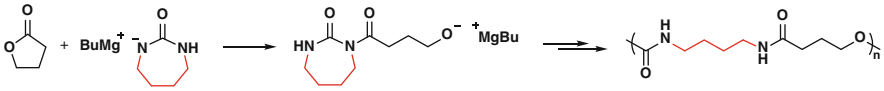
The ROP of cyclic ureas has attracted only minor interest. Dimethylene urea and trimethylene urea can be successfully ring-open using sodium hydride as initiator leading to polyureas [784]. But the synthesis of polyurethanes, starting from tetramethylene urea (TeU) and cyclic carbonates, was particularly investigated by Keul and Höcker [785–788]. It was shown that first the cyclic carbonate polymerizes, and then TeU is formally inserted into the polycarbonate chain after deprotonation of the amine by dibutylmagnesium (Bu_2Mg) (Scheme 79).

Using γ-butyrolactone (γ-BL) instead of cyclic carbonates in the presence of Bu_2Mg, alternating poly(amide urethane)s were achieved [789]. The homopolymerizations of TeU and γ-BL were not observed. TeU reacts initially with Bu_2Mg to form the salt in which the nucleophilicity of the nitrogen is enhanced and the reaction between activated TeU and γ-BL is made possible. Ring-opening leads to the AB monomer. It is followed by the nucleophilic attack of the alkoxide at the endocyclic carbonyl carbon atom, resulting in polymer after ring-opening (Scheme 80).

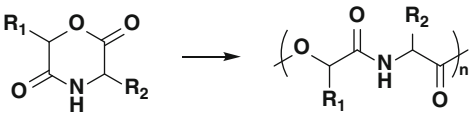
Polydepsipeptides, alternated copolymers of α-hydroxy acids and α-amino acids, belong to the poly(ester-amide) family and are interesting for their degradable character. Ring-opening polymerization of morpholine-2,5-dione (MD) and its



Scheme 79 Polyurethane synthesis by insertion and ROP of deprotonated tetramethylene urea in a polycarbonate



Scheme 80 Poly(amide urethane) synthesis by reaction between deprotonated tetramethylene urea and γ-BL

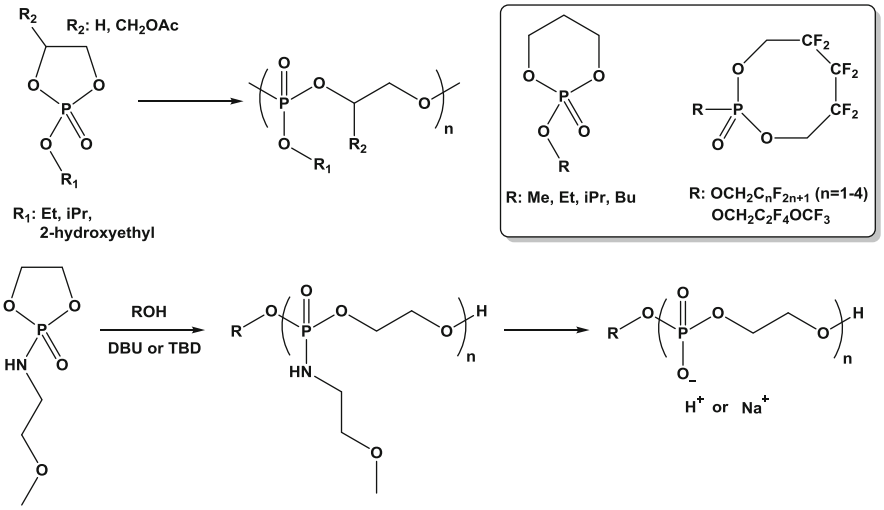


Scheme 81 Structure of cyclic depsipeptides (morpholine-2,5-dione) and corresponding polymers

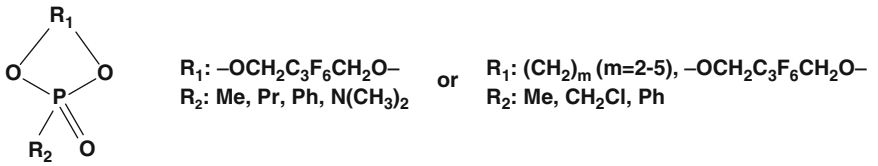
derivatives (Scheme 81), in the presence of stannous catalyst, is the main way to obtain such polymers [790]. Detailed information can be found in the review of Dijkstra [791]. AROP using potassium alkoxides was also applied to provide polymers with limited conversions and molar masses [792]. The lack of control may be explained by the presence of a proton on the amine. Block copolymers such as polymorpholine-2,5-dione-*b*-polylactide were nevertheless prepared by a two-step procedure for surfactants applications [793, 794].

7.5 Cyclic Phosphorus Monomers

Cyclic phosphorus monomer family gives rise to polymers of interest in particular in biomedical field, due to biocompatibility, biodegradability, and structural similarities to naturally occurring nucleic acids, or in flame retardant applications. Lapienis reviewed recently all ring-opening polymerizations leading to polymers containing phosphorus atoms [795]. Only few monomers are polymerized by an



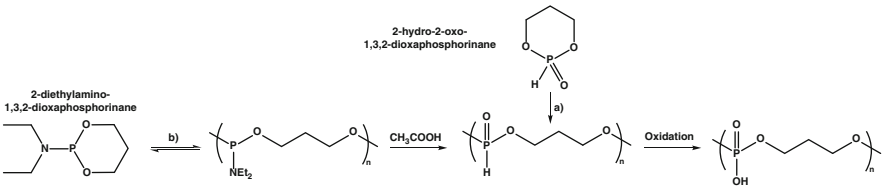
Scheme 82 Cyclic phosphoesters polymerized by AROP



Scheme 83 Cyclic phosphonates polymerized by AROP

anionic route. Poly(phosphate esters) can be prepared from cyclic phosphoesters (Scheme 82) either with alkali metal initiators [796–800] or organic initiators (tertiary amines, TBD, or DBU) [801–805]. 5-Membered phosphoesters were by far the most studied monomers. The presence of a substituent on the ring decreases the polymerizability of the monomer as high polymerization temperatures are needed to get only oligomers. 6-Membered phosphoesters are also difficult to polymerize [799]. Fluorosubstituted phosphoesters (Scheme 82) can undergo AROP with KOH, butyllithium, or triethylamine, in bulk at 220–270 °C, giving rubber-like polymers, the molar mass being highly dependent on the initiator [800]. The presence of polar agents (e.g., THF, diethyl ether, and dimethylformamide (DMF)) considerably lowers the required polymerization temperature (100 °C). The polymerization presents a living character with organic initiators, enabling the formation of random and block copolymers [802, 803].

5-, 6-, 7-, and 8-Membered cyclic phosphonates (Scheme 83) can also undergo anionic polymerization at high temperatures [806]. Very recently, it was shown that DBU can perform the synthesis of poly(ethylene methylphosphonate) with an excellent control with molar masses up to 20,000 g/mol [807]. The polymerization



Scheme 84 Examples of other cyclic phosphorus containing monomers polymerized by AROP

of cyclic [808] or bicyclic [809] *H*-phosphonate was also performed with an alkyllithium. As an example, the polymerization of 2-hydro-2-oxo-1,3,2-dioxaphosphorinane was achieved in bulk or in dichloromethane solution, initiated by n-BuLi, but also EtONa and t-BuOK, at 25–45 °C, to give a high molar mass polymer (route a, Scheme 84) [808]. Some trivalent phosphorus cyclic compounds were also polymerized by AROP with potassium or cesium alkoxides (no polymerization occurred with lithium or sodium) or potassium trimethylsilanolate (route b, Scheme 84) [810–812]. After acetolysis, poly(2-diethylamino-1,3,2-dioxaphosphorinane) gave the same polymer as the one obtained from 2-hydro-2-oxo-1,3,2-dioxaphosphorinane, which can be easily converted to polyacid after oxidation.

8 Conclusion

A large variety of cyclic monomers can be polymerized by anionic ring-opening polymerization. In spite of required rigorous experimental procedures as compared to some other polymerization routes, some industries and academic researchers used to play with such chemistry and already take advantages of some polymeric structures prepared by AROP. Indeed, thanks to the recent progress in the control of the polymerizations, functionalized polymers and copolymers (block in particular) are now available, broadening the scope of properties and thus opening many perspectives in various applications.

Abbreviations

18C6	1,4,7,10,13,16-Hexaoxacyclooctadecane (18-crown-6 ether)
ACE	Active chain end
AGE	Allyl glycidyl ether
AM	Activated monomer
AROP	Anionic ring-opening polymerization
BEMP	2-*tert*-butylimino-2-diethylamino-1,3-dimethylperhydro-1,3,2-diazaphosphorine

BL	β-butyrolactone
γ-BL	γ-butyrolactone
BO	Butylene oxide
BTMC	5-Benzyloxy-trimethylene carbonate
Bu_2Mg	Dibutylmagnesium
i-Bu_3Al	Triisobutylaluminum
BuLi	Butyllithium
CC	Cyclic carbonate
CL	ε-Caprolactone
ε-CL	ε-Caprolactam
Cp	Cyclopentadienyl
D3	Hexamethylcyclotrisiloxane
D4	Octamethylcyclotetrasiloxane
D5	Decamethylcyclopentasiloxane
D6	Dodecamethylcyclohexasiloxane
DABCO	1,4-Diazabicyclo[2.2.2]octane
DBU	1,8-Diazabicyclo[5.4.0]undec-7-ene
DHCM	3,4-Dihydrocoumarin
DMAE	2-(Dimethylamino)ethanol
DMAP	*N*,*N*-Dimethylamino pyridine
DMF	Dimethylformamide
DMO	2,2-Dimethyloxirane
DMSO	Dimethylsulfoxide
DP	Degree of polymerization
DTC	2,2-dimethyl trimethylene carbonate
EC	Ethylene carbonate
ECH	Epichlorohydrin
EEGE	2-Ethoxyethyl glycidyl ether
EO	Ethylene oxide
EtONa	Sodium ethoxide
EVGE	Ethoxy vinyl glycidyl ether
GME	Glycidyl methyl ether
GPE	Glycidyl phenyl ether
GTP	Group transfer polymerization
HMPA	Hexamethylphosphoramide
KHMDS	Potassium bis(trimethylsilyl)amide
LA	Lactide
ω-LL	ω-Lauryllactam
MAlBP	Methylaluminum bis(2,4,6-tri-*tert*-butylphenolate)
MD	Morpholine-2,5-dione
MLABz	Benzyl-β-malolactonate
MT	Methylthiirane
NHC	*N*-heterocyclic carbene
$NOct_4Br$	Tetraoctylammonium chloride

PA3	Polyamide 3
PA5	Polyamide 5
PA6	Polyamide 6
PA10	Polyamide 10
PA12	Polyamide 12
PBL	Poly(β-butyrolactone)
PBO	Poly(butylene oxide)
PC	Polycarbonate
PCL	Poly(ε-caprolactone)
PDMS	Poly(dimethyl siloxane)
PEEGE	Poly(2-ethoxyethyl glycidyl ether)
PEO	Poly(ethylene oxide)
PGME	Poly(glycidyl methyl ether)
PGPE	Poly(glycidyl phenyl ether)
PHA	Polyhydroxyalkanoate
PL	β-Propiolactone
PLA	Polylactide
PMMA	Poly(methyl methacrylate)
PMT	Polymethylthiirane
POSS	Oligomeric silsesquioxane
PO	Propylene oxide
PPL	Poly(β-propiolactone)
PPO	Poly(propylene oxide)
PPY	4-Pyrrolidinopyridine
PS	Polystyrene
PTHF	Polytetrahydrofuran
PTMC	Poly(trimethylene carbonate)
PVL	Pivalolactone (α,α-dimethyl-β-propiolactone)
P*t*BuGE	Poly(*tert*-butyl glycidyl ether)
RIM	Reaction injection molding
ROP	Ring-opening polymerization
RTM	Resin transfer molding
TBD	1,5,7-Triazabicyclo[4.4.0]dec-5-ene
t-BuGE	*tert*-butyl glycidyl ether
t-BuOK	Potassium *tert*-butoxide
$tBuP_1$	*N′*-*tert*-butyl-*N*,*N*,*N′*,*N′*,*N″*,*N″*-hexamethylphosphorimidic triamide
$tBuP_2$	1-*tert*-Butyl-2,2,4,4,4-pentakis(dimethylamino)-2λ^5,4λ^5-catenadi (phosphazene)
$tBuP_4$	1-*tert*-Butyl-4,4,4-tris(dimethylamino)-2,2-bis[tris(dimethylamino)-phosphoranylidenamino]-2-λ^5,4-λ^5-catenadi (phosphazene) (phosphazene base)
TeMC	Tetramethylene carbonate
TeU	Tetramethylene urea
THF	Tetrahydrofuran

TMC	Trimethylene carbonate
TPPAlCl	α,β,γ,δ-Tetraphenylporphyrin aluminum chloride
δ-VL	δ-Valerolactone

References

1. Flory PJ (1940) Molecular size distribution in ethylene oxide polymers. J Am Chem Soc 62:1561–1565
2. Penczek S, Cypryk M, Duda A, Kubisa P, Slomkowski S (2007) Living ring-opening polymerizations of heterocyclic monomers. Prog Polym Sci 32:247–282
3. Boileau S (1989) 32 – anionic ring-opening polymerization: epoxides and episulfides. In: Allen G, Bevington JC (eds) Comprehensive polymer science and supplements. Pergamon, Amsterdam, pp 467–487
4. Lassalle D, Boileau S, Sigwalt P (1977) Reactivities of fluorenyl species as ethylene oxide polymerization initiators-II. Mechanisms of the ring opening of ethylene oxide by fluorenyl and 9-methylfluorenyl alkali salts. Eur Polym J 13:591–597
5. Lassalle D, Boileau S, Sigwalt P (1977) Reactivities of fluorenyl species as ethylene oxide polymerization initiators-I. Ultraviolet and visible absorption spectra of 9-methylfluorenyl alkali salts. Eur Polym J 13:587–589
6. Richards DH, Szwarc M (1959) Block polymers of ethylene oxide and its analogues with styrene. Trans Faraday Soc 55:1644–1650
7. Boileau S, Deffieux A, Lassalle D, Menezes F, Vidal B (1978) Reactivities of anionic species for the ring opening of ethylene oxide. Tetrahedron Lett 19:1767–1770
8. Szwarc M (1968) Carbanions, living polymers, and electron-transfer processes. Interscience Publishers, a division of John Wiley and Sons, Inc., New York
9. Knischka R, Lutz PJ, Sunder A, Mülhaupt R, Frey H (2000) Functional poly(ethylene oxide) multiarm star polymers: core-first synthesis using hyperbranched polyglycerol initiators. Macromolecules 33:315–320
10. Feng XS, Taton D, Chaikof EL, Gnanou Y (2005) Toward an easy access to dendrimer-like poly(ethylene oxide)s. J Am Chem Soc 127:10956–10966
11. Stolarzewicz A (1986) A new chain transfer-reaction in the anionic-polymerization of 2,3-epoxypropyl phenyl ether and other oxiranes. Makromol Chem Macromol Chem Phys 187:745–752
12. Stolarzewicz A, Grobelny Z, Kowalczuk M (1995) The unusual outcome of the reaction of potassium anions with phenyl glycidyl ether. J Organomet Chem 492:111–113
13. Nenna S, Figueruelo JE (1975) Caesium as counter-ion in the anionic polymerization of ethylene oxide-II. Kinetics in HMPT. Eur Polym J 11:511–513
14. Price CC, Carmelite DD (1966) Reactions of epoxides in dimethyl sulfoxide catalyzed by potassium t-butoxide. J Am Chem Soc 88:4039–4044
15. Solov'yanov AA, Kazanskii KS (1972) Polymerization of ethylene oxide in dimethyl sulphoxide (DMSO). Polym Sci USSR 14:1196–1206
16. Kazanskii KS, Solovyanov AA, Entelis SG (1971) Polymerization of ethylene oxide by alkali metal-naphthalene complexes in tetrahydrofuran. Eur Polym J 7:1421–1433
17. Solov'yanov AA, Kazanskii KS (1972) The kinetics and mechanism of anionic polymerization of ethylene oxide in ether solvents. Polym Sci USSR 14:1186–1195
18. Pierre LES, Price CC (1956) The room temperature polymerization of propylene oxide. J Am Chem Soc 78:3432–3436

19. Allgaier J, Willbold S, Taihyun C (2007) Synthesis of hydrophobic poly(alkylene oxide)s and amphiphilic poly(alkylene oxide) block copolymers. Macromolecules 40:518–525
20. Price CC, Akkapeddi MK (1972) Kinetics of base-catalyzed polymerization of epoxides in dimethyl sulfoxide and hexamethylphosphoric triamide. J Am Chem Soc 94:3972–3975
21. Stolarzewicz A, Neugebauer D (1999) Influence of substituent on the polymerization of oxiranes by potassium hydride. Macromol Chem Phys 200:2467–2470
22. Deffieux A, Boileau S (1977) Anionic polymerization of ethylene oxide with cryptates as counterions: 1. Polymer 18:1047–1050
23. Deffieux A, Graf E, Boileau S (1981) Anionic polymerization of ethylene oxide with cryptates as counterions: 2. Polymer 22:549–552
24. Ding J, Heatley F, Price C, Booth C (1991) Use of crown ether in the anionic polymerization of propylene oxide-2. Molecular weight and molecular weight distribution. Eur Polym J 27:895–899
25. Ding J, Price C, Booth C (1991) Use of crown ether in the anionic polymerization of propylene oxide-1. Rate of polymerization. Eur Polym J 27:891–894
26. Stolarzewicz A, Neugebauer D, Grobelny Z (1995) Influence of the crown-ether concentration and the addition of tert-butyl alcohol on anionic-polymerization of (butoxymethyl) oxirane initiated by potassium tert-butoxide. Macromol Chem Phys 196:1295–1300
27. Stolarzewicz A, Neugebauer D, Grobelny J (1996) Potassium hydride – the new initiator for anionic polymerization of oxiranes. Macromol Rapid Commun 17:787–793
28. Inoue S, Sugimoto H, Aida T (1996) Metalloporphyrin catalysts for living and immortal polymerizations. Macromol Symp 101:11–18
29. Kuroki M, Watanabe T, Aida T, Inoue S (1991) Steric separation of nucleophile and Lewis acid providing dramatically accelerated reaction. High-speed polymerization of methyl methacrylate with enolate-aluminum porphyrin/sterically crowded organoaluminum systems. J Am Chem Soc 113:5903–5904
30. Endo M, Aida T, Inoue S (1987) "Immortal" polymerization of ε-caprolactone initiated by aluminum porphyrin in the presence of alcohol. Macromolecules 20:2982–2988
31. Aida T, Inoue S (1981) Living polymerization of epoxides with metalloporphyrin and synthesis of block copolymers with controlled chain lengths. Macromolecules 14:1162–1166
32. Takeuchi D, Watanabe Y, Aida T, Inoue S (1995) Lewis acid-promoted anionic polymerization of a monomer with high cationic polymerizability. Synthesis of narrow molecular weight distribution polyoxetane and polyoxetane-poly(methyl methacrylate) block copolymer with aluminum porphyrin initiators. Macromolecules 28:651–652
33. Aida T, Mizuta R, Yoshida Y, Inoue S (1981) Polymerization of epoxides catalyzed by metalloporphine. Makromol Chem Macromol Chem Phys 182:1073–1079
34. Aida T, Wada K, Inoue S (1987) Copolymerization of epoxides by aluminum porphyrin. Reactivity of (porphinato) aluminum alkoxide as growing species. Macromolecules 20:237–241
35. Yasuda T, Aida T, Inoue S (1984) Synthesis of polyester-polyether block copolymer with controlled chain length from β-lactone and epoxide by aluminum porphyrin catalyst. Macromolecules 17:2217–2222
36. Aida T, Inoue S (1996) Metalloporphyrins as initiators for living and immortal polymerizations. Acc Chem Res 29:39–48
37. Sugimoto H, Inoue S (1999) Polymerization by metalloporphyrin and related complexes. In: Jacob S, Jiang M, Kennedy JP, Li M, Sugimoto H, Xiang M, Zhou H, Inoue S (eds) Polymer synthesis/polymer-polymer complexation. Springer, Berlin/Heidelberg, pp 39–119
38. Sugimoto H, Kawamura C, Kuroki M, Aida T, Inoue S (1994) Lewis acid-assisted anionic ring-opening polymerization of epoxide by the aluminum complexes of porphyrin, phthalocyanine, tetraazaannulene, and schiff-base as initiators. Macromolecules 27:2013–2018
39. Takeuchi D, Aida T (1996) Controlled coordinate anionic polymerization of oxetane by novel initiating systems: onium salts/bulky organoaluminum diphenolates. Macromolecules 29:8096–8100

40. Braune W, Okuda J (2003) An efficient method for controlled propylene oxide polymerization: the significance of bimetallic activation in aluminum Lewis acids. Angew Chem Int Ed 42:64–68
41. Tsvetanov CB, Petrova EB, Panayotov IM (1985) Polymerization of 1,2-epoxides initiated by tetraalkyl aluminates. 1. Polymerization of ethylene-oxide in the presence of sodium tetrabutyl aluminate. J Macromol Sci A Chem A22:1309–1324
42. Billouard C, Carlotti S, Desbois P, Deffieux A (2004) "Controlled" high-speed anionic polymerization of propylene oxide initiated by alkali metal alkoxide/trialkylaluminum systems. Macromolecules 37:4038–4043
43. Carlotti S, Billouard C, Gautriaud E, Desbois P, Deffieux A (2005) Activation mechanisms of trialkylaluminum in alkali metal alkoxides or tetraalkylammonium salts / propylene oxide controlled anionic polymerization. Macromol Symp 226:61–68
44. Carlotti S, Desbois P, Billouard C, Deffieux A (2006) Reactivity control in anionic polymerization of ethylenic and heterocyclic monomers through formation of 'ate' complexes. Polym Int 55:1126–1131
45. Labbé A, Carlotti S, Billouard C, Desbois P, Deffieux A (2007) Controlled high-speed anionic polymerization of propylene oxide initiated by onium salts in the presence of triisobutylaluminum. Macromolecules 40:7842–7847
46. Desbois P, Deffieux A, Carlotti S, Billouard C (2007) Method for the anionic polymerisation of oxiranes. US 2007100097, EP1629026
47. Desbois P, Deffieux A, Carlotti S, Billouard C (2007) Method for the anionic polymerization of oxirans. US 2007173576, EP1682603
48. Rejsek V, Sauvanier D, Billouard C, Desbois P, Deffieux A, Carlotti S (2007) Controlled anionic homo- and copolymerization of ethylene oxide and propylene oxide by monomer activation. Macromolecules 40:6510–6514
49. Rejsek V, Desbois P, Deffieux A, Carlotti S (2010) Polymerization of ethylene oxide initiated by lithium derivatives via the monomer-activated approach: application to the direct synthesis of PS-b-PEO and PI-b-PEO diblock copolymers. Polymer 51:5674–5679
50. Carlotti S, Labbé A, Rejsek V, Doutaz S, Gervais M, Deffieux A (2008) Living/controlled anionic polymerization and copolymerization of epichlorohydrin with tetraoctylammonium bromide-triisobutylaluminum initiating systems. Macromolecules 41:7058–7062
51. Labbé A, Carlotti S, Deffieux A, Hirao A (2007) Controlled polymerization of glycidyl methyl ether initiated by onium salt/triisobutylaluminum and investigation of the polymer LCST. Macromol Symp 249–250:392–397
52. Gervais M, Brocas AL, Cendejas G, Deffieux A, Carlotti S (2010) Synthesis of linear high molar mass glycidol-based polymers by monomer-activated anionic polymerization. Macromolecules 43:1778–1784
53. Quirk RP, Guo Y, Wesdemiotis C, Arnould MA (2004) Investigation of ethylene oxide oligomerization during functionalization of poly(butadienyl)lithium using MALDI-TOF MS and H-1 NMR analyses. Polymer 45:3423–3428
54. Quirk RP, Ma JJ (1988) Characterization of the functionalization reaction-product of poly (styryl)lithium with ethylene-oxide. J Polym Sci A Polym Chem 26:2031–2037
55. Goeke GL, Karol F (1980) Process for preparing olefin oxide polymerization catalysts by aging the catalysts. US 4193892
56. Dimitrov I, Tsvetanov CB (2012) 4.21 – high-molecular-weight poly(ethylene oxide). In: Matyjaszewski K, Möller M (eds) Polymer science: a comprehensive reference. Elsevier, Amsterdam, pp 551–569
57. Nelles G, Rosselli S, Miteva T, Yasuda A, Tsvetanov C, Stamenova R, Berlinova I, Petrov P (2010) Method of producing a poly (ethylene oxide) copolymerised with at least one other alkylene oxide. US 2010056753
58. Petrov P, Berlinova I, Tsvetanov CB, Rosselli S, Schmid A, Zilaei AB, Miteva T, Durr M, Yasuda A, Nelles G (2008) High-molecular-weight polyoxirane copolymers and their use in high-performance dye-sensitized solar cells. Macromol Mater Eng 293:598–604

59. Petrov P, Rangelov S, Novakov C, Brown W, Berlinova I, Tsvetanov CB (2002) Core-corona nanoparticles formed by high molecular weight poly(ethylene oxide)-b-poly(alkylglycidyl ether) diblock copolymers. Polymer 43:6641–6651
60. Dimitrov P, Hasan E, Rangejov S, Trzebicka B, Dworak A, Tsvetanov CB (2002) High molecular weight functionalized poly(ethylene oxide). Polymer 43:7171–7178
61. Hasan E, Jankova K, Samichkov V, Ivanov Y, Tsvetanov CB (2002) Graft copolymers composed of high molecular weight poly(ethylene oxide) backbone and poly (N-isopropylaerlylamide) side chains and their thermoassociating properties. Macromol Symp 177:125–138
62. Berger J, Lohse F (1985) Polymerization of para-cresyl glycidyl ether induced by benzyldimethylamine. Eur Polym J 21:435–444
63. Tanaka Y, Tomio M, Kakiuchi H (1967) Oligomerization of substituted phenyl glycidyl ethers with tertiary amine. J Macromol Sci A Chem 1:471–491
64. Dell'Erba IE, Williams RJJ (2006) Homopolymerization of epoxy monomers initiated by 4-(dimethylamino)pyridine. Polym Eng Sci 46:351–359
65. Herrmann WA (2002) N-heterocyclic carbenes: a new concept in organometallic catalysis. Angew Chem Int Ed 41:1290–1309
66. Bourissou D, Guerret O, Gabbai FP, Bertrand G (2000) Stable carbenes. Chem Rev 100:39–91
67. Naumann S, Buchmeiser MR (2014) Liberation of N-heterocyclic carbenes (NHCs) from thermally labile progenitors: protected NHCs as versatile tools in organo- and polymerization catalysis. Catal Sci Technol 4:2466–2479
68. Raynaud J, Absalon C, Gnanou Y, Taton D (2009) N-heterocyclic carbene-induced zwitterionic ring-opening polymerization of ethylene oxide and direct synthesis of α, ω-difunctionalized poly(ethylene oxide)s and poly(ethylene oxide)-b-poly(ε-caprolactone) block copolymers. J Am Chem Soc 131:3201–3209
69. Raynaud J, Absalon C, Gnanou Y, Taton D (2010) N-Heterocyclic carbene-organocatalyzed ring-opening polymerization of ethylene oxide in the presence of alcohols or trimethylsilyl nucleophiles as chain moderators for the synthesis of α, ω-heterodifunctionalized poly(ethylene oxide)s. Macromolecules 43:2814–2823
70. Raynaud J, Ottou WN, Gnanou Y, Taton D (2010) Metal-free and solvent-free access to α, ω-heterodifunctionalized poly(propylene oxide)s by N-heterocyclic carbene-induced ring opening polymerization. Chem Commun 46:3203–3205
71. Maitre C, Ganachaud F, Ferreira O, Lutz JF, Paintoux Y, Hemery P (2000) Anionic polymerization of phenyl glycidyl ether in miniemulsion. Macromolecules 33:7730–7736
72. Morinaga H, Ochiai B, Endo T (2007) Metal-free ring-opening polymerization of glycidyl phenyl ether by tetrabutylammonium fluoride. Macromolecules 40:6014–6016
73. Morinaga H, Ujihara Y, Endo T (2013) Synthesis of amphiphilic block copolymer by metal-free ring-opening oligomerization of glycidyl phenyl ether initiated with tetra-n-butylammonium fluoride in the presence of poly(ethylene glycol) monomethyl ether. J Polym Sci A Polym Chem 51:4451–4458
74. Boileau S, Illy N (2011) Activation in anionic polymerization: why phosphazene bases are very exciting promoters. Prog Polym Sci 36:1132–1151
75. Schwesinger R, Schlemper H (1987) Peralkylierte polyaminophosphazene -extrem Starke neutrale stickstoffbasen. Angew Chem 99:1212–1214
76. Esswein B, Moller M (1996) Polymerization of ethylene oxide with alkyllithium compounds and the phosphazene base "tBu-P-4". Angew Chem Int Ed 35:623–625
77. Esswein B, Steidl NM, Moller M (1996) Anionic polymerization of oxirane in the presence of the polyiminophosphazene base t-Bu-P-4. Macromol Rapid Commun 17:143–148
78. Schlaad H, Kukula H, Rudloff J, Below I (2001) Synthesis of alpha, omega-heterobifunctional poly(ethylene glycol)s by metal-free anionic ring-opening polymerization. Macromolecules 34:4302–4304

79. Schmalz H, Lanzendorfer MG, Abetz V, Muller AHE (2003) Anionic polymerization of ethylene oxide in the presence of the phosphazene base (BuP4)-P-t - Kinetic investigations using in-situ FT-NIR spectroscopy and MALDI-ToF MS. Macromol Chem Phys 204:1056–1071
80. Zhao JP, Schlaad H, Weidner S, Antonietti M (2012) Synthesis of terpene-poly(ethylene oxide)s by t-BuP4-promoted anionic ring-opening polymerization. Polym Chem 3:1763–1768
81. Zhao JP, Schlaad H (2011) Controlled anionic graft polymerization of ethylene oxide directly from poly(N-isopropylacrylamide). Macromolecules 44:5861–5864
82. Zhao J, Pahovnik D, Gnanou Y, Hadjichristidis N (2014) A "catalyst switch" strategy for the sequential metal-free polymerization of epoxides and cyclic esters/carbonate. Macromolecules 47:3814–3822
83. Zhao J, Pahovnik D, Gnanou Y, Hadjichristidis N (2014) Phosphazene-promoted metal-free ring-opening polymerization of ethylene oxide initiated by carboxylic acid. Macromolecules 47:1693–1698
84. Zhao J, Pahovnik D, Gnanou Y, Hadjichristidis N (2014) Sequential polymerization of ethylene oxide, epsilon-caprolactone and L-lactide: a one-pot metal-free route to tri- and pentablock terpolymers. Polym Chem 5:3750–3753
85. Nobori T, Hayashi T, Shibahara A, Saeki T, Yamasaki S, Ohkubo K (2010) Development of novel molecular catalysts "phosphazene catalysts" for commercial production of highly advanced polypropylene glycols. Catal Surv Asia 14:164–167
86. Rexin O, Mulhaupt R (2002) Anionic ring-opening polymerization of propylene oxide in the presence of phosphonium catalysts. J Polym Sci A Polym Chem 40:864–873
87. Rexin O, Mulhaupt R (2003) Anionic ring-opening polymerization of propylene oxide in the presence of phosphonium catalysts at various temperatures. Macromol Chem Phys 204:1102–1109
88. Misaka H, Tamura E, Makiguchi K, Kamoshida K, Sakai R, Satoh T, Kakuchi T (2012) Synthesis of end-functionalized polyethers by phosphazene base-catalyzed ring-opening polymerization of 1,2-butylene oxide and glycidyl ether. J Polym Sci A Polym Chem 50:1941–1952
89. Isono T, Kamoshida K, Satoh Y, Takaoka T, Sato S-I, Satoh T, Kakuchi T (2013) Synthesis of star- and figure-eight-shaped polyethers by t-Bu-P4-catalyzed ring-opening polymerization of butylene oxide. Macromolecules 46:3841–3849
90. Misaka H, Sakai R, Satoh T, Kakuchi T (2011) Synthesis of high molecular weight and end-functionalized poly(styrene oxide) by living ring-opening polymerization of styrene oxide using the alcohol/phosphazene base initiating system. Macromolecules 44:9099–9107
91. Hans M, Keul H, Moeller M (2009) Chain transfer reactions limit the molecular weight of polyglycidol prepared via alkali metal based initiating systems. Polymer 50:1103–1108
92. Toy AA, Reinicke S, Muller AHE, Schmalz H (2007) One-pot synthesis of polyglycidol-containing block copolymers with alkyllithium initiators using the phosphazene base t-BuP4. Macromolecules 40:5241–5244
93. Isono T, Satoh Y, Miyachi K, Chen Y, S-i S, Tajima K, Satoh T, Kakuchi T (2014) Synthesis of linear, cyclic, figure-eight-shaped, and tadpole-shaped amphiphilic block copolyethers via t-Bu-P4-catalyzed ring-opening polymerization of hydrophilic and hydrophobic glycidyl ethers. Macromolecules 47:2853–2863
94. Groenewolt M, Brezesinski T, Schlaad H, Antonietti M, Groh PW, Ivan B (2005) Polyisobutylene-block-poly(ethylene oxide) for robust templating of highly ordered mesoporous materials. Adv Mater 17:1158–1162
95. Thomas A, Schlaad H, Smarsly B, Antonietti M (2003) Replication of lyotropic block copolymer mesophases into porous silica by nanocasting: Learning about finer details of polymer self-assembly. Langmuir 19:4455–4459

96. Yang H, Yan M, Pispas S, Zhang G (2011) Synthesis of poly (ethylene carbonate)-co-(ethylene oxide) copolymer by phosphazene-catalyzed ROP. Macromol Chem Phys 212:2589–2593
97. Forster S, Kramer E (1999) Synthesis of PB-PEO and PI-PEO block copolymers with alkyllithium initiators and the phosphazene base t-BuP4. Macromolecules 32:2783–2785
98. Zhao J, Alamri H, Hadjichristidis N (2013) A facile metal-free "grafting-from" route from acrylamide-based substrate toward complex macromolecular combs. Chem Commun 49:7079–7081
99. Zhao JP, Mountrichas G, Zhang GX, Pispas S (2009) Amphiphilic polystyrene-b-poly (p-hydroxystyrene-g-ethylene oxide) block-graft copolymers via a combination of conventional and metal-free anionic polymerization. Macromolecules 42:8661–8668
100. Zhao JP, Zhang GZ, Pispas S (2010) Thermoresponsive brush copolymers with poly(propylene oxide-ran-ethylene oxide) side chains via metal-free anionic polymerization "grafting from" technique. J Polym Sci A Polym Chem 48:2320–2328
101. Esswein B, Molenberg A, Moller M (1996) Use of polyiminophosphazene bases for ring-opening polymerizations. Macromol Symp 107:331–340
102. Brocas AL, Mantzaridis C, Tunc D, Carlotti S (2013) Polyether synthesis: from activated or metal-free anionic ring-opening polymerization of epoxides to functionalization. Prog Polym Sci 38:845–873
103. Obermeier B, Wurm F, Mangold C, Frey H (2011) Multifunctional poly(ethylene glycol)s. Angew Chem Int Ed 50:7988–7997
104. Mangold C, Wurm F, Frey H (2012) Functional PEG-based polymers with reactive groups via anionic ROP of tailor-made epoxides. Polym Chem 3:1714–1721
105. Thompson MS, Vadala TP, Vadala ML, Lin Y, Riffle JS (2008) Synthesis and applications of heterobifunctional poly(ethylene oxide) oligomers. Polymer 49:345–373
106. Chattopadhyay DK, Raju K (2007) Structural engineering of polyurethane coatings for high performance applications. Prog Polym Sci 32:352–418
107. Gnanou Y, Lutz P, Rempp P (1988) Synthesis of star-shaped poly(ethylene oxide). Makromol Chem Macromol Chem Phys 189:2885–2892
108. Hou S, Chaikof EL, Taton D, Gnanou Y (2003) Synthesis of water-soluble star-block and dendrimer-like copolymers based on poly(ethylene oxide) and poly(acrylic acid). Macromolecules 36:3874–3881
109. Lapienis G (2009) Star-shaped polymers having PEO arms. Prog Polym Sci 34:852–892
110. Six JL, Gnanou Y (1995) From star-shaped to dendritic poly(ethylene oxide)s – toward increasingly branched architectures by anionic-polymerization. Macromol Symp 95:137–150
111. Taton D, Saule M, Logan J, Duran R, Sijian HOU, Chaikof EL, Gnanou Y (2003) Polymerization of ethylene oxide with a calixarene-based precursor: Synthesis of eight-arm poly (ethylene oxide) stars by the core-first methodology. J Polym Sci A Polym Chem 41:1669–1676
112. Choi YR, Bae YH, Kim SW (1998) Star-shaped poly(ether-ester) block copolymers: synthesis, characterization, and their physical properties. Macromolecules 31:8766–8774
113. Comanita B, Noren B, Roovers J (1999) Star poly(ethylene oxide)s from carbosilane dendrimers. Macromolecules 32:1069–1072
114. Dworak A, Walach W (2009) Synthesis, characterization and properties of functional star and dendritic block copolymers of ethylene oxide and glycidol with oligoglycidol branching units. Polymer 50:3440–3447
115. Brocas AL, Deffieux A, Le Malicot N, Carlotti S (2012) Combination of phosphazene base and triisobutylaluminum for the rapid synthesis of polyhydroxy telechelic poly(propylene oxide). Polym Chem 3:1189–1195
116. Mosquet M, Chevalier Y, LePerchec P, Guicquero JP (1997) Synthesis of poly(ethylene oxide) with a terminal amino group by anionic polymerization of ethylene oxide initiated by aminoalcoholates. Macromol Chem Phys 198:2457–2474

117. Morinaga H, Ujihara Y, Yuto N, Nagai D, Endo T (2011) Controlled polymerization of epoxides: metal-free ring-opening polymerization of glycidyl phenyl ether initiated by tetra-n-butylammonium fluoride in the presence of protic compounds. J Polym Sci A Polym Chem 49:5210–5216
118. Wong EWC (1981) Development of a biomedical polyurethane. In: Urethane chemistry and applications, vol 172, ACS Symposium Series of American Chemical Society., pp 489–504
119. Sandler SR, Berg F (1966) Room temperature polymerization of glycidol. J Polym Sci A Polym Chem 4:1253–1259
120. Sunder A, Hanselmann R, Frey H, Mulhaupt R (1999) Controlled synthesis of hyperbranched polyglycerols by ring-opening multibranching polymerization. Macromolecules 32:4240–4246
121. Sunder A, Heinemann J, Frey H (2000) Controlling the growth of polymer trees: concepts and perspectives for hyperbranched polymers. Chem Eur J 6:2499–2506
122. Sunder A, Mulhaupt R, Haag R, Frey H (2000) Hyperbranched polyether polyols: a modular approach to complex polymer architectures. Adv Mater 12:235–239
123. Vandenberg EJ (1985) Polymerization of glycidol and its derivatives – a new rearrangement polymerization. J Polym Sci A Polym Chem 23:915–949
124. Wilms D, Stiriba SE, Frey H (2010) Hyperbranched polyglycerols: from the controlled synthesis of biocompatible polyether polyols to multipurpose applications. Acc Chem Res 43:129–141
125. Wurm F, Frey H (2011) Linear-dendritic block copolymers: the state of the art and exciting perspectives. Prog Polym Sci 36:1–52
126. Schüll C, Wilms D, Frey H (2012) 4.22 – nonlinear macromolecules by ring-opening polymerization. In: Matyjaszewski K, Möller M (eds) Polymer science: a comprehensive reference. Elsevier, Amsterdam, pp 571–596
127. Dimitrov P, Rangelov S, Dworak A, Tsvetanov CB (2004) Synthesis and associating properties of poly(ethoxyethyl glycidyl ether)/poly(propylene oxide) triblock copolymers. Macromolecules 37:1000–1008
128. Libera M, Trzebicka B, Kowalczuk A, Walach W, Dworak A (2011) Synthesis and thermoresponsive properties of four arm, amphiphilic poly(tert-butyl-glycidylether)-block-polyglycidol stars. Polymer 52:250–257
129. Libera M, Walach W, Trzebicka B, Rangelov S, Dworak A (2011) Thermosensitive dendritic stars of tert-butyl-glycidylether and glycidol – synthesis and encapsulation properties. Polymer 52:3526–3536
130. Mendrek A, Mendrek S, Trzebicka B, Kuckling D, Walach J, Adler HJ, Dworak A (2005) Polyether core-shell cylinder-polymerization of polyglycidol macromonomers. Macromol Chem Phys 206:2018–2026
131. Walach W, Trzebicka B, Justynska J, Dworak A (2004) High molecular arborescent polyoxyethylene with hydroxyl containing shell. Polymer 45:1755–1762
132. Haamann D, Keul H, Klee D, Moller M (2010) Functionalization of linear and star-shaped polyglycidols with vinyl sulfonate groups and their reaction with different amines and alcohols. Macromolecules 43:6295–6301
133. Erberich M, Keul H, Moller M (2007) Polyglycidols with two orthogonal protective groups: preparation, selective deprotection, and functionalization. Macromolecules 40:3070–3079
134. Keul H, Moller M (2009) Synthesis and degradation of biomedical materials based on linear and star shaped polyglycidols. J Polym Sci A Polym Chem 47:3209–3231
135. Mangold C, Wurm F, Obermeier B, Frey H (2010) "Functional poly(ethylene glycol)": PEG-based random copolymers with 1,2-diol side chains and terminal amino functionality. Macromolecules 43:8511–8518
136. Wurm F, Nieberle J, Frey H (2008) Synthesis and characterization of poly(glyceryl glycerol) block copolymers. Macromolecules 41:1909–1911

137. Backes M, Messager L, Mourran A, Keul H, Moeller M (2010) Synthesis and thermal properties of well-defined amphiphilic block copolymers based on polyglycidol. Macromolecules 43:3238–3248
138. Halacheva S, Rangelov S, Tsvetanov C (2006) Poly(glycidol)-based analogues to pluronic block copolymers. Synthesis and aqueous solution properties. Macromolecules 39:6845–6852
139. Huang J, Li ZY, Xu XW, Ren Y, Huang JL (2006) Preparation of novel poly(ethyleneoxide-co-glycidol)-graft-poly(epsilon-caprolactone) copolymers and inclusion complexation of the grafted chains with alpha-cyclodextrin. J Polym Sci A Polym Chem 44:3684–3691
140. Kaluzynski K, Pretula J, Lapienis G, Basko M, Bartczak Z, Dworak A, Penczek S (2001) Dihydrophilic block copolymers with ionic and nonionic blocks. I. Poly(ethylene oxide)-b-polyglycidol with OP(O)(OH)(2) COOH, or SO_3H functions: synthesis and influence for $CaCO_3$ crystallization. J Polym Sci A Polym Chem 39:955–963
141. Li ZY, Chau Y (2009) Synthesis of linear polyether polyol derivatives as new materials for bioconjugation. Bioconjugate Chem 20:780–789
142. Kochergin YS, Pyrikov AV, Kulik TA, Grigorenko TI (2010) Investigation of epoxide adhesive compositions cured with polyoxypropylene triamine. Polym Sci Ser D 3:47–49
143. Morgan RJ, Kong FM, Walkup CM (1984) Structure property relations of polyethertriamine-cured bisphenol-A-diglycidyl ether epoxies. Polymer 25:375–386
144. Poellmann K, Muenter J (2007) Polyetheramine macromonomers comprising two neighboring hydroxyl groups and their use for producing polyurethanes. US 20070376273
145. Rowton LR (1971) Polyoxypropylenediamine chain extenders for polyurethane latices CA877362
146. Yokoyama M, Okano T, Sakurai Y, Kikuchi A, Ohsako N, Nagasaki Y, Kataoka K (1992) Synthesis of poly(ethylene oxide) with heterobifunctional reactive groups at its terminals by an anionic initiator. Bioconjugate Chem 3:275–276
147. Obermeier B, Wurm F, Frey H (2010) Amino functional poly(ethylene glycol) copolymers via protected amino glycidol. Macromolecules 43:2244–2251
148. Reuss VS, Obermeier B, Dingels C, Frey H (2012) N, N-diallylglycidylamine: a Key monomer for amino-functional poly(ethylene glycol) architectures. Macromolecules 45:4581–4589
149. Meyer J, Keul H, Moller M (2011) Poly(glycidyl amine) and copolymers with glycidol and glycidyl amine repeating units: synthesis and characterization. Macromolecules 44:4082–4091
150. Du J, Murakami Y, Senyo T, Adam IK, Yagci Y (2004) Synthesis of well-defined hybrid macromonomers of poly(ethylene oxide) and their reactivity in photoinitiated polymerization. Macromol Chem Phys 205:1471–1478
151. Studer P, Breton P, Riess G (2005) Allyl end-functionalized poly(ethylene oxide)-block-poly (methylidene malonate 2.1.2) block copolymers: synthesis, characterization, and chemical modification. Macromol Chem Phys 206:2461–2469
152. Herrwerth S, Rosendahl T, Feng C, Fick J, Eck W, Himmelhaus M, Dahint R, Grunze M (2003) Covalent coupling of antibodies to self-assembled monolayers of carboxy-functionalized poly(ethylene glycol): protein resistance and specific binding of biomolecules. Langmuir 19:1880–1887
153. Harris H, Lamy Y, Lutz PJ (2006) Macromonomers as well-defined building blocks in the synthesis of hybrid octafunctional star shaped or crosslinked poly(ethylene oxide)s. Polym Prepr 47:551–552
154. Harris H, Nohra B, Gavat O, Lutz PJ (2010) New trends in poly(ethylene oxide) or polystyrene macromonomer based networks exhibiting silsesquioxane cross-linking points. Macromol Symp 291–292:43–49

155. Lee BF, Wolffs M, Delaney KT, Sprafke JK, Leibfarth FA, Hawker CJ, Lynd NA (2012) Reactivity ratios and mechanistic insight for anionic ring-opening copolymerization of epoxides. Macromolecules 45:3722–3731
156. Brocas AL, Cendejas G, Caillol S, Deffieux A, Carlotti S (2011) Controlled synthesis of polyepichlorohydrin with pendant cyclic carbonate functions for isocyanate-free polyurethane networks. J Polym Sci A Polym Chem 49:2677–2684
157. Lee BF, Kade MJ, Chute JA, Gupta N, Campos LM, Fredrickson GH, Kramer EJ, Lynd NA, Hawker CJ (2011) Poly(allyl glycidyl ether) – a versatile and functional polyether platform. J Polym Sci A Polym Chem 49:4498–4504
158. Mangold C, Dingels C, Obermeier B, Frey H, Wurm F (2011) PEG-based multifunctional polyethers with highly reactive vinyl-ether side chains for click-type functionalization. Macromolecules 44:6326–6334
159. Cheng GW, Fan XD, Tian W, Liu YY, Kong JE (2010) Synthesis of three-arm poly(ethylene glycol) by combination of controlled anionic polymerization and 'click' chemistry. Polym Int 59:543–551
160. Hua C, Peng SM, Dong CM (2008) Synthesis and characterization of linear-dendron-like poly(epsilon-caprolactone)-b-poly(ethylene oxide) copolymers via the combination of ring-opening polymerization and click chemistry. Macromolecules 41:6686–6695
161. Stefanko MJ, Gun'ko YK, Rai DK, Evans P (2008) Synthesis of functionalised polyethylene glycol derivatives of naproxen for biomedical applications. Tetrahedron 64:10132–10139
162. Wang WJ, Li T, Yu T, Zhu FM (2008) Synthesis of Multiblock Copolymers by Coupling Reaction Based on Self-Assembly and Click Chemistry. Macromolecules 41:9750–9754
163. Hiki S, Kataoka K (2007) A facile synthesis of azido-terminated heterobifunctional poly (ethylene glycol)s for "click" conjugation. Bioconjugate Chem 18:2191–2196
164. Bertozzi CR, Bednarski MD (1991) The synthesis of heterobifunctional linkers for the conjugation of ligands to molecular probes. J Org Chem 56:4326–4329
165. Iyer SS, Anderson AS, Reed S, Swanson B, Schmidt JG (2004) Synthesis of orthogonal end functionalized oligoethylene glycols of defined lengths. Tetrahedron Lett 45:4285–4288
166. Gervais M, Labbé A, Carlotti S, Deffieux A (2009) Direct synthesis of α-Azido, ω-hydroxypolyethers by monomer-Activated anionic polymerization. Macromolecules 42:2395–2400
167. Huisgen R (1984) 1,3-Dipolar Cycloaddition Chemistry. In: Padwa A (ed) 1,3-Dipolar cycloaddition chemistry. Wiley, New York, pp 1–176
168. Zeng F, Allen C (2006) Synthesis of carboxy-functionalized heterobifunctional poly(ethylene glycol) by a thiol-anionic polymerization method. Macromolecules 39:6391–6398
169. Mizrahi DM, Omer-Mizrahi M, Goldshtein J, Askinadze N, Margel S (2010) Novel Poly (ethylene glycol) Monomers Bearing Diverse Functional Groups. J Polym Sci A, Polym Chem 48:5468–5478
170. Vadala ML, Thompson MS, Ashworth MA, Lin Y, Vadala TP, Ragheb R, Riffle JS (2008) Heterobifunctional poly(ethylene oxide) oligomers containing carboxylic acids. Biomacromolecules 9:1035–1043
171. Zhang S, Du H, Sun R, Li XP, Yang DJ, Zhang SG, Xiong CD, Peng YX (2003) Synthesis of heterobifunctional poly(ethylene glycol) with a primary amino group at one end and a carboxylate group at the other end. React Funct Polym 56:17–25
172. Akiyama Y, Nagasaki Y, Kataoka K (2004) Synthesis of heterotelechelic poly(ethylene glycol) derivatives having alpha-benzaldehyde and omega-pyridyl disulfide groups by ring opening polymerization of ethylene oxide using 4-(diethoxymethyl)benzyl alkoxide as a novel initiator. Bioconjugate Chem 15:424–427
173. Labbé A, Brocas AL, Ibarboure E, Ishizone T, Hirao A, Deffieux A, Carlotti S (2011) Selective ring-opening polymerization of glycidyl methacrylate: Toward the synthesis of cross-linked (co)polyethers with thermoresponsive properties. Macromolecules 44:6356–6364

174. Jerome C, Lecomte P (2008) Recent advances in the synthesis of aliphatic polyesters by ring-opening polymerization. Adv Drug Deliv Rev 60:1056–1076
175. Lecomte P, Jerome C (2012) Recent developments in ring-opening polymerization of lactones. In: Rieger B, Kunkel A, Coates GW, Reichardt R, Dinjus E, Zevaco TA (eds) Advances in polymer science. Synthetic biodegradable polymers, vol 245. pp 173–217
176. Albertsson A-C, Varma IK, Srivastava RK (2009) Polyesters from large lactones. In: Handbook of ring-opening polymerization. Wiley-VCH Verlag GmbH & Co. KGaA, pp 287–306
177. Coulembier O, Dubois P (2009) Polyesters from β-lactones. In: Handbook of ring-opening polymerization. Wiley-VCH Verlag GmbH & Co. KGaA, pp 227–254
178. Dechy-Cabaret O, Martin-Vaca B, Bourissou D (2009) Polyesters from dilactones. In: Handbook of ring-opening polymerization. Wiley-VCH Verlag GmbH & Co. KGaA, pp 255–286
179. Dechy-Cabaret O, Martin-Vaca B, Bourissou D (2004) Controlled ring-opening polymerization of lactide and glycolide. Chem Rev 104:6147–6176
180. Duda A (2012) 4.11 – ROP of cyclic esters. Mechanisms of ionic and coordination processes. In: Matyjaszewski K, Möller M (eds) Polymer science: a comprehensive reference. Elsevier, Amsterdam, pp 213–246
181. Labet M, Thielemans W (2009) Synthesis of polycaprolactone: a review. Chem Soc Rev 38:3484–3504
182. Platel RH, Hodgson LM, Williams CK (2008) Biocompatible initiators for lactide polymerization. Polymer Reviews 48:11–63
183. Slomkowski S (2012) 4.25 – Ring-opening dispersion polymerization. In: Matyjaszewski K, Möller M (eds) Polymer science: a comprehensive reference. Elsevier, Amsterdam, pp 645–660
184. Thomas CM (2010) Stereocontrolled ring-opening polymerization of cyclic esters: synthesis of new polyester microstructures. Chem Soc Rev 39:165–173
185. Wheaton CA, Hayes PG, Ireland BJ (2009) Complexes of Mg. Ca and Zn talyas homogeneous casts for lactide polymerization. Dalton Trans (25):4832–4846
186. Gupta AP, Kumar V (2007) New emerging trends in synthetic biodegradable polymers - Polylactide: A critique. Eur Polym J 43:4053–4074
187. Zhu ZX, Deng XM, Xiong CD (2001) Anionic ring-opening polymerization of D.L-lactide. Ind J Chem B - Org Chem Med Chem 40:108–112
188. Kurcok P, Matuslonicz A, Jedlinski Z (1995) Anionic-polymerization as a tool in the synthesis of biodegradable polymers. J Polym Mater 12:161–174
189. Jedlinski Z, Kurcok P, Lenz RW (1995) Synthesis of potentially biodegradable polymers. J Macromol Sci, Pure Appl Chem A32:797–810
190. Jedlinski Z, Walach W, Kurcok P, Adamus G (1991) Polymerization of lactones.12. Polymerization of L-dilactide and L, D-dilactide in the presence of potassium methoxide. Makromol Chem. Macromol Chem Phys 192:2051–2057
191. Sipos L, Zsuga M, Kelen T (1992) Living ring-opening polymerization of L, L-lactide initiated with potassium tert-butoxide and its 18-crown-6 complex. Polym Bull 27:495–502
192. Kricheldorf HR, Kreisersaunders I (1990) Polylactones.19. Anionic-polymerization of L-lactide in solution. Makromol Chem. Macromol Chem Phys 191:1057–1066
193. Kricheldorf HR, Kreisersaunders I, Scharnagl N (1990) Anionic and pseudoanionic polymerization of lactones - a comparison. Makromol Chem, Macromol Symp 32:285–298
194. Kricheldorf HR, Boettcher C (1993) Polylactones.27. Anionic-polymerization of L-lactide - variation of endgroups and synthesis of block-copolymers with poly(ethylene oxide). Makromol Chem. Macromol Symp 73:47–64
195. Kitamura T, Matsumoto A (2007) Synthesis of poly(lactic acid) with branched and network structures containing thermally degradable junctions. Macromolecules 40:509–517
196. Stere C, Iovu M, Boborodea A, Vasilescu DS, Fazakas-Anca IS (1998) Anionic and ionic coordinative polymerization of L-lactide. Polym Adv Technol 9:322–325

197. Sipos L, Gunda T, Zsuga M (1997) The role of complex formation in the anionic polymerization of L-lactide. Polym Bull 38:609–612
198. Sipos L, Zsuga M (1997) Anionic polymerization of L-lactide effect of lithium and potassium as counterions. J Macromol Sci, Pure Appl Chem A34:1269–1284
199. Kasperczyk JE (1995) Microstructure Analysis of Poly(lactic acid) Obtained by Lithium tert-Butoxide as Initiator. Macromolecules 28:3937–3939
200. Bero M, Dobrzyński P, Kasperczyk J (1999) Synthesis of disyndiotactic polylactide. J Polym Sci A Polym Chem 37:4038–4042
201. Kricheldorf HR, Boettcher C (1993) Polylactones 26. Lithium alkoxide-initiated polymerizations of L-lactide. Makromol Chem 194:1665–1669
202. Bhaw-Luximon A, Jhurry D, Spassky N, Pensec S, Belleney J (2001) Anionic polymerization of D, L-lactide initiated by lithium diisopropylamide. Polymer 42:9651–9656
203. Emoto K, Nagasaki Y, Iijima M, Kato M, Kataoka K (2000) Preparation of non-fouling surface through the coating with core-polymerized block copolymer micelles having aldehyde-ended PEG shell. Coll Surf B Biointerf 18:337–346
204. Jule E, Nagasaki Y, Kataoka K (2002) Surface plasmon resonance study on the interaction between lactose-installed poly(ethylene glycol)-poly(D, L-lactide) block copolymer micelles and lectins immobilized on a gold surface. Langmuir 18:10334–10339
205. Jule E, Yamamoto Y, Thouvenin M, Nagasaki Y, Kataoka K (2004) Thermal characterization of poly(ethylene glycol)-poly(D, L-lactide) block copolymer micelles based on pyrene excimer formation. J Control Rel 97:407–419
206. Kim JH, Emoto K, Iijima M, Nagasaki Y, Aoyagi T, Okano T, Sakurai Y, Kataoka K (1999) Core-stabilized polymeric micelle as potential drug carrier: Increased solubilization of taxol. Polym Adv Technol 10:647–654
207. Moroishi H, Yoshida C, Murakami Y (2013) A free-standing, sheet-shaped, "hydrophobic" biomaterial containing polymeric micelles formed from poly(ethylene glycol)-poly(lactic acid) block copolymer for possible incorporation/release of "hydrophilic" compounds. Coll Surf B Biointerf 102:597–603
208. Nagasaki Y, Okada T, Scholz C, Iijima M, Kato M, Kataoka K (1998) The reactive polymeric micelle based on an aldehyde-ended poly(ethylene glycol)/poly(lactide) block copolymer. Macromolecules 31:1473–1479
209. Tanodekaew S, Pannu R, Heatley F, Attwood D, Booth C (1997) Association and surface properties of diblock copolymers of ethylene oxide and DL-lactide in aqueous solution. Macromol Chem Phys 198:927–944
210. Yang X, Grailer JJ, Pilla S, Steeber DA, Gong S, Shuai X (2010) Multifunctional polymeric vesicles for targeted drug delivery and imaging. Biofabrication 2:025004
211. Yang X, Pilla S, Grailer JJ, Steeber DA, Gong S, Chen Y, Chen G (2009) Tumor-targeting, superparamagnetic polymeric vesicles as highly efficient MRI contrast probes. J Mater Chem 19:5812–5817
212. Yasugi K, Nagasaki Y, Kato M, Kataoka K (1999) Preparation and characterization of polymer micelles from poly(ethylene glycol)-poly(D, L-lactide) block copolymers as potential drug carrier. J Control Rel 62:89–100
213. Jedlinski Z, Kurcok P, Walach W, Janeczek H, Radecka I (1993) Polymerization of lactones.17. Synthesis of ethylene glycol-L-lactide block-copolymers. Makromol Chem. Macromol Chem Phys 194:1681–1689
214. Lemmouchi Y, Perry MC, Amass AJ, Chakraorty K, Schue F (2007) Novel synthesis of biodegradable poly(lactide-co-ethylene glycol) block copolymers. J Polym Sci A, Polym Chem 45:2235–2245
215. Stefani M, Coudane J, Vert M (2006) Effects of polymerization conditions on the in vitro hydrolytic degradation of plaques of poly(DL-lactic acid-block-ethylene glycol) diblock copolymers. Polym Degrad Stab 91:2853–2859
216. Stefani M, Coudane J, Vert M (2006) In vitro ageing and degradation of PEG – PLA diblock copolymer-based nanoparticles. Polym Degrad Stab 91:2554–2559

217. Zhu ZX, Xiong CD, Zhang LL, Yuan ML, Deng XM (1999) Preparation of biodegradable polylactide-co-poly(ethylene glycol) copolymer by lactide reacted poly(ethylene glycol). Eur Polym J 35:1821–1828
218. Pannu RK, Tanodekaew S, Li W, Collett JH, Attwood D, Booth C (1999) A DSC study of the miscibility of poly(ethylene oxide)-block-poly(DL-lactide) copolymers with poly (DL-lactide). Biomaterials 20:1381–1387
219. Sipos L, Zsuga M, Deak G (1995) Synthesis of poly(L-lactide)-block-polyisobutylene-block-poly(L-lactide), a new biodegradable thermoplastic elastomer. Macromol Rapid Commun 16:935–940
220. Deng XM, Zhu ZX, Xiong CD, Zhang LL (1997) Synthesis and characterization of biodegradable block copolymers of epsilon-caprolactone and D, L-lactide initiated by potassium poly(ethylene glycol)ate. J Polym Sci A, Polym Chem 35:703–708
221. Gadzinowski M, Sosnowski S (2003) Biodegradable/biocompatible ABC triblock copolymer bearing hydroxyl groups in the middle block. J Polym Sci A Polym Chem 41:3750–3760
222. Ohya Y, Maruhashi S, Ouchi T (1998) Preparation of poly(lactic acid)-grafted amylose through the trimethylsilyl protection method and its biodegradation. Macromol Chem Phys 199:2017–2022
223. Ouchi T, Saito T, Kontani T, Ohya Y (2004) Encapsulation and/or release behavior of bovine serum albumin within and from polylactide-grafted dextran microspheres. Macromol Biosci 4:458–463
224. Nederberg F, Connor EF, Möller M, Glauser T, Hedrick JL (2001) New paradigms for organic catalysts: the first organocatalytic living polymerization. Angew Chem Int Ed 40:2712–2715
225. Dove AP (2012) Organic catalysis for ring-opening polymerization. ACS Macro Lett 1:1409–1412
226. Fèvre M, Pinaud J, Gnanou Y, Vignolle J, Taton D (2013) N-Heterocyclic carbenes (NHCs) as organocatalysts and structural components in metal-free polymer synthesis. Chem Soc Rev 42:2142–2172
227. Kamber NE, Jeong W, Waymouth RM, Pratt RC, Lohmeijer BGG, Hedrick JL (2007) Organocatalytic ring-opening polymerization. Chem Rev 107:5813–5840
228. Kiesewetter MK, Shin EJ, Hedrick JL, Waymouth RM (2010) Organocatalysis: opportunities and challenges for polymer synthesis. Macromolecules 43:2093–2107
229. Kricheldorf HR, Lomadze N, Schwarz G (2008) Cyclic polylactides by imidazole-catalyzed polymerization of L-lactide. Macromolecules 41:7812–7816
230. Katiyar V, Nanavati H (2010) Ring-opening polymerization of L-lactide using N-heterocyclic molecules: mechanistic, kinetics and DFT studies. Polym Chem 1:1491–1500
231. Brown HA, De Crisci AG, Hedrick JL, Waymouth RM (2012) Amidine-mediated zwitterionic polymerization of lactide. ACS Macro Lett 1:1113–1115
232. Myers M, Connor EF, Glauser T, Möck A, Nyce GW, Hedrick JL (2002) Phosphines: nucleophilic organic catalysts for the controlled ring-opening polymerization of lactides. J Polym Sci A Polym Chem 40:844–851
233. Zhang L, Nederberg F, Messman JM, Pratt RC, Hedrick JL, Wade CG (2007) Organocatalytic stereoselective ring-opening polymerization of lactide with dimeric phosphazene bases. J Am Chem Soc 129:12610–12611
234. Zhang L, Nederberg F, Pratt RC, Waymouth RM, Hedrick JL, Wade C (2007) Phosphazene bases: a new category of organocatalysts for the living ring-opening polymerization of cyclic esters. Macromolecules 40:4154–4158
235. Brule E, Guerineau V, Vermaut P, Prima F, Balogh J, Maron L, Slawin AMZ, Nolan SP, Thomas CM (2013) Polymerization of cyclic esters using N-heterocyclic carbene carboxylate catalysts. Polym Chem 4:2414–2423
236. Coulembier O, Lohmeijer BGG, Dove AP, Pratt RC, Mespouille L, Culkin DA, Benight SJ, Dubois P, Waymouth RM, Hedrick JL (2006) Alcohol adducts of N-heterocyclic carbenes:

latent catalysts for the thermally-controlled living polymerization of cyclic esters. Macromolecules 39:5617–5628
237. Connor EF, Nyce GW, Myers M, Mock A, Hedrick JL (2002) First example of N-heterocyclic carbenes as catalysts for living polymerization: oganocatalytic ring-opening polymerization of cyclic esters. J Am Chem Soc 124:914–915
238. Coulembier O, Dove AP, Pratt RC, Sentman AC, Culkin DA, Mespouille L, Dubois P, Waymouth RM, Hedrick JL (2005) Latent, thermally activated organic catalysts for the on-demand living polymerization of lactide. Angew Chem Int Ed 44:4964–4968
239. Dorresteijn R, Haschick R, Klapper M, Mullen K (2012) Poly(l-lactide) nanoparticles via ring-opening polymerization in non-aqueous emulsion. Macromol Chem Phys 213:1996–2002
240. Dove AP, Pratt RC, Lohmeijer BGG, Culkin DA, Hagberg EC, Nyce GW, Waymouth RM, Hedrick JL (2006) *N*-Heterocyclic carbenes: effective organic catalysts for living polymerization. Polymer 47:4018–4025
241. Jeong W, Shin EJ, Culkin DA, Hedrick JL, Waymouth RM (2009) Zwitterionic polymerization: a kinetic strategy for the controlled synthesis of cyclic polylactide. J Am Chem Soc 131:4884–4891
242. Nyce GW, Glauser T, Connor EF, Mock A, Waymouth RM, Hedrick JL (2003) In situ generation of carbenes: a general and versatile platform for organocatalytic living polymerization. J Am Chem Soc 125:3046–3056
243. Wang Y, Zhang L, Guo X, Zhang R, Li J (2013) Characteristics and mechanism of L-lactide polymerization using N-heterocyclic carbene organocatalyst. J Polym Res 20:87
244. Dove AP, Li HB, Pratt RC, Lohmeijer BGG, Culkin DA, Waymouth RM, Hedrick JL (2006) Stereoselective polymerization of rac- and meso-lactide catalyzed by sterically encumbered N-heterocyclic carbenes. Chem Commun (27):2881–2883
245. Culkin DA, Jeong WH, Csihony S, Gomez ED, Balsara NR, Hedrick JL, Waymouth RM (2007) Zwitterionic polymerization of lactide to cyclic poly(lactide) by using N-heterocyclic carbene organocatalysts. Angew Chem Int Ed 46:2627–2630
246. Shin EJ, Jones AE, Waymouth RM (2012) Stereocomplexation in cyclic and linear polylactide blends. Macromolecules 45:595–598
247. Nyce GW, Csihony S, Waymouth RM, Hedrick JL (2004) A general and versatile approach to thermally generated N-heterocyclic carbenes. Chem Eur J 10:4073–4079
248. Csihony S, Culkin DA, Sentman AC, Dove AP, Waymouth RM, Hedrick JL (2005) Single-component catalyst/initiators for the organocatalytic ring-opening polymerization of lactide. J Am Chem Soc 127:9079–9084
249. Xiao Y, Coulembier O, Koning CE, Heise A, Dubois P (2009) Cumulated advantages of enzymatic and carbene chemistry for the non-organometallic synthesis of (co)polyesters. Chem Commun 2009:2472–2474
250. Csihony S, Beaudette TT, Sentman AC, Nyce GW, Waymouth RM, Hedrick JL (2004) Bredereck's reagent revisited: latent anionic ring-opening polymerization and transesterification reactions. Adv Synth Catal 346:1081–1086
251. Coulembier O, De Winter J, Josse T, Mespouille L, Gerbaux P, Dubois P (2014) One-step synthesis of polylactide macrocycles from sparteine-initiated ROP. Polym Chem 5:2103–2108
252. Xia H, Kan S, Li Z, Chen J, Cui S, Wu W, Ouyang P, Guo K (2014) N-heterocyclic carbenes as organocatalysts in controlled/living ring-opening polymerization of O-carboxyanhydrides derived from l-lactic acid and l-mandelic acid. J Polym Sci A, Polym Chem 52:2306–2315
253. Laycock B, Halley P, Pratt S, Werker A, Lant P (2013) The chemomechanical properties of microbial polyhydroxyalkanoates. Prog Polym Sci 38:536–583
254. Jedlinski Z (1993) Novel chemistry of beta-lactones anionic-polymerization. Makromol Chem Macromol Symp 73:65–76
255. Jedlinski Z (1993) Novel degradable engineering polyesters – synthesis and applications. J Macromol Sci Pure Appl Chem A30:689–701

256. Jedliński Z, Kowalczuk M, Kurcok P (1986) Anionic ring opening polymerization by alkali metal solutions. Makromol Chem Macromol Symp 3:277–293
257. Jedlinski Z, Kurcok P, Kowalczuk M (1995) Novel anionic-polymerization of beta-lactones mediated by alkali-metal supramolecular complexes. Polym Int 37:187–190
258. Jedlinski ZJ, Kowalczuk M, Kurcok P (1994) Novel evidence on the chemistry of beta-lactone anionic-polymerization. Macromol Symp 88:217–226
259. Kricheldorf HR, Scharnagl N (1989) Polyactones. 17. Anionic polymerization of β-D, L-butyrolactone. J Macromol Sci A Chem 26:951–968
260. Lenz RW, Jedlinski Z (1996) Anionic and coordination polymerization of 3-butyrolactone. Macromol Symp 107:149–161
261. Yamashita Y, Tsuda T, Ishida H, Uchikawa A, Kuriyama Y (1968) Anionic copolymerization of β-lactones in correlation with the mode of fission. studies on the syntheses of aliphatic polyesters. XI. Makromol Chem 113:139–146
262. Jedlinski Z, Kowalczuk M, Glowkowski W, Grobelny J, Szwarc M (1991) Novel polymerization of beta-butyrolactone initiated by potassium naphthalenide in the presence of a crown-ether or a cryptand. Macromolecules 24:349–352
263. Slomkowski S, Penczek S (1976) Influence of dibenzo-18-crown-6 ether on the kinetics of anionic polymerization of β-propiolactone. Macromolecules 9:367–369
264. Deffieux A, Boileau S (1976) Use of cryptates in anionic-polymerization of lactones. Macromolecules 9:369–371
265. Jedlinski Z, Kurcok P, Adamus G, Juzwa M (2000) Biomimetic polyesters and their role in ion transport across cell membranes. Acta Biochim Polon 47:79–85
266. Kawalec M, Smiga-Matuszowicz M, Kurcok P (2008) Counterion and solvent effects on the anionic polymerization of beta-butyrolactone initiated with acetic acid salts. Eur Polym J 44:3556–3563
267. Jedlinski Z, Kowalczuk M, Adamus G, Sikorska W, Rydz J (1999) Novel synthesis of functionalized poly(3-hydroxybutanoic acid) and its copolymers. Int J Biol Macromol 25:247–253
268. Arslan H, Hazer B, Kowalczuk M (2002) Synthesis and characterization of poly (RS)-3-hydroxybutyrate telechelics and their use in the synthesis of poly(methyl methacrylate)-b-poly(3-hydroxybutyrate) block copolymers. J Appl Polym Sci 85:965–973
269. Duda A (1992) Anionic-polymerization of 4-methyl-2-oxetanone (beta-butyrolactone). J Polym Sci A Polym Chem 30:21–29
270. Kurcok P, Smiga M, Jedlinski Z (2002) beta-butyrolactone polymerization initiated with tetrabutylammonium carboxylates: a novel approach to biomimetic polyester synthesis. J Polym Sci A. Polym Chem 40:2184–2189
271. Slomkowski S, Penczek S (1980) Macroions and macroion pairs in the anionic polymerization of β-propiolactone (β-PL). Macromolecules 13:229–233
272. Camps M, Ait-Hamouda R, Boileau S, Hemery P, Lenz RW (1988) Effect of water on the anionic polymerization of.alpha.-methyl-.alpha.-n-propyl-.beta.-propiolactone. Macromolecules 21:891–894
273. Jedliński Z, Kurcok P, Lenz RW (1998) First facile synthesis of biomimetic poly-(R)-3-hydroxybutyrate via regioselective anionic polymerization of (S)-β-butyrolactone. Macromolecules 31:6718–6720
274. Hofman A, Slomkowski S, Penczek S (1984) Structure of active-centers and mechanism of the anionic-polymerization of lactones. Makromol Chem Macromol Chem Phys 185:91–101
275. Słomkowski S (1986) Kinetics of the anionic polymerization of β-propiolactone in dimethylformamide. Polymer 27:71–75
276. Sosnowski S, Slomkowski S, Penczek S (1993) On the ambident reactivity of beta-lactones in their reactions with alcoholates initiating polymerization. Macromolecules 26:5526–5527
277. Kurcok P, Kowalczuk M, Jedlinski Z (1994) On the ambident reactivity of beta-lactones in their reactions with alcoholates initiating polymerization – response. Macromolecules 27:4833–4835

278. Kurcok P, Jedlinski Z, Kowalczuk M (1993) Reactions of β-lactones with potassium alkoxides and their complexes with 18-crown-6 in aprotic solvents. J Org Chem 58:4219–4220
279. Dale J, Schwartz JE (1986) Macrocyclic oligolactones by oligomerization of simple lactones. Acta Chem Scand Ser B Org Chem Biochem 40:559–567
280. Jedlinski Z, Kowalczuk M, Kurcok P (1991) What is the real mechanism of anionic-polymerization of beta-lactones by potassium alkoxides – a critical approach. Macromolecules 24:1218–1219
281. Kurcok P, Kowalczuk M, Hennek K, Jedlinski Z (1992) Anionic-polymerization of beta-lactones initiated with alkali-metal alkoxides – reinvestigation of the polymerization mechanism. Macromolecules 25:2017–2020
282. Jedlinski Z (1998) Regioselective ring-opening anionic polymerization of beta-lactones. Macromol Symp 132:377–383
283. Jedlinski Z, Adamus G, Kowalczuk M, Schubert R, Szewczuk Z, Stefanowicz P (1998) Electrospray tandem mass spectrometry of poly(3-hydroxybutanoic acid) end groups analysis and fragmentation mechanism. Rapid Commun Mass Spectrom 12:357–360
284. Scandola M, Focarete ML, Gazzano M, Matuszowicz A, Sikorska W, Adamus G, Kurcok P, Kowalczuk M, Jedlinski Z (1997) Crystallinity-induced biodegradation of novel (R, S)-beta-butyrolactone -b-pivalolactone copolymers. Macromolecules 30:7743–7748
285. Jedlinski Z (2002) Single-electron and two-electron transfer in the anionic polymerization of vinyl monomers and the ring-opening polymerization of lactones. J Polym Sci A, Polym Chem 40:2158–2165
286. Jedlinski Z, Kowalczuk M, Kurcok P (1992) Polymerization of beta-lactones initiated by alkali-metal naphthalenides – a convenient route to telechelic polymers. J Macromol Sci Pure Appl Chem A29:1223–1230
287. Kurcok P, Matuszowicz A, Jedlinski Z (1995) Anionic-polymerization of beta-lactones initiated with potassium hydride – a convenient route to polyester macromonomers. Macromol Rapid Commun 16:201–206
288. Grobelny Z, Stolarzewicz A, Morejko B, Pisarski W, Maercker A, Skibiński A, Krompiec S, Rzepa J (2006) C−O and Not C−C bond cleavage starts the polymerization of β-butyrolactone with potassium anions of alkalide. Macromolecules 39:6832–6837
289. Jedlinski Z, Kowalczuk M (1989) Nature of the active centers and the propagation mechanism of the polymerization of.beta.-propiolactones initiated by potassium anions. Macromolecules 22:3242–3244
290. Jedliński Z, Kowalczuk M, Grobelny Z, Stolarzewicz A (1983) Polymerization of 2-oxetanone initiated by alkali metal solutions. Makromol Chem Rapid Commun 4:355–358
291. Jedlinski Z, Kowalczuk M, Kurcok P, Brzoskowska L, Franek J (1987) Anionic block polymerization of beta-lactones initiated by potassium solutions.1. Synthesis of poly (4-methyl-2-oxetanone-block-2-oxetanone). Makromol Chem Macromol Chem Phys 188:1575–1582
292. Jedlinski Z, Kurcok P, Kowalczuk M (1985) Polymerization of.beta.-lactones initiated by potassium solutions. Macromolecules 18:2679–2683
293. Jedliński Z, Kurcok P, Kowalczuk M, Kasperczyk J (1986) Anionic polymerization of 4-methyl-2-oxetanone. Makromol Chem 187:1651–1656
294. Jedliński Z, Adamus G, Kowalczuk M (1995) Synthesis of novel functional poly[(R, S)-ß-hydroxybutyrate] containing phosphonoacetate end groups. Macromol Rapid Commun 16:59–65
295. Jedlinski Z, Kowalczuk M, Kurcok P, Adamus G, Matuszowicz A, Sikorska W, Gross RA, Xu J, Lenz RW (1996) Stereochemical control in the anionic polymerization of beta-butyrolactone initiated with alkali-metal alkoxides. Macromolecules 29:3773–3777
296. Kurcok P, Kowalczuk M, Adamus G, Jedliński Z, Lenz RW (1995) Degradability of poly (β-hydroxybutyrate)s. Correlation with chemical microstructure. J Macromol Sci A Chem 32:875–880

297. Corley LS, Vogl O, Biela T, Michalski J, Penczek S, Słombowski S (1980) Optically active zwitterions. Makromol Chem Rapid Commun 1:715–718
298. Jaacks V, Mathes N (1970) Formation of macrozwitterions in the polymerization of β-lactones initiated by tertiary amines. 2nd communication on macrozwitterions1. Makromol Chem 131:295–303
299. Kricheldorf HR, Scharnagl N, Jedlinski Z (1996) Polylactones.33. The role of deprotonation in the anionic polymerization of beta-propiolactone. Polymer 37:1405–1411
300. Mathes N, Jaacks V (1971) Formation of Macrozwitterions in the polymerization of β-propiolactone initiated by betaine. 4th Communication on Macrozwitterions. Makromol Chem 142:209–225
301. Yamashita Y, Ito K, Nakakita F (1969) Initiation mechanism for the anionic polymerization of β-propiolactone by pyridine. Makromol Chem 127:292–295
302. Etienne Y, Soulas R (1963) Suppression du Stade d'Initiation dans une polycondensation du second type: ouverture des β-lactones par les Bétaïnes. J Polym Sci C Polym Symp 4:1061–1074
303. Coulembier O, Delva X, Hedrick JL, Waymouth RM, Dubois P (2007) Synthesis of biomimetic poly(hydroxybutyrate): alkoxy- and carboxytriazolines as latent ionic initiator. Macromolecules 40:8560–8567
304. Jaffredo CG, Carpentier J-F, Guillaume SM (2012) Controlled ROP of β-butyrolactone simply mediated by amidine, guanidine, and phosphazene organocatalysts. Macromol Rapid Commun 33:1938–1944
305. Kawalec M, Coulembier O, Gerbaux P, Sobota M, De Winter J, Dubois P, Kowalczuk M, Kurcok P (2012) Traces do matter-Purity of 4-methyl-2-oxetanone and its effect on anionic ring-opening polymerization as evidenced by phosphazene superbase catalysis. React Funct Polym 72:509–520
306. Jeong W, Hedrick JL, Waymouth RM (2007) Organic spirocyclic initiators for the ring-expansion polymerization of beta-lactones. J Am Chem Soc 129:8414–8415
307. Bigdeli E, Lenz RW (1978) Polymerization of alpha, alpha-disubstituted beta-propiolactones and lactams.14. Substituent, solvent, and counterion effects in anionic-polymerization of lactones. Macromolecules 11:493–496
308. Cornibert J, Marchessault RH, Allegrezza AE, Lenz RW (1973) Crystalline, thermal, and mechanical properties of the polyester of α-methyl-α- n-propyl-β-propiolactone. Macromolecules 6:676–681
309. Haggiage J, Hémery P, Boileau S, Lenz RW (1983) Anionic polymerization of α, α-disubstituted β-propiolactones with cryptates as counterions. Polymer 24:578–582
310. Hall HK (1969) The Nucleophile-Initiated Polymerization of α, α-disubstituted β-Lactones. Macromolecules 2:488–497
311. Jedlinski Z, Kurcok P, Kowalczuk M, Matuszowicz A, Dubois P, Jerome R, Kricheldorf HR (1995) Anionic-polymerization of pivalolactone initiated by alkali-metal alkoxides. Macromolecules 28:7276–7280
312. Kurcok P, Matuszowicz A, Jedlinski Z, Kricheldorf HR, Dubois P, Jerome R (1995) Substituent effect in anionic-polymerization of beta-lactones initiated by alkali-metal alkoxides. Macromol Rapid Commun 16:513–519
313. Lenz RW, Dror M, Jorgensen R, Marchessault RH (1978) Polymerization of α, α-disubstituted-β-propiolactones and lactams. 9. ABA block copolymers of α-methyl-α-butyl-β-propiolactone and pivalolactone. Polym Eng Sci 18:937–942
314. Spassky N, Leborgne A, Reix M, Prud'homme RE, Bigdeli E, Lenz RW (1978) Preparation and properties of optically active poly(α-methyl-α-n-propyl-β-propiolactone). Macromolecules 11:716–719
315. Yamashita Y, Hane T (1973) Block copolymerization. VI. Polymerization of pivalolactone with macromolecular initiators from polystyrene and polytetrahydrofuran. J Polym Sci Polym Chem Ed 11:425–434

316. Kricheldorf HR, Garaleh M, Schwarz G (2005) Tertiary amine-initiated zwitterionic polymerization of pivalolactone – a reinvestigation by means of Maldi-Tof mass spectrometry. J Macromol Sci Pure Appl Chem A42:139–148
317. Adamus G (2009) Molecular level structure of (R, S)-3-hydroxybutyrate/(R, S)-3-hydroxy-4-ethoxybutyrate copolyesters with dissimilar architecture. Macromolecules 42:4547–4557
318. Adamus G, Kowalczuk M (2008) Anionic ring-opening polymerization of beta-alkoxymethyl-substituted beta-lactones. Biomacromolecules 9:696–703
319. Barbaud C, Fay F, Abdillah F, Randriamahefa S, Guerin P (2004) Synthesis of new homopolyester and copolyesters by anionic ring-opening polymerization of alpha, alpha', beta-trisubstituted beta-lactones. Macromol Chem Phys 205:199–207
320. Bear MM, Cammas S, Langlois V, Guerin P (1997) Chemoenzymatic synthesis of poly (2R,3S)-benzyl beta-3-methylmalate : beta-methylaspartase as a versatile enzyme in the preparation of the chiral precursor. CR Acad Sci Ser B Mecan Phys Chim Astron 325:165–172
321. Bear MM, Monne C, Robic D, Campion G, Langlois V, Rimbault A, Bourbouze R, Guerin P (1998) Synthesis and polymerization of benzyl (3R,4R)-3-methylmalolactonate via enzymatic preparation of the chiral precursor. Chirality 10:727–733
322. Bizzarri R, Chiellini F, Ober CK, Saltzman WM, Solaro R (2002) Influence of structural parameters on the ring-opening polymerization of new alkyl malolactonate monomers and on the biocompatibility of polymers therefrom. Macromol Chem Phys 203:1684–1693
323. Bizzarri R, Chiellini F, Solaro R, Chiellini E, Cammas-Marion S, Guerin P (2002) Synthesis and characterization of new malolactonate polymers and copolymers for biomedical applications. Macromolecules 35:1215–1223
324. Boutault K, Cammas S, Huet F, Guerin P (1995) Polystereoisomers with 2 stereogenic centers of malic-acid 2-methylbutyl ester configurational structure/properties relationship. Macromolecules 28:3516–3520
325. Brestaz M, Desilles N, Le G, Bunel C (2011) Polyester from dimethylketene and acetaldehyde: direct copolymerization and beta-lactone ring-opening polymerization. J Polym Sci A Polym Chem 49:4129–4138
326. Cammas S, Boutault K, Huet F, Guerin P (1994) 4-alkyloxycarbonyl-2-oxetanones with 2 stereogenic centers as precursors of malic-acid alkyl esters polystereoisomers. Tetrahedron Asym 5:1589–1597
327. Cammas S, Renard I, Langlois V, Guerin P (1996) Poly(beta-malic acid): obtaining high molecular weights by improvement of the synthesis route. Polymer 37:4215–4220
328. Cammas-Marion S, Bear MM, Harada A, Guerin P, Kataoka K (2000) New macromolecular micelles based on degradable amphiphilic block copolymers of malic acid and malic acid ester. Macromol Chem Phys 201:355–364
329. Coulembier O, Degee P, Barbaud C, Guerin P, Dubois P (2004) New amphiphilic graft copolymer based on poly(beta-malic acid): synthesis and characterization. Polym Bull 51:365–372
330. Coulembier O, Degee P, Cammas-Marion S, Guerin P, Dubois P (2002) New amphiphilie poly (R, S)-beta-malic acid-b-epsilon-caprolactone diblock copolymers by combining anionic and coordination-insertion ring-opening polymerization. Macromolecules 35:9896–9903
331. Coulembier O, Degee P, Dubois P (2006) Synthesis and micellization properties of novel symmetrical poly (epsilon-caprolactone-b-R, S beta-malic acid-b-epsilon-caprolactone) triblock copolymers. Macromol Chem Phys 207:484–491
332. Coulembier O, Degee P, Gerbaux P, Wantier P, Barbaud C, Flammang R, Guerin P, Dubois P (2005) Synthesis of amphiphilic poly((R, S)-beta-malic acid)-graft-poly(epsilon-caprolactone): "grafting from" and "grafting through" approaches. Macromolecules 38:3141–3150

333. Coulembier O, Degee P, Hedrick JL, Dubois P (2006) From controlled ring-opening polymerization to biodegradable aliphatic polyester: especially poly(beta-malic acid) derivatives. Prog Polym Sci 31:723–747
334. Coulembier O, Ghisdal J, Degee P, Dubois P (2007) Benzyl beta-malolactonate: synthesis, copolymerization and design of novel biodegradable macromolecular surfactants. Arkivoc 2007:57–70
335. Coulembier O, Mespouille L, Hedrick JL, Waymouth RM, Dubois P (2006) Metal-free catalyzed ring-opening polymerization of, beta-lactones: synthesis of amphiphilic triblock copolymers based on poly(dimethylmalic acid). Macromolecules 39:4001–4008
336. De Winter J, Coulembier O, Gerbaux P, Dubois P (2010) High molecular weight poly(alpha, alpha', beta-trisubstituted beta-lactones) as generated by metal-free phosphazene catalysts. Macromolecules 43:10291–10296
337. Guerin P, Vert M, Braud C, Lenz RW (1985) Optically-active poly (beta-malic-acid). Polym Bull 14:187–192
338. LeboucherDurand MA, Langlois V, Guerin P (1996) Poly(beta-malic acid) derivatives with unsaturated lateral groups: epoxidation as model reaction of the double bonds reactivity. React Funct Polym 31:57–65
339. LeboucherDurand MA, Langlois V, Guerin P (1996) 4-carboxy-2-oxetanone as a new chiral precursor in the preparation of functionalized racemic or optically active poly(malic acid) derivatives. Polym Bull 36:35–41
340. Mabille C, Masure M, Hemery P, Guerin P (1998) Obvious complexity of the anionic polymerization of malolactonic acid esters. Polym Bull 40:381–387
341. Moine L, Cammas S, Amiel C, Guerin P, Sebille B (1997) Polymers of malic acid conjugated with the 1-adamantyl moiety as lipophilic pendant group. Polymer 38:3121–3127
342. Monne C, Robic D, Campion G, Bourbouze R, Rimbault A, Masure M, Langlois V, Hemery P, Guerin P (1996) Enantiospecific enzymatic preparation of (2S,3S)-3-alkylaspartic acids of current interest in the synthesis of stereoregular poly beta-(2S,3S)-3-alkylmalic acids as new optically active functional polyesters. Chirality 8:300–304
343. Ouhib F, Randriamahefa S, Guerin P, Barbaud C (2005) Synthesis of new statistical and block co-polyesters by ROP of alpha, alpha, beta-trisubstituted beta-lactones and their characterizations. Design Monom Polym 8:25–35
344. Jaffredo CG, Carpentier J-F, Guillaume SM (2013) Organocatalyzed controlled ROP of [small beta]-lactones towards poly(hydroxyalkanoate)s: from [small beta]-butyrolactone to benzyl [small beta]-malolactone polymers. Polym Chem 4:3837–3850
345. Jaffredo CG, Carpentier J-F, Guillaume SM (2013) Poly(hydroxyalkanoate) block or random copolymers of β-butyrolactone and benzyl β-malolactone: a matter of catalytic tuning. Macromolecules 46:6765–6776
346. Lenz RW, Vert M (1979) Preparation and properties of poly(b-malic acid): a functional polyester of potential biomedical importance. Polym Prepr 20:608–611
347. Sosnowski S, Slomkowski S, Penczek S (1991) Kinetics of the anionic-polymerization of epsilon-caprolactone with K+ (dibenzo-18-crown-6 ether) counterion – propagation via macroions and macroion pairs. Makromol Chem Macromol Chem Phys 192:735–744
348. Sosnowski S, Słomkowski S, Penczek S, Reibel L (1983) Kinetics of ϵ-caprolactone polymerization and formation of cyclic oligomers. Makromol Chem 184:2159–2171
349. Sosnowski SS, Slomkowski SS, Penczek SS (1983) Kinetics of anionic polymerization of ε-caprolactone (εCL). Propagation of poly-ε=CL-K+ ion pairs. J Macromol Sci A Chem 20:979–988
350. Mingotaud AF, Cansell F, Gilbert N, Soum A (1999) Cationic and anionic ring-opening polymerization in supercritical CO_2. Preliminary results. Polym J 31:406–410
351. Ito K, Hashizuka Y, Yamashita Y (1977) Equilibrium cyclic oligomer formation in the anionic polymerization of iε-caprolactone. Macromolecules 10:821–824
352. Ito K, Yamashita Y (1978) Propagation and depropagnation rates in the anionic polymerization of ε-caprolactone cyclic oligomers. Macromolecules 11:68–72

353. Morton M, Wu M (1985) Organolithium polymerization of ?-caprolactone. In: Ring-opening polymerization, ACS Symposium Series of American Chemical Society., pp 175–182
354. Bero M, Adamus G, Kasperczyk J, Janeczek H (1993) Synthesis of block copolymers of ε-caprolactone and lactide in the presence of lithium *t*-butoxide. Polym Bull 31:9–14
355. Hofman A, Slomkowski S, Penczek S (1987) Polymerization of ε-caprolactone with kinetic suppression of macrocycles. Makromol Chem Rapid Commun 8:387–391
356. Perret R, Skoulios A (1972) Synthèse et caractérisation de quelques poly-ε-caprolactones. Makromol Chem 152:291–303
357. Yuan ML, Xiong CD, Deng XM (1998) Ring-opening polymerization of epsilon-caprolactone initiated by cyclopentadienyl sodium. J Appl Polym Sci 67:1273–1276
358. Deng X, Yuan M, Xiong C, Li X (1999) Polymerization of lactides and lactones. IV Ring-opening polymerization of ε-caprolactone by rare earth phenyl compounds. J Appl Polym Sci 73:1401–1408
359. Stere C, Iovu MC, Iovu H, Boborodea A, Vasilescu DS, Read SJ (2001) Anionic and ionic coordinative polymerization of epsilon-caprolactone. Polym Adv Technol 12:300–305
360. Bhaw-Luximon A, Jhurry D, Motala-Timol S, Lochee Y (2005) Polymerization of ε-caprolactone and its copolymerization with γ-butyrolactone using metal complexes. Macromol Symp 231:60–68
361. Gorrasi G, Pappalardo D, Pellecchia C (2012) Polymerization of epsilon-caprolactone by sodium hydride: from the synthesis of the polymer samples to their thermal, mechanical and barrier properties. React Funct Polym 72:752–756
362. Gitsov I, Rashkov IB, Panayotov IM (1990) Anionic-polymerization of lactones initiated by alkali graphitides.5. Initiation mechanism and nature of the active-centers. J Polym Sci A Polym Chem 28:2115–2126
363. Gitsov I, Rashkov IB, Panayotov IM, Golub A (1989) Anionic-polymerization of lactones initiated by alkali graphitides.4. Copolymerization of epsilon-caprolactone initiated by KC24. J Polym Sci A Polym Chem 27:639–646
364. Mazier C, Douillard C, Merle G, Pascault JP (1980) Anionic-polymerization of lactones initiated by KC 24 intercalation compounds – characterization of obtained polymers. Eur Polym J 16:773–777
365. Rashkov I, Panayotov I, Gitsov I (1981) Mechanism of the anionic-polymerization of lactones, initiated by intercalation graphite compounds. Polym Bull 4:97–103
366. Rashkov IB, Gitsov I (1984) Anionic-polymerization of lactones initiated by alkali graphitides.3. Polymerization of delta-valerolactone initiated by KC24. J Polym Sci A Polym Chem 22:905–910
367. Rashkov IB, Gitsov I, Panayotov IM (1983) Anionic-polymerization of lactones initiated by alkali graphitides.2. Changes in the KC24 structure during polymerization of lactones. J Polym Sci A Polym Chem 21:937–941
368. Rashkov IB, Gitsov I, Panayotov IM, Pascault JP (1983) Anionic-polymerization of lactones initiated by alkali graphitides.1. Polymerization of epsilon-caprolactone initiated by KC24. J Polym Sci A Polym Chem 21:923–936
369. Kurcok P, Penczek J, Franek J, Jedlinski Z (1992) Anionic-polymerization of lactones.14. Anionic block copolymerization of delta-valerolactone and L-lactide initiated with potassium methoxide. Macromolecules 25:2285–2289
370. Zhu ZX, Xiong CD, Zhang LL, Deng XM (1997) Synthesis and characterization of poly (epsilon-caprolactone) – poly(ethylene glycol) block copolymer. J Polym Sci A Polym Chem 35:709–714
371. Mao J, Gan Z (2009) The influence of pendant hydroxyl groups on enzymatic degradation and drug delivery of amphiphilic poly glycidol-block-(epsilon-caprolactone) copolymers. Macromol Biosci 9:1080–1089
372. Brown HA, Xiong S, Medvedev GA, Chang YA, Abu-Omar MM, Caruthers JM, Waymouth RM (2014) Zwitterionic ring-opening polymerization: models for kinetics of cyclic poly (caprolactone) synthesis. Macromolecules 47:2955–2963

373. Naumann S, Schmidt FG, Frey W, Buchmeiser MR (2013) Protected N-heterocyclic carbenes as latent pre-catalysts for the polymerization of epsilon-caprolactone. Polym Chem 4:4172–4181
374. Kamber NE, Jeong W, Gonzalez S, Hedrick JL, Waymouth RM (2009) N-heterocyclic carbenes for the organocatalytic ring-opening polymerization of epsilon-caprolactone. Macromolecules 42:1634–1639
375. Shin EJ, Brown HA, Gonzalez S, Jeong W, Hedrick JL, Waymouth RM (2011) Zwitterionic copolymerization: synthesis of cyclic gradient copolymers. Angew Chem Int Ed 50:6388–6391
376. Sen TK, Sau SC, Mukherjee A, Modak A, Mandal SK, Koley D (2011) Introduction of abnormal N-heterocyclic carbene as an efficient organocatalyst: ring opening polymerization of cyclic esters. Chem Commun 47:11972–11974
377. Prasad AV, Zhu Y (2013) Syntheses of cyclic poly(lactones) by zwitterionic ring opening polymerization catalyzed by N-heterocyclic carbene. J Appl Polym Sci 128:3411–3416
378. Shin EJ, Jeong W, Brown HA, Koo BJ, Hedrick JL, Waymouth RM (2011) Crystallization of cyclic polymers: synthesis and crystallization behavior of high molecular weight cyclic poly (epsilon-caprolactone)s. Macromolecules 44:2773–2779
379. Zhang R, Zhang L, Wang J, Guo X (2013) Ring-opening copolymerization of ε-caprolactone with 2,2-dimethyltrimethylene carbonate using N-heterocyclic carbene organocatalysts. Polym Bull 70:1289–1301
380. Alamri H, Zhao J, Pahovnik D, Hadjichristidis N (2014) Phosphazene-catalyzed ring-opening polymerization of [epsilon]-caprolactone: influence of solvents and initiators. Polym Chem. doi:10.1039/c1034py00493k
381. Guillerm B, Lemaur V, Ernould B, Cornil J, Lazzaroni R, Gohy J-F, Dubois P, Coulembier O (2014) A one-pot two-step efficient metal-free process for the generation of PEO-b-PCL-b-PLA amphiphilic triblock copolymers. RSC Adv 4:10028–10038
382. Okada M, Sumitomo H, Atsumi M, Hall HK (1991) Ring-opening polymerization of bicyclic oxalactones and oxalactams. Makromol Chem Macromol Symp 42–3:355–364
383. Jedlinski Z, Juzwa M, Adamus G, Kowalczuk M, Montaudo M (1996) Anionic polymerization of pentadecanolide. A new route to a potentially biodegradable aliphatic polyester. Macromol Chem Phys 197:2923–2929
384. Nomura R, Ueno A, Endo T (1994) Anionic ring-opening polymerization of macrocyclic esters. Macromolecules 27:620–621
385. Habaue S, Asai M, Morita M, Okamoto Y, Uyama H, Kobayashi S (2003) Chemospecific ring-opening polymerization of alpha-methylenemacrolides. Polymer 44:5195–5200
386. Illy N, Taylan E, Brissault B, Wojno J, Boileau S, Barbier V, Penelle J (2013) Synthesis and anionic ring-opening polymerization of crown-ether-like macrocyclic dilactones: an alternative route to peg-containing polyesters PEG-containing polyesters and related networks. Eur Polym J 49:4087–4097
387. Kudoh R, Sudo A, Endo T (2009) Synthesis of eight-membered lactone having tertiary amine moiety by ring-expansion reaction of 1,3-benzoxazine and its anionic ring-opening polymerization behavior. Macromolecules 42:2327–2329
388. Chung K, Takata T, Endo T (1995) Anionic ring-opening copolymerization of bicyclic bis (gamma-lactone)s with monofunctional and bifunctional epoxides via double ring-opening isomerization of the bis(gamma-lactone)s and volume change during copolymerization. Macromolecules 28:3048–3054
389. Chung K, Takata T, Endo T (1995) Anionic alternating ring-opening copolymerization of spirocyclic bis(gamma-lactone)s with bisepoxides and volume change during the copolymerization. Macromolecules 28:1711–1713
390. Chung KW, Takata T, Endo T (1995) Anionic copolymerization of bicyclic bis(gamma-lactone)s with poly(glycidyl methacrylate) and volume change during the copolymerization. Macromolecules 28:4044–4046

391. Endo T, Sanda F (1996) Molecular design of novel network polymers. Angew Makromol Chem 240:171–180
392. Ohsawa S, Morino K, Sudo A, Endo T (2010) Alternating copolymerization of bicyclic bis (gamma-butyrolactone) and epoxide through Zwitterion process by phosphines. Macromolecules 43:3585–3588
393. Ohsawa S, Morino K, Sudo A, Endo T (2011) Synthesis of a reactive polyester bearing alpha, beta-unsaturated ketone groups by anionic alternating copolymerization of epoxide and bicyclic bis(gamma-butyrolactone) bearing isopropenyl group. Macromolecules 44:1814–1820
394. Ohsawa S, Morino K, Sudo A, Endo T (2012) Synthesis of bicyclic bis(gamma-butyrolactone) derivatives bearing sulfide moieties and their alternating copolymers with epoxide. J Polym Sci A Polym Chem 50:4666–4673
395. Tadokoro A, Takata T, Endo T (1993) Anionic ring-opening alternating copolymerization of a bicyclic bis(gamma-lactone) with an epoxide – a novel ring-opening polymerization of a monomer containing a gamma-lactone structure. Macromolecules 26:4400–4406
396. Takata T, Tadokoro A, Chung K, Endo T (1995) Anionic ring-opening alternating copolymerizations of bicyclic and spirocyclic bis(gamma-lactone)s with epoxides via a tandem double ring-opening isomerization of the bislactones. Macromolecules 28:1340–1345
397. Zhang CX, Ochiai B, Endo T (2005) Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry study on copolymers obtained by the alternating copolymerization of bis(gamma-lactone) and epoxide with potassium tert-butoxide. J Polym Sci A Polym Chem 43:2643–2649
398. Endo T, Sudo A (2009) Development and application of novel ring-opening polymerizations to functional networked polymers. J Polym Sci A Polym Chem 47:4847–4858
399. Sudo A, Uenishi K, Endo T (2008) Anionic copolymerization of epoxide with bifunctional aromatic lactone derived from 2-methylresorcinol. J Polym Sci A Polym Chem 46:3447–3451
400. Sudo A, Uenishi K, Endo T (2009) Anionic alternating copolymerization of epoxide and 3,4-dihydrocoumarin and its application to networked polymers. Polym Int 58:970–975
401. Sudo A, Zhang Y, Endo T (2011) Anionic alternating copolymerization of epoxide and six-membered lactone bearing naphthyl moiety. J Polym Sci A Polym Chem 49:619–624
402. Uenishi K, Sudo A, Endo T (2008) Anionic alternating copolymerization of 3,4-dihydrocoumarin and glycidyl ethers: a mew approach to myester synthesis. J Polym Sci A Polym Chem 46:4092–4102
403. Uenishi K, Sudo A, Endo T (2009) Synthesis of polyester having sequentially ordered two orthogonal reactive groups by anionic alternating copolymerization of epoxide and bislactone. J Polym Sci A Polym Chem 47:6750–6757
404. Uenishi K, Sudo A, Endo T (2009) Anionic alternating copolymerization of a bifunctional six-membered lactone and glycidyl phenyl ether: selective synthesis of a linear polyester having lactone moiety. J Polym Sci A Polym Chem 47:1661–1672
405. Sudo A, Uenishi K, Endo T (2007) Imidazole-promoted copolymerization of epoxide and 3,4-dihydrocoumarin and its application to a high-performance curing system. J Polym Sci A Polym Chem 45:3798–3802
406. Sekiguchi H (1984) Lactam and cyclic imides in ring-opening polymerization. In: Ivin J, Saegusa T (eds) Ring-opening polymerization. Elsevier, London, pp 809–818
407. Puffr R (1991) Lactam-based polyamides, vol 1, Puffr R, Kubánek V (eds). CRC Press, Boca Raton
408. Reimschuessel HK (1969) Kinetics and Mechanisms of polymerization. In: Frisch K, Reegen S (eds) Ring-opening polymerizations, vol 2. Marcel Dekker, New York, pp 303–326
409. Reimschuessel HK (1977) Nylon 6. Chemistry and mechanisms. J Polym Sci Macromol Rev 12:65–139
410. Šebenda J (1976) Chapter 6: Lactams. In: Bamford CH, Tipper CFH (eds) Comprehensive chemical kinetics. Elsevier, Amsterdam, pp 379–471

411. Hashimoto K (2000) Ring-opening polymerization of lactams. Living anionic polymerization and its applications. Prog Polym Sci 25:1411–1462
412. Roda J (2009) Polyamides. In: (ed) Handbook of ring-opening polymerization. Wiley-VCH Verlag GmbH & Co. KGaA, pp 165–195
413. Russo S, Casazza E (2012) 4.14 – Ring-opening polymerization of cyclic amides (lactams). In: Matyjaszewski K, Möller M (eds) Polymer science: a comprehensive reference. Elsevier, Amsterdam, pp 331–396
414. Sebenda J (1972) Lactam polymerization. J Macromol Sci A Chem A 6:1145–1199
415. Fiala F, Kralicek J (1978) Polymerization of lactams.15. Polymerization of lactames in presence of n-benzoyllactames and pentamethylguanidine. Angew Makromol Chem 71:29–41
416. Sekiguchi H, Tsourkas PR, Coutin B (1973) Anionic polymerization of alpha-pyrrolidone and alpha-piperidone using their quaternary ammonium salts as catalysts. J Polym Sci C Polym Symp 42:51–61
417. Huisgen R, Brade H, Walz H, Glogger I (1957) Mittlere ringe.7. Die eigenschaften aliphatischer lactame und die cis-trans-isomerie der saureamidgruppe. Chem Ber 90:1437–1447
418. Schwesinger R, Hasenfratz C, Schlemper H, Walz L, Peters EM, Peters K, Vonschnering HG (1993) How strong and how hindered can uncharged phosphazene bases be. Angew Chem Int Ed 32:1361–1363
419. Tang JS, Dopke J, Verkade JG (1993) Synthesis of new exceedingly strong nonionic bases – RN=P(MeNCH2CH2)3N. J Am Chem Soc 115:5015–5020
420. Naumann S, Epple S, Bonten C, Buchmeiser MR (2013) Polymerization of epsilon-caprolactam by latent precatalysts based on protected N-heterocyclic carbenes. ACS Macro Lett 2:609–612
421. Naumann S, Schmidt FG, Speiser M, Böhl M, Epple S, Bonten C, Buchmeiser MR (2013) Anionic ring-opening homo- and copolymerization of lactams by latent, protected N-heterocyclic carbenes for the preparation of PA 12 and PA 6/12. Macromolecules 46:8426–8433
422. Mougin N, Rempp P, Gnanou Y (1992) New activating agents for the anionic-polymerization of lactams. Macromolecules 25:6739–6743
423. Mougin N, Veith CA, Cohen RE, Gnanou Y (1992) Anionic-polymerization of lactams in the presence of metal dialkoxyaluminum hydrides - presentation of a new mechanism. Macromolecules 25:2004–2016
424. Mougin N, Rempp P, Gnanou Y (1993) Synthesis and characterization of polysiloxane-polyamide block and graft-copolymers. J Polym Sci A Polym Chem 31:1253–1260
425. Bolgov SA, Begishev VP, Malkin AY, Frolov VG (1981) Role of the functionality of activators during isothermal crystallization accompanying the activated anionic polymerization of ϵ-caprolactam. Polym Sci USSR 23:1485–1492
426. Sibal PW, Camargo RE, Macosko CW (1983) Designing nylon-6 polymerization systems for RIM. Polym Process Eng 1:147–169
427. Stehlicek J, Sebenda J (1987) Anionic-polymerization of episilon-caprolactam.60. Ionization and solvation changes in the initial-stage of the anionic-polymerization of lactams in tetrahydrofuran. Eur Polym J 23:237–242
428. Petit D, Jerome R, Teyssie P (1979) Anionic block co-polymerization of epsilon-caprolactam. J Polym Sci A Polym Chem 17:2903–2916
429. Ricco L, Russo S, Orefice G, Riva F (2001) Caprolactam-laurolactam copolymers: fast activated anionic synthesis, thermal properties and structural investigations. Macromol Chem Phys 202:2114–2121
430. Hu GH, Li HX, Feng LF (2006) Follow-up of the course of the anionic ring-opening polymerization of lactams onto an isocyanate-bearing polymer backbone in the melt. J Appl Polym Sci 102:4394–4403

431. Mateva R, Filyanova R, Velichkova R, Gancheva V (2003) Anionic copolymerization of hexanelactam with functionalized polyisoprene. J Polym Sci A Polym Chem 41:487–496
432. Petrov P, Mateva R, Dimitrov R, Rousseva S, Velichkova R, Bourssukova M (2002) Structure and thermal behavior of nylon-6/polytetrahydrofuran triblock copolymers obtained via anionic polymerization. J Appl Polym Sci 84:1448–1456
433. Ricco L, Russo S, Orefice G, Riva F (1999) Anionic poly(epsilon-caprolactam): relationships among conditions of synthesis, chain regularity, reticular order, and polymorphism. Macromolecules 32:7726–7731
434. Russo S, Biagini E, Bonta G (1991) Novel synthetic approaches to poly(epsilon-caprolactam)-based materials. Makromol Chem Macromol Symp 48–9:31–46
435. Daniel L, Brozek J, Roda J, Kralicek J (1982) Polymerization of lactams.52. Anionic-polymerization of 2-pyrrolidone accelerated with CO_2.1. Makromol Chem Macromol Chem Phys 183:2719–2729
436. Merna J, Chromcova D, Brozek J, Roda J (2006) Polymerization of lactams: 97. Anionic polymerization of epsilon-caprolactam activated by esters. Eur Polym J 42:1569–1580
437. Roda J, Brozek J, Kralicek J (1980) Polymerization of lactams.37. Isolation and characterization of alkali carboxylates of 2-pyrrolidone. Makromol Chem Rapid Commun 1:165–169
438. Sittler E, Sebenda J (1968) Alkaline polymerization of 6-caprolactam. 34. Kinetics of polymerization of caprolactam initiated by sodium caprolactam. Coll Czech Chem Commun 33:3182–3190
439. Barzakay S, Levy M, Vofsi D (1965) On mechanism of anionic polymerization of lactams. J Polym Sci B Polym Lett 3:601–605
440. Rached R, Hoppe S, Fonteix C, Schrauwen C, Pla F (2005) New developments for modelling and simulation of activated anionic polymerization of lauryllactam. Chem Eng Sci 60:2715–2727
441. Frunze TM, Kotelnikov VA, Kurashev VV, Arakyan YA, Danilevskaya LB, Davtyan SP (1983) IUPAC macro 83, Bucharest, p 233
442. Alfonso GC, Chiappori C, Razore S, Russo S (1985) Activated anionic polymerization of ε-caprolactam for RIM process. In: Krestan JE (University of Detroit) (ed) Reaction injection molding. ACS symposium series, vol 270. American Chemical Society, pp 163–179
443. Mendichi R, Russo S, Ricco L, Schieroni AG (2004) Hexafluoroisopropanol as size exclusion chromatography mobile phase for polyamide 6. J Separat Sci 27:637–644
444. Udipi K, Dave RS, Kruse RL, Stebbins LR (1997) Polyamides from lactams via anionic ring-opening polymerization.1. Chemistry and some recent findings. Polymer 38:927–938
445. Stehlicek J, Sebenda J (1986) Anionic-polymerization of 6-caprolactam.58. The relative rates of elementary reactions in the activated anionic-polymerization of epsilon-caprolactam in tetrahydrofuran. Eur Polym J 22:5–11
446. Russo S, Imperato A, Mariani A, Parodi F (1995) The fast activation of epsilon-caprolactam polymerization in quasi-adiabatic conditions. Macromol Chem Phys 196:3297–3303
447. Champetier G, Sekiguchi H (1960) Mécanisme réactionnel de la polymérisation anionique des lactames. J Polym Sci 48:309–319
448. Sekiguchi H (1960) Mécanisme réactionnel de la polymérisation catalytique alcaline de l'alpha-pyrrolidone (iii). Bull Soc Chim Fr 1835–1838
449. Sekiguchi H (1963) Mécanisme réactionnel de la polymérisation alcaline des lactames. J Polym Sci A, General Papers 1:1627–1633
450. Frunze TM, Kotel'nikov VA, Volkova TV, Kurašev VV, Davtjan SP, Stankevič IV (1981) The active centres in the anionically activated polymerization of ε-caprolactam. Acta Polym 32:31–35
451. Frunze TM, Kotelnikov VA, Volkova TV, Kurashov VV (1981) Ions and ion-pairs in anionic activated polymerization of epsilon-caprolactam. Eur Polym J 17:1079–1084
452. Bonta G, Ciferri A, Russo S (1977) Specific interactions of lithium chloride in the anionic polymerization of lactams. In: Saegusa T (Kyoto University), Goethals E (University of

Ghent) (eds) Ring-opening polymerization. ACS symposium series, vol 59. American Chemical Society, pp 216–232
453. Cefelin P, Stehlice J, Cefelin P, Sebenda J (1974) Alkaline polymerization of 6-caprolactam.54. Effect of cation on formation of keto structures during activated anionic-polymerization of lactams. Coll Czech Chem Commun 39:2212–2220
454. Šebenda J (1989) 35 – Anionic ring-opening polymerization: lactams. In: Allen G, Bevington JC (eds) Comprehensive polymer science and supplements. Pergamon, Amsterdam, pp 511–530
455. Cefelin P, Stehlice.J, Sebenda J (1973) Anionic polymerization of caprolactam. 47. Effect of polymerization conditions upon keto groups content in anionic polycaprolactam. J Polym Sci C Polym Symp 79–88
456. Coutin B, Sekiguchi H (1977) Dissociation of alkaline and quaternary ammonium-salts of 2-piperidone in polymerization of 2-piperidone. J Polym Sci A Polym Chem 15:2539–2541
457. Alfonso GC, Cirillo G, Russo S, Turturro A (1983) Adiabatic polymerization of epsilon-caprolactam in presence of calcium-chloride – thermodynamic and kinetic aspects. Eur Polym J 19:949–953
458. Greenberg A, Hsing HJ, Liebman JF (1995) Aziridinone and 2-azetidinone and their protonated structures – an ab-initio molecular-orbital study making comparisons with bridgehead bicyclic lactams and acetamide. J Molecul Struct Theochem 338:83–100
459. Dybal J, Schneider B, Doskocilova D, Baldrian J, Pavlikova H, Kvarda J, Prokopova I (1997) Spectral and structural characterization of a cyclic trimeric model of poly(6-hexanelactam). Polymer 38:2483–2491
460. Schneider B, Kvarda J, Dybal J, Schmidt P, Suchoparek M, Prokopova I (1993) Molecular-structure of a cyclic dimeric model of poly(6-hexanelactam). Coll Czech Chem Commun 58:2403–2414
461. Budin J, Brozek J, Roda J (2006) Polymerization of lactams, 96. anionic copolymerization of epsilon-caprolactam with omega-laurolactam. Polymer 47:140–147
462. Luisier A, Bourban PE, Manson JAE (2002) Initiation mechanisms of an anionic ring-opening polymerization of lactam-12. J Polym Sci A Polym Chem 40:3406–3415
463. Mateva R, Delev O, Rousseva S (1997) Structure of poly-omega-dodecalactam obtained in bulk by an anionic mechanism. Eur Polym J 33:1377–1382
464. Malkin AY, Ivanova SL, Frolov VG, Ivanova AN, Andrianova ZS (1982) Kinetics of anionic-polymerization of lactams – (solution of non-isothermal kinetic problems by the inverse method). Polymer 23:1791–1800
465. Rusu G, Ueda K, Rusu E, Rusu M (2001) Polyamides from lactams by centrifugal molding via anionic ring-opening polymerization. Polymer 42:5669–5678
466. Budin J, Roda J, Brozek J, Kriz J (2006) Anionic copolymerization of epsilon-caprolactam with omega-laurolactam. Macromol Symp 240:78–82
467. Chromcova D, Baslerova L, Roda J, Brozek J (2008) Polymerization of lactams. 99 Preparation of polyesteramides by the anionic copolymerization of epsilon-caprolactam and epsilon-caprolactone. Eur Polym J 44:1733–1742
468. Fang XM, Hutcheon R, Scola DA (2000) Microwave syntheses of poly(epsilon-caprolactam-co-epsilon-caprolactone). J Polym Sci A Polym Chem 38:1379–1390
469. Goodman I, Vachon RN (1984) Copolyesteramides.2. Anionic copolymers of epsilon-caprolactam with epsilon-caprolactone – preparation and general-properties. Eur Polym J 20:529–537
470. Kim BJ, White JL (2003) Continuous polymerization of lactam – lactone block copolymers in a twin-screw extruder. J Appl Polym Sci 88:1429–1437
471. Kim I, White JL (2003) Anionic copolymerization of lauryl lactam and polycaprolactone for the production of a poly(ester amide) triblock copolymer. J Appl Polym Sci 90:3797–3805
472. Kim I, White JL (2005) Reactive copolymerization of various monomers based on lactams and lactones in a twin-screw extruder. J Appl Polym Sci 96:1875–1887

473. Bernaskova A, Chromcova D, Brozek J, Roda J (2004) Polymerization of lactams, 95 – part 94 – preparation of polyesteramides by the anionic polymerization of epsilon-caprolactam in the presence of poly(epsilon-caprolactone). Polymer 45:2141–2148
474. Novakova V, Sobotik R, Matenova J, Roda J (1996) Polymerization of lactams.87. – Block copolymers of poly(epsilon-caprolactam) and polybutadiene prepared by anionic polymerization.1. Preparation and properties. Angew Makromol Chem 237:123–141
475. Petrov P, Jankova K, Mateva R (2003) Polyamide-6-b-polybutadiene block copolymers: synthesis and properties. J Appl Polym Sci 89:711–717
476. Roda J (2000). In: Baltá Calleja FJ, Roslaniec Z (eds) Block copolymers. Marcel Dekker, Basel, p 93
477. Sobotik R, Srubar R, Roda J (1997) Polymerization of lactams.88. Copolymers poly(epsilon-caprolactam)-block-polybutadiene prepared by anionic polymerization.3. Model polymerizations initiated with potassium salt of epsilon-caprolactam and accelerated with isocyanates and their derivatives. Macromol Chem Phys 198:1147–1163
478. Coutinho FMB, Sobrinho AAB (1991) Thermal and mechanical-properties of some caprolactam-poly(propylene oxide) block copolymers. Eur Polym J 27:105–108
479. Kim KJ, Hong DS, Tripathy AR, Kyu T (1999) Toughening and phase separation behavior of nylon 6-PEG block copolymers and in situ nylon 6-PEG blend via in situ anionic polymerization. J Appl Polym Sci 73:1285–1303
480. Maier S, Loontjens T, Scholtens B, Mulhaupt R (2003) Isocyanate-free route to caprolactam-blocked oligomeric isocyanates via carbonylbiscaprolactam- (CBC-) mediated end group conversion. Macromolecules 36:4727–4734
481. Stehlicek J, Chauhan GS, Znasikova M (1992) Preparation of polymeric initiators of the anionic-polymerization of lactams from polyetherdiols. J Appl Polym Sci 46:2169–2175
482. Yeh JL, Kuo JF, Chen CY (1993) Adiabatic anionic-polymerization of caprolactam in the presence of n-acylated caprolactam macroactivator – kinetic-study. J Appl Polym Sci 50:1671–1681
483. Zhilkova K, Mateva R (2008) Anionic block polymerization of hexanelactam and dodecalactam in the presence of a polymeric activator. J Univ Chem Technol Metal 43:291–296
484. Mateva R, Filyanova R, Dimitrov R, Velichkova R (2004) Structure, mechanical, and thermal behavior of nylon 6-polyisoprene block copolymers obtained via anionic polymerization. J Appl Polym Sci 91:3251–3258
485. Owen MJ, Thompson J (1972) Siloxane modification of polyamides. Brit Polym J 4:297–303
486. Allen WT, Eaves DE (1977) Caprolactam based block copolymers using polymeric activators. Angew Makromol Chem 58:321–343
487. Hu GH, Cartier H, Feng LF, Li BG (2004) Kinetics of the in situ polymerization and in situ compatibilization of poly(propylene) and polyamide 6 blends. J Appl Polym Sci 91:1498–1504
488. Hu G-H, Li H, Feng L-F (2005) Rate of the activated anionic polymerisation of ε-caprolactam onto an isocyanate bearing polypropylene in the melt. Polymer 46:4562–4570
489. Teng J, Otaigbe JU, Taylor EP (2004) Reactive blending of functionalized polypropylene and polyamide 6: in situ polymerization and in situ compatibilization. Polym Eng Sci 44:648–659
490. Zhang CL, Feng LF, Hoppe S, Hu GH (2008) Grafting of polyamide 6 by the anionic polymerization of epsilon-caprolactam from an isocyanate bearing polystyrene backbone. J Polym Sci A Polym Chem 46:4766–4776
491. Biernacki P, Chrzczon S, Wlodarcz M (1971) Molecular weight distribution of polycaproamide obtained by anionic polymerization of caprolactam in solvent. Eur Polym J 7:739–747
492. Biernacki P, Wlodarczyk M (1975) Study of molecular-weight of polycaproamide obtained by anionic-polymerization of caprolactam in solvent. Eur Polym J 11:107–109
493. Biernacki P, Wlodarczyk M (1980) Chemical-structure of polycaproamide obtained by anionic-polymerization of caprolactam in solvent. Eur Polym J 16:843–848

494. Dan F, Vasiliu-Oprea C (1998) On the relationship between synthesis parameters and morphology of the anionic polycaproamide obtained in organic media. III. Macroporous powders obtained using CO_2 and carbodiimides as activating compounds. J Appl Polym Sci 67:231–243
495. Vasiliu-Oprea C, Dan F (1996) On the relation between synthesis parameters and morphology of anionic polycaproamide obtained in organic media. I. Influence of the Na[O $(CH_2)_2OCH_3]_2AlH_2$/isophorone diisocyanate catalytic system. J Appl Polym Sci 62:1517–1527
496. Vasiliu-Oprea C, Dan F (1997) On the relation between synthesis parameters and morphology of anionic polycaproamide obtained in organic media. II. Influence of the Na[O $(CH_2)_2OCH_3]_2AIH_2$/aliphatic diisocyanates catalytic systems. J Appl Polym Sci 64:2575–2583
497. Ricco L, Monticelli O, Russo S, Paglianti A, Mariani A (2002) Fast-activated anionic polymerization of epsilon-caprolactam in suspension, 1 – role of the continuous phase on characteristics and properties of powdered PA6. Macromol Chem Phys 203:1436–1444
498. Crespy D, Landfester K (2005) Anionic polymerization of epsilon-caprolactam in miniemulsion: synthesis and characterization of polyamide-6 nanoparticles. Macromolecules 38:6882–6887
499. Pei AH, Liu AD, Xie TX, Yang GS (2006) A new strategy for the preparation of polyamide-6 microspheres with designed morphology. Macromolecules 39:7801–7804
500. Hedrick RM, Gabbert JD, Wohl MH (1985) Nylon 6 RIM. In: Kresta JE (University of Detroit) (ed) Reaction injection molding. ACS symposium series, vol 270. American Chemical Society, pp 135–162
501. Illing G (1969) Direct extrusion of nylon products from lactams. Mod Plast 46:70–76
502. Macosko CW (1989) RIM fundamentals of reaction injection molding. Hanser Publications, Munich
503. Du LB, Yang GS (2010) A super-toughened nylon 12 blends via anionic ring-opening polymerization of lauryllactam in a twin screw extruder. Preparation, morphology, and mechanical properties. Polym Eng Sci 50:1178–1185
504. Hu GH, Cartier H, Plummer C (1999) Reactive extrusion: toward nanoblends. Macromolecules 32:4713–4718
505. Rothe B, Elas A, Michaeli W (2009) In situ polymerisation of polyamide-6 nanocompounds from caprolactam and layered silicates. Macromol Mater Eng 294:54–58
506. Wollny A, Nitz H, Faulhammer H, Hoogen N, Mulhaupt R (2003) In situ formation and compounding of polyamide 12 by reactive extrusion. J Appl Polym Sci 90:344–351
507. Yan DG, Yang GS (2009) Synthesis and properties of homogeneously dispersed polyamide 6/MWNTs nanocomposites via simultaneous in situ anionic ring-opening polymerization and compatibilization. J Appl Polym Sci 112:3620–3626
508. Yang M, Gao Y, He JP, Li HM (2007) Preparation of polyamide 6/silica nanocomposites from silica surface initiated ring-opening anionic polymerization. Expr Polym Lett 1:433–442
509. Sebenda J, Hauer J (1981) Living polymerization of lactams and synthesis of monodisperse polyamides. Polym Bull 5:529–534
510. Sebenda J, Hauer J, Svetlik J (1986) An unusual kinetics of anionic-polymerization of 4-membered lactams. J Polym Sci Polym Symp 74(1):303–310
511. Hashimoto K, Hotta K, Okada M, Nagata S (1995) Synthesis of monodisperse polyamides by living anionic-polymerization of beta-lactams in the mixture of N, N-dimethylacetamide and lithium-chloride. J Polym Sci A Polym Chem 33:1995–1999
512. Hashimoto K, Oi T, Yasuda J, Hotta K, Okada M (1997) Molecular weight distribution of polyamides obtained in anionic polymerization of methyl-substituted beta-lactams and aminolysis of their N-benzoyl lactams. J Polym Sci A Polym Chem 35:1831–1838

513. Hashimoto K, Yasuda J, Kobayashi M (1999) Proton transfer-controlled anionic polymerization of methyl-substituted beta-lactams with potassium t-butoxide and subsequent coupling reaction with saccharides. J Polym Sci A Polym Chem 37:909–915
514. Zhang JH, Gellman SH, Stahl SS (2010) Kinetics of anionic ring-opening polymerization of variously substituted beta-lactams: homopolymerization and copolymerization. Macromolecules 43:5618–5626
515. Tachibana K, Hashimoto K, Tansho N, Okawa H (2011) Chemical modification of chain end in nylon 4 and improvement of its thermal stability. J Polym Sci A Polym Chem 49:2495–2503
516. Roda J, Votrubcova Z, Kralicek J, Stehlicek J, Pokorny S (1981) Polymerization of lactams.39. Condensation as side reaction in the anionic-polymerization of 2-pyrrolidone. Makromol Chem Macromol Chem Phys 182:2117–2126
517. Schirawski G (1972) Studies on anionic polymerization of pyrrolidone. Makromol Chem 161:57–68
518. Sekiguchi H (1960) Etude cinétique de la polymérisation catalytique de l'alpha-pyrrolidone (ii). Bull Soc Chim Fr 1831–1834
519. Roda J, Kralicek J (1982) Process for the anionic polymerization of 2-pyrrolidone with fast freezing step US 4,343,933
520. Costa G, Nencioni M, Russo S, Semeghini GL (1981) The anionic-polymerization of 2-pyrrolidone in bulk and in suspension. Makromol Chem Macromol Chem Phys 182:1399–1405
521. Hashimoto K, Sudo M, Sugimura T, Inagaki Y (2004) Synthesis of novel block copolymers containing polyamide4 segments and control of their biodegradability. J Appl Polym Sci 92:3492–3498
522. Kawasaki N, Yamano N, Takeda S, Ando H, Nakayama A (2012) Synthesis of an azo macromolecular initiator composed of polyamide 4 and its initiation activity for the radical polymerization of vinyl monomers. J Appl Polym Sci 126:E425–E432
523. Chuchma F, Trska P, Roda J, Kralicek J (1983) Polymerization of lactams.57. GLC and NMR analysis of the anionic co-polymers of 2-pyrrolidone with 6-caprolactam and 8-octanelactam. Polymer 24:1491–1494
524. Komoto H (1968) Anionic copolymerization of omega-lactams with omega-lactones. Makromol Chem, Macromol Chem Phys 115:33–42
525. Stehlicek J, Sebenda J (1986) Anionic-polymerization of epsilon-caprolactam.59. Effect of the ratio of reacting components, of the medium and of the ring size on the initial-stage of the anionic-polymerization of lactams. Eur Polym J 22:769–773
526. Hall HK (1958) Polymerization and ring strain in bridged bicyclic compounds. J Am Chem Soc 80:6412–6420
527. Hall HK (1960) Synthesis and polymerization of atom-bridged bicyclic lactams. J Am Chem Soc 82:1209–1215
528. Hashimoto K, Sugata T, Imanishi SI, Okada M (1994) Synthesis of saccharide-conjugated polyamides by quasi-living anionic-polymerization of a bicyclic lactam. J Polym Sci A Polym Chem 32:1619–1625
529. Hashimoto K, Sumitomo H, Washio A (1989) Preparation of monodisperse hydrophilic polyamide by anionic-polymerization of bicyclic oxalactam. J Polym Sci A Polym Chem 27:1915–1923
530. Clarson SJ, Semlyen JA (1993) Siloxane polymers. Prentice Hall, Englewood Cliffs
531. Cypryk M (2012) 4.17 – Polymerization of cyclic siloxanes, silanes, and related monomers. In: Matyjaszewski K, Möller M (eds) Polymer science: a comprehensive reference. Elsevier, Amsterdam, pp 451–476
532. Ganachaud F, Boileau S (2009) Siloxane-containing polymers. In: (ed) Handbook of ring-opening polymerization. Wiley-VCH Verlag GmbH & Co. KGaA, pp 65–95

533. Chojnowski J, Cypryk M (2000) Synthesis of linear polysiloxanes. In: Jones R, Ando W, Chojnowski J (eds) Silicon containing polymers. Kluwer Academic Publishers, Dordrecht, pp 3–42
534. Yilgor E, Yilgor I (2014) Silicone containing copolymers: synthesis, properties and applications. Prog Polym Sci. doi:10.1016/j.progpolymsci.2013.1011.1003
535. Sigwalt P (1981) Ring-opening polymerizations of heterocycles with organometallic catalysts. Angew Makromol Chem 94:161–180
536. Butts M, Cella J, Wood CD, Gillette G, Kerboua R, Leman J, Lewis L, Rajaraman S, Rubinsztajn S, Schattenmann F, Stein J, Wengrovius J, Wicht D (2004) Silicones. In: Encyclopedia of polymer science and technology. John Wiley & Sons, Inc, Hoboken, pp 765–841
537. Noll W (1968) Chemistry and technology of silicones. Academic, New York
538. Fortuniak W, Chojnowski J, Sauvet G (2001) Controlled synthesis of siloxane polymers and siloxane-siloxane block copolymers with 3-chloropropyl groups pendant to the siloxane chain. Macromol Chem Phys 202:2306–2313
539. Takiguchi T, Sakurai M, Kishi T, Ichimura J, Iizuka Y (1960) Preparation of hexaphenylcyclotrisiloxane by the reaction of diphenyldichlorosilane with zinc oxide. J Org Chem 25:310–311
540. Voronkov MG, Basenko SV (1995) From ephemers to monomers, oligomers and polymers - new methods for the generation and transformation of silanones. J Organomet Chem 500:325–329
541. Embery C, Clarke S, Matisons J (2003) Ring-opening polymerization of poly(siloxane) materials. In: Nalwa HS (ed) Handbook of organic–inorganic hybrid materials and nanocomposites, vol 2. American Scientific Publishers, Stevenson Ranch, pp 331–347
542. Bellas V, Iatrou H, Hadjichristidis N (2000) Controlled anionic polymerization of hexamethylcyclotrisiloxane. Model linear and miktoarm star co- and terpolymers of dimethylsiloxane with styrene and isoprene. Macromolecules 33:6993–6997
543. Chojnowski J, Mazurek M (1975) Anionic-polymerization of siloxanes - mechanism of initiation with triorganosilanolates. Makromol Chem, Macromol Chem Phys 176:2999–3023
544. Wilczek L, Kennedy JP (1987) Aggregation in the anionic-polymerization of hexamethylcyclotrisiloxane with lithium counterion. Polym J 19:531–538
545. Kopylov VM, Prokhodko PL, Kovyazin VA (1982) polymerization of hexamethylcyclotrisiloxane by alpha, omega-bis-(tetramethylammonium) oligodimethylsiloxanolate in the presence of trimethylsilanol. Vysokomol Soedin A 24:1751–1756
546. Wright P (1984). In: Ivin J, Saegusa T (ed) Ring-opening polymerization. Elsevier, London, p 1055
547. Boileau S (1981) Use of cryptates in anionic polymerization of heterocyclic compounds. In: James E. McGrath (Virginia Polytechnic Institute and State University) (ed) Anionic Polymerization Kinetics, Mechanisms, and Synthesis. ACS symposium series, vol 166. American Chemical Society, pp 283–305
548. Dickstein WH, Lillya CP (1989) Blocked amine functional initiator for anionic-polymerization. Macromolecules 22:3882–3885
549. Hubert S, Hemery P, Boileau S (1986) Anionic-polymerization of cyclosiloxanes with cryptates as counterions – new results. Makromol Chem Macromol Symp 6:247–252
550. Molenberg A, Siffrin S, Moller M, Boileau S, Teyssie D (1996) Well defined columnar liquid crystalline polydiethylsiloxane. Macromol Symp 102:199–207
551. Suzuki T (1989) Preparation of poly(dimethylsiloxane) macromonomers by the initiator method.2. Polymerization mechanism. Polymer 30:333–337
552. Veith CA, Cohen RE (1989) Kinetic modeling and optimization of the trifluoropropylmethylsiloxane polymerization. J Polym Sci A Polym Chem 27:1241–1258
553. Zhang Y, Zhang ZJ, Wang Q, Xie ZM (2007) Synthesis of well-defined difunctional polydimethylsiloxane with an efficient dianionic initiator for ABA triblock copolymer. J Appl Polym Sci 103:153–159

554. Beckmann J, Dakternieks D, Lim AEK, Lim KF, Jurkschat K (2006) Understanding ring strain and ring flexibility in six- and eight-membered cyclic organometallic group 14 oxides. J Molecul Struct Theochem 761:177–193
555. Mazurek M, Chojnowski J (1977) Anionic-polymerization of siloxanes.2. Internal multifunctional assistance of siloxane system to siloxane bond-cleavage by alkali-metal silanolates. Makromol Chem Macromol Chem Phys 178:1005–1017
556. Ritch JS, Chivers T (2007) Silicon analogues of crown ethers and cryptands: a new chapter in host-guest chemistry? Angew Chem Int Ed 46:4610–4613
557. Su SX, Zhang ZJ, Zheng ZM, Xie ZM (2004) Anionic non-equilibrium ring-opening polymerization of octamethylcyclotetrasiloxane (D-4) initiated by silazyl-lithiums. Polym Int 53:149–152
558. Molenberg A, Moller M (1995) A fast catalyst system for the ring-opening polymerization of cyclosiloxanes. Macromol Rapid Commun 16:449–453
559. Molenberg A, Moller M (1997) Polymerization of cyclotrisiloxanes by organolithium compounds and P-2-Et base. Macromol Chem Phys 198:717–726
560. Grzelka A, Chojnowski J, Fortuniak W, Taylor RG, Hupfield PC (2004) Kinetics of the anionic ring opening polymerization of cyclosiloxanes initiated with a superbase. J Inorg Organomet Polym 14:85–99
561. Hupfield PC, Taylor RG (1999) Ring-opening polymerization of siloxanes using phosphazene base catalysts. J Inorg Organomet Polym 9:17–34
562. Bessmertnykh A, Ben F, Baceiredo A, Mignani G (2003) Anionic ring-opening polymerization of cyclic organosiloxanes using phosphorus ylides as strong non-ionic bases. J Organomet Chem 686:281–285
563. Rodriguez M, Marrot S, Kato T, Sterin S, Fleury E, Baceiredo A (2007) Catalytic activity of N-heterocyclic carbenes in ring opening polymerization of cyclic siloxanes. J Organomet Chem 692:705–708
564. Saam JC (1999) Stereoregular polysiloxanes via ring-opening polymerization, a review. J Inorg Organomet Polym 9:3–16
565. Clarson SJ (2000) Synthesis of linear polysiloxanes. In: Jones R, Ando W, Chojnowski J (eds) Silicon containing polymers. Kluwer Academic Publishers, Dordrecht, p 139
566. Andrianov KA, Godovskii IK, Svistunov VS, Papkov VS, Zhdanov AA, Slonimskii GL (1977) Polymerization of some organocyclosiloxanes in solid-phase. Dokl Akad Nauk Sssr 234:1326–1328
567. Andrianov KA, Temnikovskii VA, Khananashvili LM, Zavin BG, Kuznetsova AG, Golubtsov SA, Ivanov VI (1969) Solid-state polymerization of organocyclosiloxanes. Vysokomol Soedin B 11:637–638
568. Buzin MI, Gerasimov MV, Obolonkova ES, Papkov VS (1997) Solid-state polymerization of hexaphenylcyclotrisiloxane. J Polym Sci A Polym Chem 35:1973–1984
569. Unno M, Takada K, Kawaguchi Y, Matsumoto H (2005) Supramolecular aggregates of silanols and solid-state synthesis of siloxanes. Mol Cryst Liq Cryst 440:259–264
570. Barrere M, Ganachaud F, Bendejacq D, Dourges MA, Maitre C, Hemery P (2001) Anionic polymerization of octamethylcyclotetrasiloxane in miniemulsion II. Molar mass analyses and mechanism scheme. Polymer 42:7239–7246
571. Degunzbourg A, Favier JC, Hemery P (1994) Anionic-polymerization of octamethylcyclotetrasiloxane in aqueous emulsion.1. Preliminary-results and kinetic-study. Polym Int 35:179–188
572. Barrere M, Maitre C, Dourges MA, Hemery P (2001) Anionic polymerization of 1,3,5-tris (trifluoropropylmethyl)cyclotrisiloxane (F-3) in miniemulsion. Macromolecules 34:7276–7280
573. Caille JR, Teyssie D, Bouteiller L, Bischoff R, Boileau S (2000) Ring-opening polymerization in aqueous emulsion applied to the preparation of interpenetrating networks based on telechelic polysiloxanes. Macromol Symp 153:161–166

574. Ivanenko C, Maitre C, Ganachaud F, Hemery P (2003) Multiblock silicones, 1 – vinyl functionalized polydimethylsiloxane. e-Polymers 3:111–125
575. Aoyagi T, Tadenuma R, Nagase Y (1996) Novel silicones for transdermal therapeutic system.6. Preparation of oligodimethylsiloxane containing 2-pyrrolidone moiety as a terminal group and its enhancing effect on transdermal drug penetration. Macromol Chem Phys 197:677–686
576. Elkins CL, Long TE (2004) Living anionic polymerization of hexamethylcyclotrisiloxane (D-3) using functionalized initiation. Macromolecules 37:6657–6659
577. Kazama H, Tezuka Y, Imai K (1991) Synthesis and reactions of uniform-size poly(dimethylsiloxane)s having carboxylic-acid as a single end group and both end groups. Macromolecules 24:122–125
578. Kumar A, Eichinger BE (1990) Anionic polymerization of hexamethylcyclotrisiloxane with acetylacetone initiator to form telechelic polymer. Macromolecules 23:5358
579. Saxena A, Rajaraman S, Leatherman M (2007) Synthesis of narrowly dispersed bis-hydride-capped polydimethylsiloxane using difunctional anionic initiator based on 1,3-diisopropenylbenzene. Macromolecules 40:752–755
580. Suzuki T, Yamada S, Okawa T (1993) Synthesis of polydimethylsiloxanes containing aminosilyl or amidosilyl groups at one chain end. Polym J 25:411–416
581. Yin R, Hogenesch TE (1993) Synthesis and characterization of narrow molecular-weight distribution polystyrene poly(dimethylsiloxane) macrocyclic block-copolymers and their isobaric precursors. Macromolecules 26:6952–6957
582. Chang TC, Chen YC, Ho SY, Chiu YS (1996) The effect of silicon and phosphorus on the degradation of poly(methyl methacrylate). Polymer 37:2963–2968
583. Miura Y, Hirota K, Moto H, Yamada B (1999) High-yield synthesis of functionalized alkoxyamine initiators and approach to well-controlled block copolymers using them. Macromolecules 32:8356–8362
584. Miura Y, Miyake K (2005) Synthesis of poly(dimethylsiloxane)-containing diblock and triblock copolymers by the combination of anionic ring-opening polymerization of hexamethylcyclotrisiloxane and nitroxide-mediated radical polymerization of methyl acrylate, isoprene, and styrene. J Polym Sci A Polym Chem 43:6153–6165
585. Miura Y, Sakai Y, Taniguchi I (2003) Syntheses of well-defined poly(siloxane)-b-poly (styrene) and poly(norbomene)-b-poly(styrene) block copolymers using functional alkoxyamines. Polymer 44:603–611
586. Pollack SK, Singer DU, Morgan AM (1999) Siloxane/styrene copolymers via nitroxide-mediated radical polymerization. Polym Prepr 40:370
587. Rheingans O, Hugenberg N, Harris JR, Fischer K, Maskos M (2000) Nanoparticles built of cross-linked heterotelechelic, amphiphilic poly(dimethylsiloxane)-b-poly(ethylene oxide) diblock copolymers. Macromolecules 33:4780–4790
588. Tezuka Y, Nobe S, Shiomi T (1995) Synthesis and surface formation of 3-component copolymers having polystyrene-block-poly(dimethylsiloxane) graft segments. Macromolecules 28:8251–8258
589. Aoyagi T, Takamura Y, Nakamura T, Nagase Y (1992) Preparation of pyridyl-terminated oligodimethylsiloxane and siloxane-grafted copolymers containing pyridyl groups at the side-chain ends. Polymer 33:1530–1536
590. Suzuki T, Lo PY (1991) Preparation of poly(dimethylsiloxane) macromonomers having ethynylene functionality by the initiator method. Macromolecules 24:460–463
591. Fragouli P, Iatrou H, Hadichristidis N, Sakurai T, Matsunaga Y, Hirao A (2006) Synthesis of well-defined miktoarm star polymers of poly(dimethylsiloxane) by the combination of chlorosilane and benzyl chloride linking chemistry. J Polym Sci A Polym Chem 44:6587–6599
592. Hammouch SO, Beinert GJ, Zilliox JG, Herz JE (1995) Synthesis and characterization of monofunctional polydimethylsiloxanes with a narrow molecular-weight distribution. Polymer 36:421–426

593. Chojnowski J, Cypryk M, Fortuniak W, Rozga-Wijas K, Scibiorek M (2002) Controlled synthesis of vinylmethylsiloxane-dimethylsiloxane gradient, block and alternate copolymers by anionic ROP of cyclotrisiloxanes. Polymer 43:1993–2001
594. Cypryk M, Kazmierski K, Fortuniak W, Chojnowski J (2000) Microstructure of the copolymer chain generated by anionic ring-opening polymerization of a model cyclotrisiloxane with mixed siloxane units. Macromolecules 33:1536–1545
595. Cypryk M, Delczyk B, Juhari A, Koynov K (2009) Controlled synthesis of trifluoropropylmethylsiloxane-dimethylsiloxane gradient copolymers by anionic ROP of cyclotrisiloxanes. J Polym Sci A Polym Chem 47:1204–1216
596. Liu LH, Yang SY, Zhang ZJ, Wang Q, Xie ZM (2003) Synthesis and characterization of poly (diethylsiloxane) and its copolymers with different diorganosiloxane units. J Polym Sci A Polym Chem 41:2722–2730
597. Ziemelis MJ, Saam JC (1989) Sequence distribution in poly(dimethylsiloxane-co-methylvinylsiloxanes). Macromolecules 22:2111–2116
598. Abe Y, Gunji T (2004) Oligo- and polysiloxanes. Prog Polym Sci 29:149–182
599. Baney RH, Itoh M, Sakakibara A, Suzuki T (1995) Silsesquioxanes. Chem Rev 95:1409–1430
600. Cordes DB, Lickiss PD, Rataboul F (2010) Recent developments in the chemistry of cubic polyhedral oligosilsesquioxanes. Chem Rev 110:2081–2173
601. Loy DA, Shea KJ (1995) Bridged polysilsesquioxanes – highly porous hybrid organic–inorganic materials. Chem Rev 95:1431–1442
602. Li HY, Yu DS, Zhang JY (2005) A novel and facile method for direct synthesis of cross-linked polysiloxanes by anionic ring-opening copolymerization with Ph-12-POSS/D-4/Ph8D4. Polymer 46:5317–5323
603. Li HY, Zhang JY, Xu RW, Yu DS (2006) Direct synthesis and characterization of cross-linked polysiloxanes via anionic ring-opening copolymerization with octaisobutyl-polyhedral oligomeric silsesquioxane and octamethylcyclotetrasiloxane. J Appl Polym Sci 102:3848–3856
604. Suryanarayanan B, Peace BW, Mayhan KG (1974) Anionic-polymerization of 2,2,5,5-tetramethyl-1-oxa-2,5-disilacyclopentane. J Polym Sci A Polym Chem 12:1089–1107
605. Suryanarayanan B, Peace BW, Mayhan KG (1974) Anionic-polymerization of a series of 5-membered cyclocarbosiloxanes. J Polym Sci A Polym Chem 12:1109–1123
606. Ziatdinov VR, Cai GP, Weber WP (2002) Anionic ring-opening polymerization of trimethylsiloxy-substituted 1-oxa-2,5-disilacyclopentanes: synthesis of trimethylsiloxy-substituted poly 1-oxa-2,5-disila-1,5-pentanylene s. Macromolecules 35:2892–2897
607. Lohmeijer BGG, Dubois G, Leibfarth F, Pratt RC, Nederberg F, Nelson A, Waymouth RM, Wade C, Hedrick JL (2006) Organocatalytic living ring-opening polymerization of cyclic carbosiloxanes. Org Lett 8:4683–4686
608. Brown HA, Chang YA, Waymouth RM (2013) Zwitterionic polymerization to generate high molecular weight cyclic poly(carbosiloxane)s. J Am Chem Soc 135:18738–18741
609. Li YN, Kawakami Y (1999) Synthesis and polymerization of an optically active bifunctional disiloxane. 2. Preparation of optically active (S)-2-(1-naphthyl)-2-phenyl-5,5-dimethyl-1-oxa-2,5-disilacyclopentane and its ring-opening polymerization. Macromolecules 32:548–553
610. Li YN, Kawakami Y (2000) Stereoselective feature in anionic ring-opening polymerization of 2-(1-naphthyl)-2-phenyl-5,5-dimethyl-1-oxa-2,5-disilacyclopentane and influence of tacticity on the thermal property of polymers. Macromolecules 33:1560–1564
611. Chojnowski J, Kurjata J (1995) Selective anionic ring-opening polymerization of permethyltetrasila-1,4-dioxane, d-2(2) – transformation of poly(silaether) in polysiloxane and polysilylene. Macromolecules 28:2996–2999
612. Steward OW, Williams JL (1988) New mechanisms for the base-catalyzed cleavage of Si-Si bonds in organopolysilanes – the base-catalyzed solvolysis of pentaphenyldisilanecarboxylic acid and pentaphenyldisilanol in ethanol water media. J Organomet Chem 341:199–211

613. Zundel T, Baran J, Mazurek M, Wang JS, Jerome R, Teyssie P (1998) Climbing back up the nucleophilic reactivity scale. Use of cyclosila derivatives as reactivity boosters in anionic polymerization. Macromolecules 31:2724–2730
614. Cypryk M, Chrusciel J, Fossum E, Matyjaszewski K (1993) Ring-opening polymerization of strained cyclotetrasilanes as a new route towards well-defined polysilylenes. Makromol Chem Macromol Symp 73:167–176
615. Cypryk M, Gupta Y, Matyjaszewski K (1991) Anionic ring-opening polymerization of 1,2,3,4-tetramethyl-1,2,3,4-tetraphenylcyclotetrasilane. J Am Chem Soc 113:1046–1047
616. Fossum E, Gordonwylie SW, Matyjaszewski K (1994) Identification of the stereoisomers of 1,2,3,4-tetramethyl-1,2,3,4-tetraphenylcyclotetrasilane. Organometallics 13:1695–1698
617. Fossum E, Matyjaszewski K (1995) Ring-opening polymerization of cyclotetrasilanes – microstructure and mechanism. Macromolecules 28:1618–1625
618. Fossum E, Matyjaszewski K, Sheiko SS, Moller M (1997) Morphology of polystyrene-block-poly(methylphenylsilylene). Macromolecules 30:1765–1767
619. Suzuki M, Kotani J, Gyobu S, Kaneko T, Saegusa T (1994) Synthesis of sequence-ordered polysilane by anionic ring-opening polymerization of phenylnonamethylcyclopentasilane. Macromolecules 27:2360–2363
620. Koopmann F, Frey H (1996) Synthesis of poly(silylenemethylene)s symmetrically substituted with alkyl side groups containing 4–6 carbon atoms. Macromolecules 29:3701–3706
621. Matsumoto K, Nishimura M, Yamaoka H (2000) Organolithium-induced anionic polymerization of 1,1,3,3-tetramethyl-1,3-disilacyclobutane in the presence of hexamethylphosphoramide. Macromol Chem Phys 201:805–808
622. Matsumoto K, Shimazu H, Deguchi M, Yamaoka H (1997) Anionic ring-opening polymerization of silacyclobutane derivatives. J Polym Sci A Polym Chem 35:3207–3216
623. Matsumoto K, Shinohata M, Yamaoka H (2000) Anionic ring-opening polymerization of phenylsilacyclobutanes. Polym J 32:354–360
624. Ogawa T, Lee SD, Murakami M (2002) Synthesis of siloxane-crosslinked polysilyienemethylenes by chlorodephenylation. J Polym Sci A Polym Chem 40:416–422
625. Theurig M, Weber WP (1992) Stereoselective anionic ring-opening polymerization of 1,1-dimethyl-1-silacyclobutene – characterization of poly(1,1-dimethyl-1-sila-cis-but-2-ene). Polym Bull 28:17–21
626. Finkelshtein ES, Ushakov NV, Krasheninnikov EG, Yampolskii YP (2004) New polysilalkylenes: synthesis and gas-separation properties. Russ Chem Bull 53:2604–2610
627. Kawahara S, Nagai A, Kazama T, Takano A, Isono Y (2004) Preparation of poly (1,1-dimethyl silabutane) by anionic polymerization and its crystallization. Macromolecules 37:315–321
628. Kakihana Y, Uenishi K, Imae I, Kawakami Y (2005) Anionic ring-opening polymerization of optically pure 1-methyl-1-(1-naphthyl)-2,3-benzosilacyclobut-2-ene. Macromolecules 38:6321–6326
629. Kloninger C, Rehahn M (2004) 1,1-dimethylsilacyclobutane-mediated living anionic block copolymerization of 1 dimethylsilaferrocenophane and methyl methacrylate. Macromolecules 37:1720–1727
630. Sheridan JB, Gomez P, Manners I (1996) Transition metal-catalyzed ring-opening copolymerization of silicon-bridged 1 ferrocenophanes and sila- or disilacyclobutanes: synthesis of poly(ferrocenylsilane)-poly(carbosilane) random copolymers. Macromol Rapid Commun 17:319–324
631. Sheikh MRK, Tharanikkarasu K, Imae I, Kawakami Y (2001) Silacyclobutane as "carbanion pump" in anionic polymerization. 2. Effective trapping of the initially formed carbanion by diphenylethylene. Macromolecules 34:4384–4389
632. Bruzaud S, Soum A (1996) Anionic ring-opening polymerization of cyclodisilazanes.1. General aspects. Macromol Chem Phys 197:2379–2391

633. Cazalis C, Mingotaud AF, Soum A (1997) Anionic ring-opening polymerization of cyclodisilazanes.3. Influence of the silicon substituent on the kinetics of polymerization. Macromol Chem Phys 198:3441–3450
634. Duguet E, Schappacher M, Soum A (1992) High molar mass polysilazane – a new polymer. Macromolecules 25:4835–4839
635. Soum A (2000) Polysilazanes in Silicon containing polymers: the science and technology of their synthesis and applications. In: Jones R, Ando W, Chojnowski J (eds) Silicon containing polymers. Kluwer Academic Publishers, Dordrecht, pp 323–349
636. Matsumoto K, Nakashita J, Matsuoka H (2006) Synthesis of silicon nitride based ceramic nanoparticles by the pyrolysis of silazane block copolymer micelles. J Polym Sci A Polym Chem 44:4696–4707
637. Rulkens R, Lough AJ, Manners I (1994) Anionic ring-opening oligomerization and polymerization of silicon-bridged 1 ferrocenophanes – characterization of short-chain models for poly (ferrocenylsilane) high polymers. J Am Chem Soc 116:797–798
638. Rider DA, Manners I (2007) Synthesis, self-assembly, and applications of polyferrocenylsilane block copolymers. Polym Rev 47:165–195
639. Bellas V, Rehahn M (2007) Polyferrocenylsilane-based polymer systems. Angew Chem Int Ed 46:5082–5104
640. Rokicki G (2000) Aliphatic cyclic carbonates and spiroorthocarbonates as monomers. Prog Polym Sci 25:259–342
641. Rokicki G, Parzuchowski PG (2012) 4.12 – ROP of cyclic carbonates and ROP of macrocycles. In: Matyjaszewski K, Möller M (eds) Polymer science: a comprehensive reference. Elsevier, Amsterdam, pp 247–308
642. Keul H (2009) Polycarbonates. In: (ed) Handbook of ring-opening polymerization. Wiley-VCH Verlag GmbH & Co. KGaA, pp 307–327
643. Tempelaar S, Mespouille L, Coulembier O, Dubois P, Dove AP (2013) Synthesis and post-polymerisation modifications of aliphatic poly(carbonate)s prepared by ring-opening polymerisation. Chem Soc Rev 42:1312–1336
644. Mespouille L, Coulembier O, Kawalec M, Dove AP, Dubois P (2014) Implementation of metal-free ring-opening polymerization in the preparation of aliphatic polycarbonate materials. Prog Polym Sci 39:1144–1164
645. Vogdanis L, Heitz W (1986) Carbon dioxide as a monomer, 3. The polymerization of ethylene carbonate. Makromol Chem Rapid Commun 7:543–547
646. Vogdanis L, Martens B, Uchtmann H, Hensel F, Heitz W (1990) Synthetic and thermodynamic investigations in the polymerization of ethylene carbonate. Makromol Chem 191:465–472
647. Elmer AM, Jannasch P (2006) Synthesis and characterization of poly(ethylene oxide-co-ethylene carbonate) macromonomers and their use in the preparation of crosslinked polymer electrolytes. J Polym Sci A Polym Chem 44:2195–2205
648. Keki S, Torok J, Deak G, Zsuga M (2004) Mechanism of the anionic ring-opening oligomerization of propylene carbonate initiated by the tert-butylphenol/$KHCO_3$ system. Macromol Symp 215:141–150
649. Kéki S, Török J, Deák G, Zsuga M (2001) Ring-opening oligomerization of propylene carbonate initiated by the bisphenol a/KHCO3 system: a matrix-assisted laser desorption/ionization mass spectrometric study of the oligomers formed. Macromolecules 34:6850–6857
650. Lee J-C, Litt MH (2000) Ring-opening polymerization of ethylene carbonate and depolymerization of poly(ethylene oxide-co-ethylene carbonate). Macromolecules 33:1618–1627
651. Rokicki G, Rakoczy P, Parzuchowski P, Sobiecki M (2005) Hyperbranched aliphatic polyethers obtained from environmentally benign monomer: glycerol carbonate. Green Chem 7:529–539
652. Wu M, Guo J, Jing H (2008) Organic base catalyzed oligomerization of propylene carbonate and bisphenol A: unexpected polyether diol formation. Catal Commun 9:120–125

653. Rokicki G, Jezewski P (1988) Polycarbonates from cyclic carbonates, carbanions, and dihalo compounds. Polym J 20:499–509
654. Rokicki G, Pawlicki J, Kuran W (1985) Poly(ether-carbonate)s from diphenolates, cyclic carbonates, and dihalo compounds. Polym J 17:509–516
655. Bialas NJ, Kühling S, Keul H, Höcker H (1990) On the behaviour of benzo-1,3-dioxolan-2-one and benzo-1,3-dioxan-2-one versus carbanionic species. Makromol Chem 191:1165–1175
656. Azechi M, Matsumoto K, Endo T (2013) Anionic ring-opening polymerization of a five-membered cyclic carbonate having a glucopyranoside structure. J Polym Sci A Polym Chem 51:1651–1655
657. Haba O, Furuichi N, Akashika Y (2009) Anionic ring-opening copolymerization of L-lactide with a five-membered cyclic carbonate having a glucopyranoside structure. Polym J 41:702–708
658. Haba O, Tomizuka H, Endo T (2005) Anionic ring-opening polymerization of methyl 4,6-O-benzylidene-2,3-O-carbonyl-alpha-D-glucopyranoside: a first example of anionic ring-opening polymerization of five-membered cyclic carbonate without elimination of CO2. Macromolecules 38:3562–3563
659. Hocker H, Keul H (1992) Initiation and growth mechanisms of the ring-opening polymerization of cyclic carbonates. Makromol Chem Macromol Symp 54–5:9–11
660. Hocker H, Keul H (1994) Controlled copolymer structures via anionic insertion polymerization of cyclic carbonates. Macromol Symp 85:211–215
661. Hocker H, Keul H, Kuhling S, Hovestadt W (1991) Ring-opening polymerization and copolymerization of cyclic carbonates. Makromol Chem Macromol Symp 42–3:145–153
662. Hocker H, Keul H, Kuhling S, Hovestadt W, Muller A, Wurm B (1993) Ring-opening polymerization and copolymerization of cyclic carbonates with a variety of initiating systems. Makromol Chem Macromol Symp 73:1–5
663. Hocker H, Keul H, Kuhling S, Hovestadt W, Muller AJ (1991) The anionic ring-opening polymerization and copolymerization of cyclic carbonates. Makromol Chem Macromol Symp 44:239–245
664. Carothers WH, Dorough GH, Van Natta FJ (1932) Studies of polymerization and ring formation. X The reversible polymerization of six-membered cyclic esters. J Am Chem Soc 54:761–772
665. Carothers WH, Van Natta FJ (1930) Studies on polymerization and ring formation. III Glycol esters of carbonic acid. J Am Chem Soc 52:314–326
666. Keul H, Bacher R, Hocker H (1986) Anionic ring-opening polymerization of 2,2-dimethyltrimethylene carbonate. Makromol Chem Macromol Chem Phys 187:2579–2589
667. Kuhling S, Keul H, Hocker H (1989) Active species in the anionic ring-opening polymerization of cyclic carbonates. Makromol Chem Macromol Chem Phys 190:9–13
668. Kuhling S, Keul H, Hocker H (1990) Polymers from 2-allyloxymethyl-2-ethyltrimethylene carbonate and copolymers with 2,2-dimethyltrimethylene carbonate obtained by anionic ring-opening polymerization. Makromol Chem Macromol Chem Phys 191:1611–1622
669. Kühling S, Keul H, Höcker H (1992) Copolymerization of 2,2-dimethyltrimethylene carbonate with 2-allyloxymethyl-2-ethyltrimethylene carbonate and with ε-caprolactone using initiators on the basis of Li, Al, Zn and Sn. Makromol Chem 193:1207–1217
670. Kuhling S, Keul H, Hocker H, Buysch HJ, Schon N, Leitz E (1991) Polymerization of 5,5-(bicyclo 2.2.1 hept-2-en-5,5-ylidene)-1,3-dioxan-2-one and copolymerization with 5,5-dimethyl-1,3-dioxan-2-one. Macromolecules 24:4229–4235
671. Matsuo J, Sanda F, Endo T (1998) A novel observation in anionic ring-opening polymerization behavior of cyclic carbonates having aromatic substituents. Macromol Chem Phys 199:2489–2494
672. Sanda F, Kamatani J, Endo T (2001) Synthesis and anionic ring-opening polymerization behavior of amino acid-derived cyclic carbonates. Macromolecules 34:1564–1569

673. Albertsson AC, Sjoling M (1992) Homopolymerization of 1,3-dioxan-2-one to high-molecular-weight poly(trimethylene carbonate). J Macromol Sci Pure Appl Chem 29:43–54
674. Kuhling S, Keul H, Hocker H, Buysch HJ, Schon N (1991) Synthesis of poly(2-ethyl-2-hydroxymethyltrimethylene carbonate). Makromol Chem Macromol Chem Phys 192:1193–1205
675. Matsuo J, Aoki K, Sanda F, Endo T (1998) Substituent effect on the anionic equilibrium polymerization of six-membered cyclic carbonates. Macromolecules 31:4432–4438
676. Miyagawa T, Shimizu M, Sanda F, Endo T (2005) Six-membered cyclic carbonate having styrene moiety as a chemically recyclable monomer. Construction of novel cross-linking-de-cross-linking system of network polymers. Macromolecules 38:7944–7949
677. Endo T, Kakimoto K, Ochiai B, Nagai D (2005) Synthesis and chemical recycling of a polycarbonate obtained by anionic ring-opening polymerization of a bifunctional cyclic carbonate. Macromolecules 38:8177–8182
678. Morikawa H, Sudo A, Nishida H, Endo T (2005) Volume-expandable monomer 5,5-dimethyl-1,3-dioxolan-2-one: Its copolymerization behavior with epoxide and its applications to shrinkage-controlled epoxy-curing systems. J Appl Polym Sci 96:372–378
679. Murayama M, Sanda F, Endo T (1998) Anionic ring-opening polymerization of a cyclic carbonate having a norbornene structure with amine initiators. Macromolecules 31:919–923
680. Nederberg F, Lohmeijer BGG, Leibfarth F, Pratt RC, Choi J, Dove AP, Waymouth RM, Hedrick JL (2007) Organocatalytic ring opening polymerization of trimethylene carbonate. Biomacromolecules 8:153–160
681. Nederberg F, Trang V, Pratt RC, Mason AF, Frank CW, Waymouth RM, Hedrick JL (2007) New ground for organic catalysis: A ring-opening polymerization approach to hydrogels. Biomacromolecules 8:3294–3297
682. Mindemark J, Hilborn J, Bowden T (2007) End-group-catalyzed ring-opening polymerization of trimethylene carbonate. Macromolecules 40:3515–3517
683. Parzuchowski PG, Jaroch M, Tryznowski M, Rokicki G (2008) Synthesis of new glycerol-based hyperbranched polycarbonates. Macromolecules 41:3859–3865
684. Seow WY, Yang YY (2009) Functional polycarbonates and their self-assemblies as promising non-viral vectors. J Control Rel 139:40–47
685. Wang Z, Zhang L, Wang J, Wang Y, Guo X, Liu C (2012) Ring-opening polymerization of 2,2-dimethyltrimethylene carbonate using imidazol-2-ylidenes. Polym Bull 68:141–150
686. Brignou P, Carpentier JF, Guillaume SM (2011) Metal- and organo-catalyzed ring-opening polymerization of alpha-methyl-trimethylene carbonate: insights into the microstructure of the polycarbonate. Macromolecules 44:5127–5135
687. Helou M, Brusson J-M, Carpentier JF, Guillaume SM (2011) Functionalized polycarbonates from dihydroxyacetone: insights into the immortal ring-opening polymerization of 2,2-dimethoxytrimethylene carbonate. Polym Chem 2:2789–2795
688. Helou M, Miserque O, Brusson J-M, Carpentier J-F, Guillaume SM (2010) Organocatalysts for the controlled "immortal" ring-opening polymerization of six-membered ring cyclic carbonates: a metal-free, green process. Chem Eur J 16:13805–13813
689. Guerin W, Helou M, Slawinski M, Brusson J-M, Carpentier J-F, Guillaume SM (2014) Macromolecular engineering via ring-opening polymerization (3): trimethylene carbonate block copolymers derived from glycerol. Polym Chem 5:1229–1240
690. Feng J, Wang X-L, He F, Zhuo R-X (2007) Non-catalyst synthesis of functionalized biodegradable polycarbonate. Macromol Rapid Commun 28:754–758
691. Kricheldorf HR, Lee SR, WeegenSchulz B (1996) Polymers of carbonic acid.12. Spontaneous and hematin-initiated polymerizations of trimethylene carbonate and neopentylene carbonate. Macromol Chem Phys 197:1043–1054
692. Liao L, Zhang C, Gong S (2007) Rapid synthesis of poly(trimethylene carbonate) by microwave-assisted ring-opening polymerization. Eur Polym J 43:4289–4296
693. Pawlowski P, Szymanski A, Kozakiewicz J, Przybylski J, Rokicki G (2005) Poly(urethane-urea)s based on oligocarbonatediols comprising bis(carbamate)alkanes. Polym J 37:742–753

694. Weilandt KD, Keul H, Höcker H (1996) Synthesis and ring-opening polymerization of 2-acetoxymethyl-2-alkyltrimethylene carbonates and of 2-methoxycarbonyl-2-methyltrimethylene carbonate; a comparison with the polymerization of 2,2-dimethyltrimethylene carbonate. Macromol Chem Phys 197:3851–3868
695. Keul H, Hocker H (1986) Block polymers obtained by means of anionic-polymerization - polystyrene-block-poly(epsilon-caprolactone) and polystyrene-block-poly(2,3-dimethyltrimethylene carbonate). Makromol Chem Macromol Chem Phys 187:2833–2839
696. Muller AJ, Keul H, Hocker H (1993) Synthesis and thermal-properties of poly (2,2-dimethyltrimethylene carbonate)-block-poly(tetrahydrofuran)-block-poly(2,2-dimethyltrimethyle ne carbonate). Eur Polym J 29:1171–1178
697. Keul H, Muller AJ, Hocker H, Sylvester G, Schon N (1993) Preparation of polymers with polycarbonate sequences and their depolymerization – an example of thermodynamic recycling. Makromol Chem Macromol Symp 67:289–298
698. Muller AJ, Keul H, Hocker H (1991) Lithium and potassium alcoholates of poly(ethylene glycol)s as initiators for the anionic-polymerization of 2,2-dimethyltrimethylene carbonate - synthesis of AB and ABA block copolymers. Eur Polym J 27:1323–1330
699. Gerhard-Abozari E, Keul H, Höcker H (1994) Copolymers with soft and hard segments based on 2,2-dimethyltrimethylene carbonate and ε-caprolactone. Macromol Chem Phys 195:2371–2380
700. Muller AJ, Keul H, Hocker H (1994) Poly(2,2-dimethyltrimethylene carbonate)-block-poly (dimethylsiloxane)-block-poly(2,2-dimethyltrimethyl ene carbonate) - synthesis and thermal-properties. Polym Int 33:197–204
701. Hovestadt W, Keul H, Hocker H (1991) Poly(methyl methacrylate)-block-poly(2,2-dimethyltrimethylene carbonate) - site transformation from a group transfer polymerization to an anionic ring-opening polymerization. Makromol Chem Macromol Chem Phys 192:1409–1418
702. Keul H, Hocker H, Leitz E, Ott KH, Morbitzer L (1988) Copolymers obtained by means of anionic ring-opening polymerization - poly(2,2-dimethyltrimethylene carbonate-tapered-epsilon-caprolactone). Makromol Chem Macromol Chem Phys 189:2303–2321
703. Keul H, Hocker H, Leitz E, Ott KH, Morbitzer L (1990) Copolymers obtained by means of anionic ring-opening polymerization – poly(2,2-dimethyltrimethylene carbonate)-block-polypivalolactone. Makromol Chem Macromol Chem Phys 191:1975–1990
704. Keul H, Schmidt P, Robertz B, Hocker H (1995) Copolymerization of 2,2-dimethyltrimethylene carbonate and cyclic esters. Macromol Symp 95:243–253
705. Morinaga H, Ujihara Y, Endo T (2012) Metal-free ring-opening block copolymerization of glycidyl phenyl ether with trimethylene carbonate initiated by tetra-n-butylammonium fluoride. J Polym Sci A, Polym Chem 50:3461–3465
706. Edlund U, Albertsson A-C (1999) Copolymerization and polymer blending of trimethylene carbonate and adipic anhydride for tailored drug delivery. J Appl Polym Sci 72:227–239
707. Sanda F, Kamatani J, Endo T (1999) The first anionic ring-opening polymerization of cyclic monothiocarbonate via selective ring-opening with C-S bond cleavage. Macromolecules 32:5715–5717
708. Kakimoto K, Nemoto N, Sanda F, Endo T (2002) Anionic ring-opening polymerization of cyclic thiocarbonates containing norbornene and norbornane groups undergoing volume expansion on polymerization. Chem Lett 31:156–157
709. Kricheldorf HR, Damrau D-O (1998) Polymers of carbonic acid, 26. Synthesis and ionic polymerization of 1,3-dioxane-2-thione. Macromol Chem Phys 199:2589–2596
710. Matsuo J, Sanda F, Endo T (1997) Anionic ring-opening polymerization behavior of a seven-membered cyclic carbonate 1,3-dioxepan-2-one. J Polym Sci A Polym Chem 35:1375–1380
711. Brignou P, Gil MP, Casagrande O, Carpentier JF, Guillaume SM (2010) Polycarbonates derived from green acids: ring-opening polymerization of seven-membered cyclic carbonates. Macromolecules 43:8007–8017

712. Kricheldorf HR, Jenssen J (1989) Polymers of carbonic acid—2. synthesis and polymerization of 2,2'-dihydroxybiphenyl carbonate (4,5,6,7-dibenzo-2-oxo-1,3-dioxacycloheptane). Eur Polym J 25:1273–1279
713. Keul H, Deisel F, Höcker H, Leitz E, Ott K-H, Buysch H-J, Schön N (1991) Aromatic polycarbonates by means of anionic ring-opening polymerization: bisphenol-A-polycarbonate and poly(4,8-dicyclohexyl-2,10-dimethyl-6-oxo-12 H-dibenzo[d, g]-[1,3]dioxocin). Makromol Chem Rapid Commun 12:133–139
714. Takata T, Matsuoka H, Endo T (1991) Synthesis and anionic ring-opening polymerization of a novel aromatic cyclic carbonate having binaphthyl structure. Chem Lett 2091–2094
715. Brunelle DJ, Evans TL, Boden EP (1993) Preparation and ring-opening polymerization of cyclic oligomeric aromatic carbonates. Ind J Technol 31(4–6):234–246
716. Weilandt KD, Keul H, Höcker H (1996) Synthesis and polymerization of bis(hexamethylene carbonate) and bis(2,2,3,3,4,4,5,5-octafluorohexamethylene carbonate). Macromol Chem Phys 197:2539–2551
717. Mitsuhashi T (1989) Structure and reactivity. Wiley-VCH Verlag GmbH, Weinheim, pp 179–230
718. Chakrabarti P, Seiler P, Dunitz JD, Schluter AD, Szeimies G (1981) Experimental-evidence for the absence of bonding electron-density between inverted carbon-atoms. J Am Chem Soc 103:7378–7380
719. Cho I (2000) New ring-opening polymerizations for copolymers having controlled microstructures. Prog Polym Sci 25:1043–1087
720. Hall HK, Ykman P (1976) Addition polymerization of cyclobutene and bicyclobutane monomers. J Polym Sci Macromol Rev 11:1–45
721. Levin MD, Kaszynski P, Michl J (2000) Bicyclo 1.1.1 pentanes, n staffanes, 1.1.1 propellanes, and tricyclo 2.1.0.0(2,5) pentanes. Chem Rev 100:169–234
722. Penelle J (2000) Synthetic control over substituent location on carbon-chain polymers using ring-opening polymerization of small cycloalkanes. In: Boffa LS (Exxon Research & Engineering Company), Novak BM (North Carolina State University) (eds) Transition metal catalysis in macro-molecular design. ACS symposium series, vol 760. American Chemical Society, pp 59–76
723. Penelle J (2009) Polymerization of cycloalkanes. In: Handbook of ring-opening polymerization. Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, pp 329–357
724. Kagumba LC, Penelle J (2005) Anionic ring-opening polymerization of alkyl 1-cyanocyclopropanecarboxylates. Macromolecules 38:4588–4594
725. Penelle J, Herion H, Xie T, Gorissen P (1998) Synthesis and characterization of a model carbon-chain polymer substituted by two esters on every third atom via anionic ring-opening polymerization of a cyclopropane-1,1-dicarboxylate. Macromol Chem Phys 199:1329–1336
726. Penelle J, Xie T (2000) Ring-opening polymerization of diisopropyl cyclopropane-1,1-dicarboxylate under living anionic conditions: A kinetic and mechanistic study. Macromolecules 33:4667–4672
727. Penelle J, Xie T (2001) Synthesis, characterization, and thermal properties of poly (trimethylene-1,1-dicarboxylate) polyelectrolytes. Macromolecules 34:5083–5089
728. Xie T, Penelle J, Verraver M (2002) Experimental investigation on the reliability of routine SEC-MALLS for the determination of absolute molecular weights in the oligomeric range. Polymer 43:3973–3977
729. Illy N, Boileau S, Buchmann W, Penelle J, Barbier V (2010) Control of End groups in anionic polymerizations using phosphazene bases and protic precursors as initiating system (XH-^{t}BuP_4 approach): application to the Ring-opening polymerization of 1,1-dicyanocyclopropane. Macromolecules 43:8782–8789
730. Illy N, Boileau S, Penelle J, Barbier V (2009) Metal-free activation in the anionic ring-opening polymerization of cyclopropane derivatives. Macromol Rapid Commun 30:1731–1735

731. Kagumba LC, Penelle J (2000) Ring-opening polymerization of 1,1-dicyanocyclopropane. Polym Prepr 41:1290
732. Alder RW, Anderson KR, Benjes PA, Butts CP, Koutentis PA, Orpen AG (1998) Polymers and oligomers with transverse aromatic groups and tightly controlled chain conformations. Chem Commun 309–310
733. Cho I, Ahn KD (1979) Polymerizations of substituted cyclopropanes.2. Anionic-polymerization of 1,1-disubstituted 2-vinylcyclopropanes. J Polym Sci A Polym Chem 17:3183–3191
734. Cho I, Kim JB (1980) Polymerization of substituted cyclopropanes.3. Anionic polymerizations of 2-substituted cyclopropane-1,1-dicarbonitriles. J Polym Sci A Polym Chem 18:3053–3057
735. Cho I, Kim WT (1986) Exploratory ring-opening polymerization.12. Polymerization of substituted spiro 2,5 octa-4,7-diene-6-ones and spiro cyclopropane-1,4'-(1'-naphthalenone). J Polym Sci C Polym Lett 24:109–111
736. Cho I, Kim WT (1987) Polymerization systems driven by aromatization energy - anionic-polymerization of 4-allylidene-2,6-dimethyl-2,5-cyclohexadien-1-one and spiro 2,5 octadienone derivatives. J Polym Sci A Polym Chem 25:2791–2798
737. Kim JB, Cho IH (1997) Synthesis and electronic effect of the substituents on anionic ring-opening polymerization of para-substituted phenyl cyclopropanes. Tetrahedron 53:15157–15166
738. Lee JY, Cho I (1986) Synthesis and ring-opening polymerization of 1,2-disubstituted cyclobutanes. Bull Kor Chem Soc 7:210–213
739. Yokozawa T, Miyamoto Y, Futamura S (1993) Synthesis of alternating copolymer of tetracyanoethylene and ethyl vinyl ether by ring-opening polymerization. Makromol Chem Rapid Commun 14:245–249
740. Barfield M, Chan RJH, Hall HK, Mou YH (1986) C-13 NMR-studies of sequence distributions in polymers having all rings in the backbone - 1-substituted 1,3-poly(bicyclobutanes). Macromolecules 19:1343–1349
741. Hall HK, Blanchar EP, Cherkofs SC, Sieja JB, Sheppard WA (1971) Synthesis and polymerization of 1-bicyclobutanecarbonitriles. J Am Chem Soc 93:110–120
742. Hall HK, Padias AB (2003) Bicyclobutanes and cyclobutenes: unusual carbocyclic monomers. J Polym Sci A Polym Chem 41:625–635
743. Hall HK, Smith CD, Blanchar EP, Cherkofs SC, Sieja JB (1971) Synthesis and polymerization of bridgehead-substituted bicyclobutanes. J Am Chem Soc 93:121–130
744. Kawauchi T, Nakamura M, Kitayama T, Padias AB, Hall HK (2005) Structural analyses of methyl bicyclobutane-1-carboxylate oligomers formed with tert-butyllithium/aluminum bisphenoxide and mechanistic aspect of the polymerization. Polym J 37:439–448
745. Kitayama T, Kawauchi T, Chen XP, Padias AB, Hall HK (2002) Stereospecific anionic polymerization of methyl bicyclobutane-1-carboxylate. Macromolecules 35:3328–3330
746. Hall HK (1971) Synthesis and polymerization studies of bicyclo 2.1.0 pentene-1-carbonitrile and bicyclo 3.1.0 hexane-1-carbonitrile. Macromolecules 4:139–142
747. Kaszynski P, Michl J (1988) N staffanes - a molecular-size tinkertoy construction set for nanotechnology - preparation of end-functionalized telomers and a polymer of 1.1.1 propellane. J Am Chem Soc 110:5225–5226
748. Schluter AD (1988) Poly(1.1.1 propellane) - a novel rigid-rod polymer obtained by ring-opening polymerization breaking a carbon carbon sigma-bond. Macromolecules 21:1208–1211
749. Schluter AD (1988) The central propellane bond as polymerizable cc single bond – poly (tricyclo 4.2.0.02,7 octane-1,7-diyl) – a poly(1.1.1 propellane). Angew Chem Int Ed 27:296–298
750. Goethals EJ, Dervaux B (2012) 4.13 – ROP of cyclic amines and sulfides. In: Matyjaszewski K, Möller M (eds) Polymer science: a comprehensive reference. Elsevier, Amsterdam, pp 309–330

751. Boileau S, Champetier G, Sigwalt P (1963) Polymérisation anionique du sulfure de propylène. Makromol Chem 69:180–192
752. Boileau S, Raynal JM, Sigwalt P, Coste J (1962) Chimie macromoléculaire – hauts polymères du sulfure d'éthylène. CR Acad Sci 254:2774–2776
753. Sigwalt P, Spassky N (1984) In: Ivin J, Saegusa T (eds) Ring-opening polymerization. Elsevier, London, p 603
754. Favier JC, Boileau S, Sigwalt P (1968) Kinetics of anionic polymerization of propylene sulfide in tetrahydrofuran.i. Bifunctional polymers with a sodium counter-ion at −30 °C. Eur Polym J 4:3–12
755. Aida T, Kawaguchi K, Inoue S (1990) Zinc N-substituted porphyrins as novel initiators for the living and immortal polymerizations of episulfide. Macromolecules 23:3887–3892
756. Morgan DR, Williams GT, Wragg RT (1970) Polyamines as polymerization catalysts for alkylene sulphide. Eur Polym J 6:309–317
757. Nicol E, Bonnans-Plaisance C, Levesque G (1999) A new initiator system for the living thiiranes ring-opening polymerization: a way toward star-shaped polythiiranes. Macromolecules 32:4485–4487
758. Bonnans-Plaisance C, Levesque G (1989) Homo- and copolymerization of unprotected 2-(hydroxymethyl)thiirane initiated by quaternary ammonium salts of dithiocarboxylic acids. Macromolecules 22:2020–2023
759. Rehor A, Tirelli N, Hubbell JA (2002) A new living emulsion polymerization mechanism: episulfide anionic polymerization. Macromolecules 35:8688–8693
760. Kilcher G, Wang L, Tirelli N (2008) Role of thiol-disulfide polymerization exchange in episulfide polymerization. J Polym Sci A Polym Chem 46:2233–2249
761. Napoli A, Tirelli N, Kilcher G, Hubbell JA (2001) New synthetic methodologies for amphiphilic multiblock copolymers of ethylene glycol and propylene sulfide. Macromolecules 34:8913–8917
762. Wang L, Kilcher G, Tirelli N (2007) Synthesis and properties of amphiphilic star polysulfides. Macromol Biosci 7:987–998
763. Suzuki A, Nagai D, Ochiai B, Endo T (2004) Star-shaped polymer synthesis by anionic polymerization of propylene sulfide based on trifunctional initiator derived from trifunctional five-membered cyclic dithiocarbonate. Macromolecules 37:8823–8824
764. Boileau S, Sigwalt P (1965) Copolymères séquencés à partir des épisulfures. CR Acad Sci 261:132–134
765. Boileau S, Sigwalt P (1973) Block copolymers of epoxyethane with epithioalkanes. Makromol Chem Macromol Chem Phys 171:11–18
766. Bonnans-Plaisance C, Guerin P, Levesque G (1995) Preparation and characterization of poly (thiirane) block copolymers with pendent hydroxy groups. Polymer 36:201–208
767. Gourdenne A, Sigwalt P (1967) Stability of the living polymers of dienes in relation with the preparation of block copolymers. Eur Polym J 3:481–499
768. Morton M, Kammerec RF, Fetters LJ (1971) Synthesis and properties of block polymers. 2. Poly(alpha-methylstyrene)-poly(propylene sulfide)-poly(alpha-methylstyrene). Macromolecules 4:11–15
769. Nevin RS, Pearce EM (1965) Alkylene sulfide block copolymers. J Polym Sci B Polym Lett 3:487–490
770. Watanabe Y, Aida T, Inoue S (1990) Visible-light-mediated living and immortal polymerizations of epoxides initiated with zinc-complexes of N-substituted porphyrins. Macromolecules 23:2612–2617
771. Bonnans-Plaisance C, Corvazier L, Emery J, Nicol E (1998) Functional polythiiranes 9: stilbene mesogen side chain polythiirane. Polym Bull 41:525–532
772. Bonnans-Plaisance C, Corvazier L, Skoulios A (1997) Functional polythiiranes: 5. Side chain liquid crystalline polythiiranes. Polymer 38:3843–3854
773. Bonnans-Plaisance C, Retif P (1999) Functional polythiiranes 6: hydrolysis of side chains ester and monothioacetal functions of comb-like polythiiranes. React Funct Polym 39:9–18

774. Bonnans-Plaisance C, Rétif P, Levesque G (1995) Functional polythiiranes 4. Polym Bull 34:141–147
775. Hirata M, Ochiai B, Endo T (2010) Synthesis of refractive star-shaped polysulfide by anionic polymerization of phenoxy propylene sulfide using an initiating system consisting of trifunctional thiol derived from five-membered cyclic dithiocarbonate and amine. J Polym Sci A Polym Chem 48:525–531
776. Nicol E, Bonnans-Plaisance C, Dony P, Levesque G (2001) Synthesis of end-functionalized star-shaped poly(methylthiirane)s. Macromol Chem Phys 202:2843–2852
777. Lazcano S, Bello A, Marco C, Fatou JG (1989) Anionic synthesis and thermal-properties of poly(3,3-diethylthietane). Polym Bull 21:571–576
778. Lazcano S, Marco C, Fatou JG, Bello A (1989) Growth-rates and regime transitions in poly (3,3-dimethylthietane). Eur Polym J 25:1213–1218
779. Machon JP, Nicco A (1971) Synthesis of homopolymers of thietane of determined molecular mass. Eur Polym J 7:353–361
780. Morton M, Kammerec RF (1970) Nucleophilic substitution at bivalent sulfur - reaction of alkyllithium with cyclic sulfides. J Am Chem Soc 92:3217–3218
781. Saegusa T, Kobayashi S, Hayashi K, Yamada A (1978) Preparation and chelating properties of mercaptoethylated and dithiocarboxylated poly(styrene-g-ethylenimine)s. Polym J 10:403–408
782. Yingyongnarongkul B-E, Howarth M, Elliott T, Bradley M (2004) Solid-phase synthesis of 89 polyamine-based cationic lipids for DNA delivery to mammalian cells. Chem Eur J 10:463–473
783. Stewart IC, Lee CC, Bergman RG, Toste FD (2005) Living ring-opening polymerization of N-sulfonylaziridines: synthesis of high molecular weight linear polyamines. J Am Chem Soc 127:17616–17617
784. Hall HK, Schneider AK (1958) Polymerization of cyclic esters, urethans, ureas and imides. J Am Chem Soc 80:6409–6412
785. Keul H, Hocker H (2000) Expected and unexpected reactions in ring-opening (co)polymerization. Macromol Rapid Commun 21:869–883
786. Schmitz F, Keul H, Hocker H (1997) Alternating copolymers of tetramethylene urea with 2,2-dimethyltrimethylene carbonate and ethylene carbonate; preparation of the corresponding polyurethanes. Macromol Rapid Commun 18:699–706
787. Schmitz F, Keul H, Hocker H (1998) Copolymerization of 2,2-dimethyltrimethylene carbonate with tetramethylene urea: a new route to the polyurethane. Polymer 39:3179–3186
788. Ubaghs L, Novi C, Keul H, Hocker H (2004) Copolymerization of ethylene carbonate and 1,2-propylene carbonate with tetramethylene urea and characterization of the polyurethanes. Macromol Chem Phys 205:888–896
789. Ubaghs L, Waringo M, Keul H, Hocker H (2004) Copolymers and terpolymers of tetramethylene urea, gamma-butyrolactone, and ethylene carbonate or 1,2-propylene carbonate. Macromolecules 37:6755–6762
790. Jorres V, Keul H, Hocker H (1998) Polymerization of (3S,6S)-3-isopropyl-6-methyl-2,5-morpholinedione with tin octoate and tin acetylacetonate. Macromol Chem Phys 199:835–843
791. Dijkstra PJ (2009) Polymerization of cyclic depsipeptides, ureas and urethanes. In: Handbook of ring-opening polymerization. Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, pp 123–140
792. Ouchi T, Miyazaki H, Arimura H, Tasaka F, Hamada A, Ohya Y (2002) Synthesis of biodegradable amphiphilic AB-type diblock copolymers of lactide and depsipeptide with pendant reactive groups. J Polym Sci A Polym Chem 40:1218–1225
793. Ouchi T, Toyohara M, Arimura H, Ohya Y (2002) Preparation of poly(L-lactide)-based microspheres having a cationic or anionic surface using biodegradable surfactants. Biomacromolecules 3:885–888

794. Yongzhen L, Jidong H, Guozhen C, Weina H, Zheng P (2010) Synthesis of polymorpholine-2,5-dione-block-polylactide by two-step anionic ring-opening polymerization. J Appl Polym Sci 118:2005–2008
795. Lapienis G (2012) 4.18 - ring-opening polymerization of cyclic phosphorus monomers. In: Matyjaszewski K, Möller M (eds) Polymer science: a comprehensive reference. Elsevier, Amsterdam, pp 477–505
796. Łapienis G, Penczek S (1977) Kinetics and thermodynamics of anionic polymerization of 2-methoxy-2-oxo-1,3,2-dioxaphosphorinane. J Polym Sci Polym Chem Ed 15:371–382
797. Libiszowski J, Kałużynski K, Penczek S (1978) Polymerization of cyclic esters of phosphoric acid. VI. Poly(alkyl ethylene phosphates). Polymerization of 2-alkoxy-2-oxo-1,3,2-dioxaphospholans and structure of polymers. J Polym Sci Polym Chem Ed 16:1275–1283
798. Vogt W, Pflüger R (1975) Polymere ester von säuren des Phosphors, 3. Polymerisation des 2-Äthoxy-2-oxo-1,3,2-dioxaphospholans. Makromol Chem 1:97–110
799. Vogt W, Siegfried R (1976) Polymere ester von säuren des phosphors, 4. Polymerisation des 2-äthoxy-2-oxo-4,5-dihydro-1,3,2-dioxaphosphorins. Makromol Chem 177:1779–1789
800. Sharov VN, Sharov VN, Bartashe VA, Klebansk AL (1972) Polymers based on cyclic polyfluoroalkylene polyfluoroalkyl phosphates. Vysokomol Soedin A 14:653–661
801. Iwasaki Y, Yamaguchi E (2010) Synthesis of well-defined thermoresponsive polyphosphoester macroinitiators using organocatalysts. Macromolecules 43:2664–2666
802. Liu J, Pang Y, Huang W, Zhai X, Zhu X, Zhou Y, Yan D (2010) Controlled topological structure of copolyphosphates by adjusting pendant groups of cyclic phosphate monomers. Macromolecules 43:8416–8423
803. Steinbach T, Schroder R, Ritz S, Wurm FR (2013) Microstructure analysis of biocompatible phosphoester copolymers. Polym Chem 4:4469–4479
804. Zhang S, Wang H, Shen Y, Zhang F, Seetho K, Zou J, Taylor J-SA, Dove AP, Wooley KL (2013) A simple and efficient synthesis of an acid-labile polyphosphoramidate by organobase-catalyzed ring-opening polymerization and transformation to polyphosphoester Ionomers by acid treatment. Macromolecules 46:5141–5149
805. Yasuda H, Sumitani M, Lee K, Araki T, Nakamura A (1982) High molecular weight poly (2-methoxy-1,3,2-dioxaphospholane 2-oxide) by ring-opening catalysis of tertiary amines. Initiation and stepwise propagation mechanisms as studied by the stoichiometric reaction with triethylamine. Macromolecules 15:1231–1237
806. Sharov VN, Klebansk AL (1973) Polymers based on cyclic polyfluoroalkylene alkyl(aryl) phosphonates. Vysokomol Soedin A 15:2453–2457
807. Steinbach T, Ritz S, Wurm FR (2014) Water-soluble poly(phosphonate)s via living ring-opening polymerization. ACS Macro Lett 3:244–248
808. Kałuzynski K, Libiszowski J, Penczek S (1977) Poly(2-hydro-2-oxo-1,3,2-dioxaphosphorinane). Preparation and NMR spectra. Makromol Chem 178:2943–2947
809. Łapienis G, Penczek S (1990) Synthesis of poly(alkylene phosphate)s with n-containing bases in the side chains. III. N1-oxoethyleneuracil on the poly(trimethylene phosphate) chain. J Polym Sci A Polym Chem 28:1519–1526
810. Pretula J, Kałużyński K, Penczek S (1984) Living reversible anonic polymerization of N, N-diethylamine-1,3,2-dioxaphosphorinan. J Polym Sci Polym Chem Ed 22:1251–1258
811. Kałużyński K, Penczek S (1987) Polymerization of 2-diethylamino-1,3,2-dioxaphosphorinane, 2. Kinetics. Makromol Chem 188:1713–1721
812. Lapienis G, Penczek S, Pretula J (1983) Poly (dialkylphosphates) based on deoxyribose. Macromolecules 16:153–158