8

CATIONIC POLYMERIZATIONS

FILIP E. DU PREZ, ERIC J. GOETHALS, AND RICHARD HOOGENBOOM

8.1 INTRODUCTION

Since the discovery of "living" polymerizations by Swarc in 1956 [1], the area of synthesis and application of well-defined polymer structures has been developed. The livingness of a polymerization is defined as the absence of termination and transfer reactions during the course of the polymerization. If there is also fast initiation and chain-end fidelity, which are prerequisites for the so-called controlled polymerization, well-defined polymers are obtained that have a narrow molar mass distribution as well as defined end groups. Such well-defined polymers can be prepared by various types of living and controlled polymerization techniques, including anionic polymerization [2], controlled radical polymerization [3–5], and cationic polymerization [6, 7].

This chapter provides an overview of the most important living cationic polymerization methods, namely carbocationic polymerizations of vinyl monomers and cationic ring-opening polymerizations (ROPs) of heterocyclic monomers, as depicted in Scheme 8.1. In general, cationic polymerization can be regarded as chain-growth polymerizations based on positively charged propagating species. During initiation, these cationic species are formed and propagation occurs by nucleophilic attack of the monomer onto this ionic species, resulting in chain growth while the newly added monomer remains as cationic chain end. Finally, addition of another nucleophile or a second monomer can be used to introduce chain-end functionality or for the preparation of block copolymers, respectively. Despite the tremendous growth of controlled radical polymerizations in recent decades, living cationic polymerization provides access to additional defined polymer structures that cannot easily be achieved by controlled radical polymerization methods, including poly(vinyl ether)s, poly(isobutene) as well as polyamines, poly(cyclic imino ether)s and poly(ethers). This additional monomer pool, which is only accessibly by living cationic polymerization methods, clearly demonstrates that it is an important tool for polymer chemists.

This chapter will first discuss the living carbocationic polymerization of the three most important monomer classes: isobutene, vinyl ethers, and styrenics. The second part of the chapter will focus on living cationic ROP of cyclic ethers, cyclic imines, and cyclic imino ethers. For more detailed discussions on carbocationic polymerizations [8–14] and cationic ROPs [15–18] in general, the readers are referred to previous literature [19].

8.2 CARBOCATIONIC POLYMERIZATION

Cationic polymerization of vinyl monomers involves the highly reactive carbenium ions, which can only be formed when they are stabilized by the substituents on the vinyl group. Stabilization of the carbenium ion can be achieved by resonance structures, as is the case for vinyl ether and styrenic monomers, or by an inductive effect, which is the stabilizing mechanism for 1,1-disubstituted alkenes. Despite this stabilization, the reactivity of such carbenium ions is still very high, giving rise to the occurrence of side reactions, such as isomerization, hydride abstraction, as well as various transfer reactions. Moreover, carbocationic polymerizations are very sensitive to minor nucleophilic impurities. Nonetheless, in recent years a range of less sensitive polymerization initiators have been developed that can be used in aqueous environment [20].

The counteranion in carbocationic polymerizations is of major importance to "regulate" the reactivity of the

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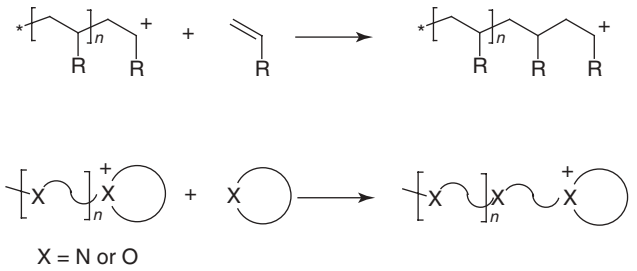
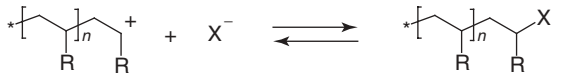


Scheme 8.1 Schematic representation of the propagation step, that is, monomer addition, in carbocationic polymerizations (top) and cationic ring-opening polymerizations (bottom). Counteranions have been omitted for clarity.

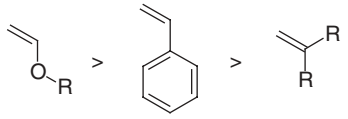
cationic species. Initial studies involved non-nucleophilic counteranions, such as BF_4^-, PF_6^-, SbF_6^-, or ClO_4^-, completely exposing the carbenium ions resulting in uncontrolled cationic polymerizations. In contrast, the use of strong nucleophilic counteranions, such as chloride, can lead to recombination of the carbenium ion and counteranion leading to covalently bound species, which do not propagate and, thus, terminate the polymerization. Importantly, an intermediate situation can be reached with a continuous equilibrium between cationic and covalent species by adjusting the nucleophilicity of the counteranion and the propagating carbenium ions. In this intermediate situation, the concentration of the highly reactive carbenium ions is lowered by reversibly shielding it as covalent species, which are referred to as the "dormant" species (Scheme 8.2) [21]. The main propagation reaction occurs by monomer addition to the carbenium ions which are much more electrophilic than the covalent "dormant" species. Such a polymerization mechanism, involving an equilibrium between active and "dormant" species, should be called "living" polymerization, as proposed by the IUPAC Macromolecular Division [22], on the conditions that the exchange reactions are fast compared to the propagation rate and that transfer and termination reactions are absent. This polymerization mechanism is sometimes also referred to as "quasi-living" polymerization.

It should be noted, however, that Scheme 8.2 depicts a highly simplified mechanism for "living" carbocationic polymerizations and it is in most cases not possible to find a counteranion with intermediate reactivity that spontaneously establishes an equilibrium between cationic and covalent species. Instead, the counteranion is generally a halide that preferably forms a covalent species with the carbenium ion. The addition of a Lewis acid as co-initiator is required to activate the covalently bound halide, resulting in the cationic carbenium ion. Alternatively, a nucleophile or electron donor can be added to the cationic polymerization, to reversibly form a stable cationic addition product with the carbenium ion. Both these deactivation mechanisms are depicted in Scheme 8.3. To achieve a "living" cationic polymerization it is of critical importance to have fast deactivation equilibria. In addition, the position of the equilibria should be carefully optimized for each monomer by variation of, for example, temperature, solvent, initiator, as well as the addition of halide activators or nucleophilic deactivators.

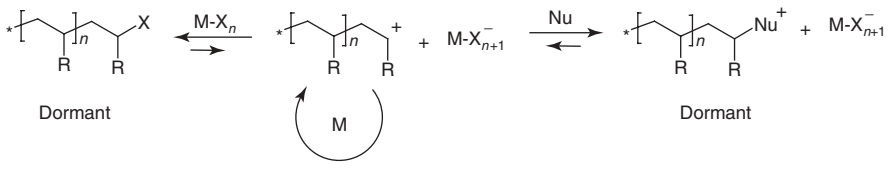
The following sections will provide an overview of the "living" carbocationic polymerizations of the three most important monomer families, namely, isobutene, vinyl ethers, and styrenics. The reactivity of the monomers for carbocationic polymerization is directly related to the stabilization of the formed carbenium ion: vinyl ethers are the most reactive monomers, followed by styrenics and, finally, 1,1-disubstituted alkenes (Scheme 8.4). As a direct consequence of this stabilization, the reactivity of the formed carbocations is opposite to that of the monomer.



Scheme 8.2 Schematic representation of the continuous equilibration between active cationic carbenium ions and covalent "dormant" species.



Scheme 8.4 Reactivity order for the most common classes of monomers for carbocationic polymerization.



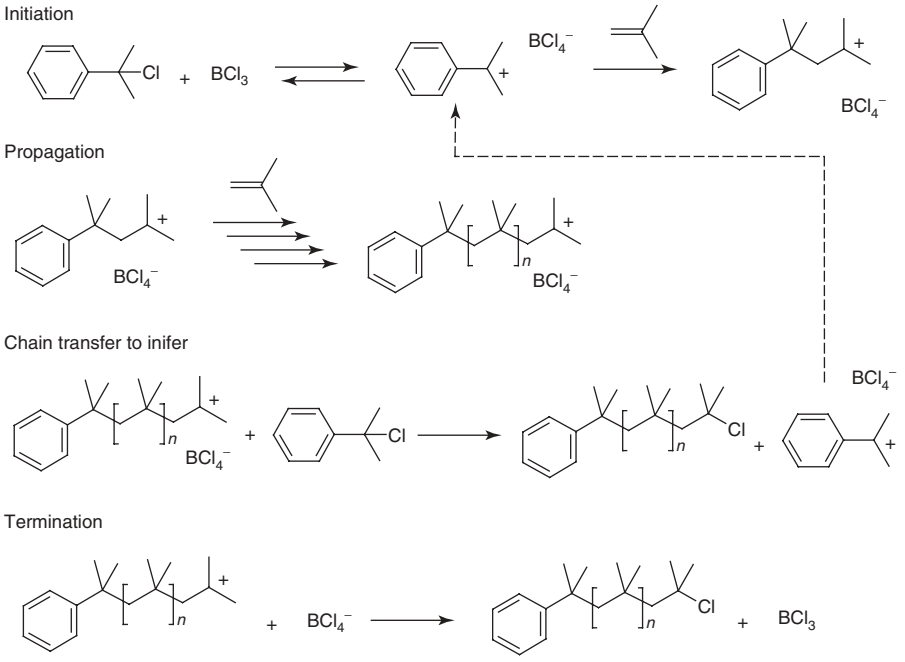
Scheme 8.3 Schematic representation of the "living" carbocationic polymerization based on covalent halide species and an activator (left) or based on the addition of a nucleophilic deactivator (right). X represents a halide; M, a metal; and Nu, a nucleophile.

8.2.1 Isobutene

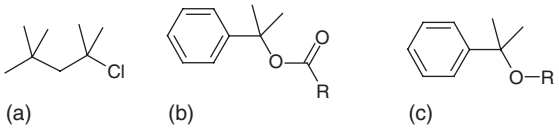
The most studied monomer for cationic polymerization is isobutene, which is related to the inductive stabilization of the formed carbenium ions. Polyisobutene (PIB) has been produced since 1943 on an industrial scale by carbocationic polymerization. PIB is an interesting polymer material with high stability and a low glass transition temperature ($-70\,^{\circ}C$), and is particularly suited for low temperature elastomer applications. The majority of industrial PIB contains a diene comonomer, such as isoprene, making it suitable as "butyl rubber" that can be vulcanized by the conventional methods used in rubber industry based on the presence of a minor fraction of unsaturated bonds. The industrial, uncontrolled cationic polymerization of isobutene is performed at very low temperatures, usually $-90\,^{\circ}C$, in methyl chloride using Lewis acid initiators yielding PIB with a hydrogen atom as initiating fragment and an unsaturated bond at the chain end due to various transfer and isomerization reactions [23].

To fully exploit the beneficial properties of PIB in, for example, polyurethanes, thermoplastic elastomers, and sealants, controlled polymerization methods are required that provide access to controlled end-group functionalities. The controlled polymerization of isobutene was first reported by Kennedy, which was based on the "inifer" technique. This so-called "inifer" that is added to provide control over the polymerization is a compound that acts both as the initiator and the transfer agent. The inifer deliberately induces chain transfer to control the molecular weight of the PIB, whereby each transfer step generates a new chain. A combination of cumyl chloride and boron trichloride was used for the inifer polymerization of isobutene, whereby the cumyl group is introduced as initiator fragment and the end group of the resulting PIB is a chloride (Scheme 8.5) [24, 25]. Initiation occurs by activation of cumyl chloride with BCl_3 followed by addition of the monomer to the formed cation (propagation). Chain transfer to cumyl chloride results in a dead polymer chain as well as a new cationic initiating fragment. In addition, termination by halogen transfer from BCl_4^- to the cationic propagating species can also occur, resulting in regeneration of BCl_3 which can activate the remaining cumyl chloride initiator. As such, the molecular weight of the PIB is not very well controlled, but the end groups of the PIB can be defined. Telechelic PIB became available via this inifer polymerization method when using bifunctional initiators. This initial controlled polymerization method does not allow reactivation of the formed covalent isobutyl halide end groups, which would be a prerequisite for a "living" polymerization.

The first hint toward a "living" cationic polymerization of isobutene was provided by Nuyken and coworkers in 1982 when they reported that the cationic polymerization of isobutene could be initiated by 2-chloro-2,4,4-trimethylpentane (Scheme 8.6), which is a low molecular weight analog of the covalent chloride-terminated PIB, in a polar solvent at $-85\,^{\circ}C$ [26]. This work indicated that the irreversible termination reaction in the inifer polymerization mechanism could become reversible in a more polar medium, which was indeed demonstrated by Kennedy who



Scheme 8.5 Inifer mechanism for the cationic polymerization of isobutene.



Scheme 8.6 Structures of (a) 2-chloro-2,4,4-trimethylpentane, (b) cumyl esters, and (c) cumyl ethers used as initiators for the cationic polymerization of isobutene.

reported the cationic polymerization of isobutene based on a combination of the inifer and "living" polymerization mechanisms [27]. It was proposed that, during the initial stages of the polymerization the inifer mechanism (Scheme 8.5) was dominant, whereas after complete consumption of the cumyl chloride the "living" polymerization mechanism based on reversible termination/activation was active (Scheme 8.3, left).

Already before reporting this combined inifer and "living" polymerization approach, Kennedy and coworkers developed a controlled isobutene polymerization method based on cumyl ester initiators (Scheme 8.6) with boron trichloride as activator and incremental monomer addition [28]. The "livingness" of the polymerization was demonstrated by the linear increase of number-average molar mass and the constant number of polymer chains (N) with the amount of PIB obtained (w_{PIB}, as measure for conversion) as well as the narrowing of the molar mass distribution with conversion (Fig. 8.1) [28].

Moreover, the absence of unsaturations in the resulting polymers clearly indicated the absence of chain transfer reactions. Similar "living" polymerization characteristics were reported for cationic isobutene polymerizations initiated with cumyl methyl ethers (Scheme 8.6) with BCl_3 as activator [29, 30] as well as with cumyl ethers and cumyl esters as initiators together with titanium tetrachloride as activator [31].

Originally it was proposed that these polymerizations occurred by monomer insertion into the polarized alkyl–oxygen bonds. However, this should lead to PIB with ether or ester end groups, which was not observed. Instead, the resulting PIBs contained tertiary chloride end groups, which led to the proposal of a polymerization mechanism involving rapid halogen exchange (Scheme 8.7) [32]. The initial step of the polymerization is the activation of the cumyl initiator resulting from ionization by the activator. Depending on the reactivity of the ionized complex, the monomer, and the activator, two polymerization routes can be followed separately or simultaneously. In route 1, the isobutene monomer is directly added to the ionized complex until the covalent dormant chloride PIB adduct is formed together with $CH_3OCOMtCl_{n-1}$. The latter acts as electron donor and is the key element to obtain a "living"

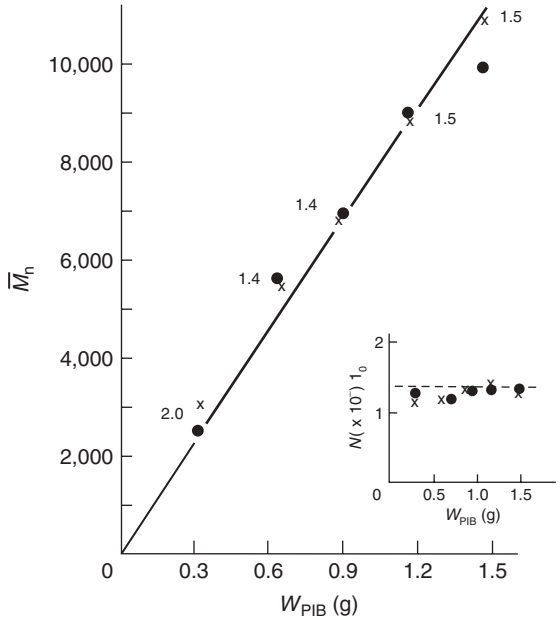
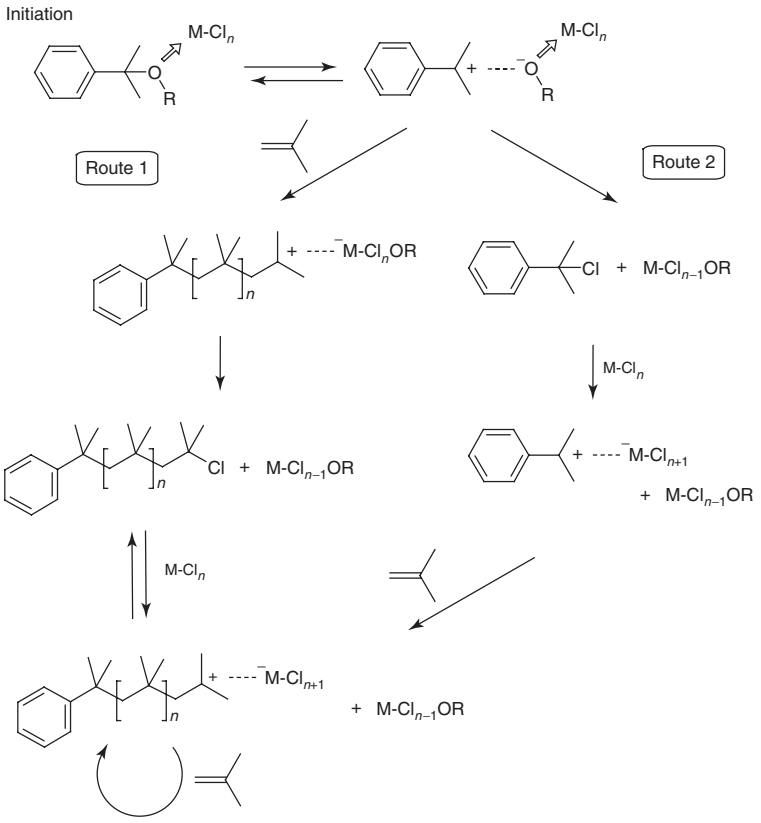


Figure 8.1 The first example of a "living" cationic polymerization of isobutene using cumyl acetate as initiator and BCl_3 as activator in dichloromethane at $-30\,^{\circ}C$. Number-average molar mass, polydispersity index (numbers in the plot), and number of polymer chains (inset) are reported as a function of the mass of PIB obtained. *Source*: Reprinted with permission from Faust R, Kennedy JP. J Polym Sci A Polym Chem 1987; 25:1847 [28]. Copyright 1987 John Wiley and Sons, Inc.

polymerization. The dormant PIB is in continuous equilibrium with the cationic species in the presence of excess activator and the electron donor, resulting in the "living" polymerization. When following route 2, the ionized complex is directly transformed into cumyl chloride and the $CH_3OCOMtCl_{n-1}$ electron donor. Subsequently, the cumyl chloride is transformed into the cationic initiating species by excess activator, which, after monomer addition, eventually results in the same "living" polymerization equilibrium between the dormant covalent species and the cationic PIB.

The "livingness" of the previously described systems is based on a complex initiation procedure involving the *in situ* formation of an electron donor complex. A simplified "living" polymerization procedure for isobutene was reported by Kennedy involving the addition of external electron donors, including amides, esters, amines, or sulfoxides [33]. The isobutene polymerization initiated by cumyl chloride or cumyl methyl ether with $TiCl_4$ as activator and N,N-dimethylacetamide or N,N,N',N'-tetramethyl ethylenediamine (TMEDA) as electron donor resulted in PIBs with high molar mass ($M_n > 10^5$ g/mol) and very narrow polydispersities ($M_w/M_n < 1.1$). The effect of the electron donor on the molar mass distribution is illustrated in Figure 8.2, showing



Scheme 8.7 Mechanism for the "living" polymerization of isobutene with cumyl esters or cumyl ethers as initiator and BCl_3 or $TiCl_4$ as activator. M = B or Ti; R = alkyl or acyl.

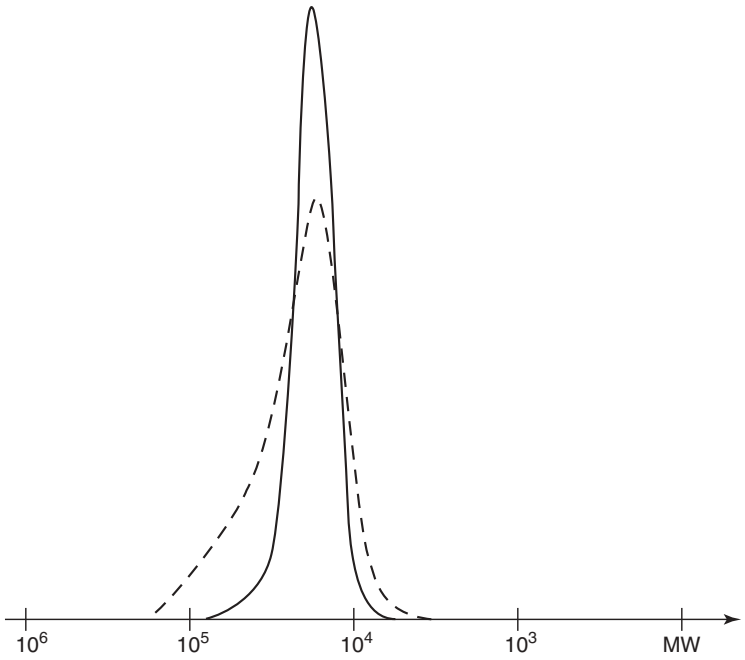


Figure 8.2 Poly(isobutene) molar mass distributions obtained using cumyl chloride as initiation and $TiCl_4$ as activator with (solid line) and without (dashed line) ethyl acetate as electron donor. *Source*: Reprinted with permission from Kaszas G, Puskas JE, Kennedy JP. Polym Bull 1988;20:413 [33]. Copyright 1988 Springer-Verlag.

the PIB molar mass distribution obtained with and without ethyl acetate as electron donor.

All these developed "living" cationic polymerization methods for isobutene provide defined tertiary chloride end groups, opening up possibilities for further end-group functionalization. A representative example was reported by Ivan and Kennedy, who described the quantitative conversion of the chloride into allyl-terminated PIB, which was converted into epoxy and hydroxyl-functional PIBs [34].

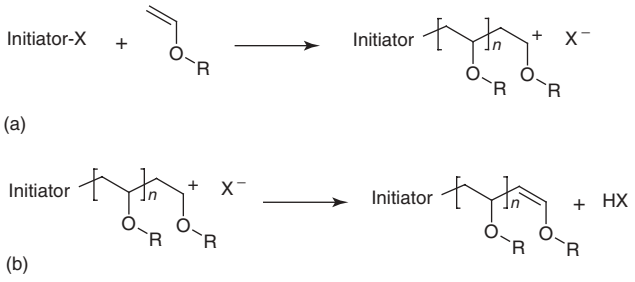
In addition to such postpolymerization modification methods, it is possible to directly include functionalities in PIB during the polymerization process by using pseudohalide initiators, such as azide and thiocyanate, instead of halides [35]. Cheradame reported the use of cumyl azide and bifunctional 1,4-bis(1-azidomethylethyl)benzene initiators with $AlEt_2Cl$ as Lewis acid activator for the polymerization of isobutene directly resulting in the mono-azido and bisazido telechelic PIBs, respectively (Scheme 8.8) [36, 37].

Direct end-capping of living PIB chains with a nucleophile is challenging because of the very high reactivity of the tertiary PIB carbenium ion. Faust *et al*. demonstrated that the living PIB chains react with 1,1-diphenylethylene (DPE) monomer, whereby the resulting DPE carbenium ion is more stable than the PIB carbenium ion. As a result, isobutene is not added to this relatively stable carbenium ion, while homopolymerization also does not occur because of the steric bulk of the phenyl rings [38]. Therefore, the living PIB chain ends can be quantitatively transformed into a single cationic DPE adduct, which has been utilized to couple various nucleophilic end-capping agents, including methanol, ammonia, and silanol ethers. Moreover, the less reactive DPE carbenium ion facilitates the initiation of more reactive monomers, such as styrenics [39, 40] as well as vinylethers [41, 42], resulting in PIB-containing block copolymers. Especially, ABA triblock copolymers with a PIB soft middle block and hard polystyrene outer blocks are interesting thermoplastic elastomers based on the presence of hard polystyrene microdomains that act as physical crosslinks.

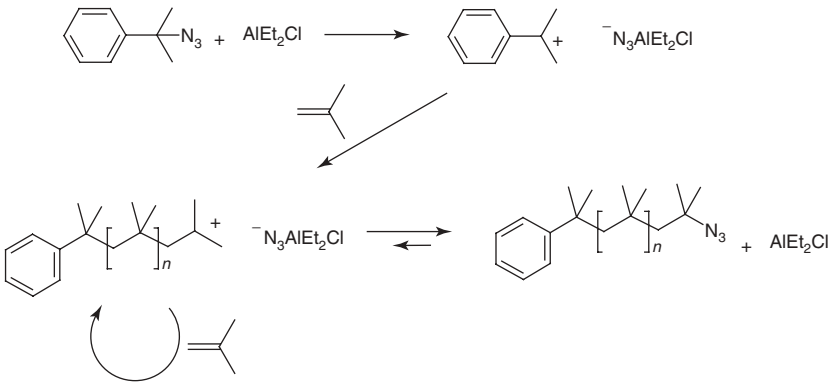
8.2.2 Vinyl Ethers

Vinyl ethers are another important class of monomers for carbocationic polymerizations that cannot be easily polymerized with radical polymerization methods because of insufficient activation of the double bond leading to very slow polymerization and low polymerization degrees. The uncontrolled cationic polymerization of vinyl ethers using strong acidic initiators, such as boron trifluoride and stannyl tetrachloride, is a well-established industrial method giving very high polymerization rates [43]. These very fast uncontrolled cationic polymerizations of vinyl ether result in carbocationic polymerization in combination with a range of chain-transfer- and termination reactions, leading to unsaturated end groups, for example, by hydrogen abstraction (Scheme 8.9).

Even though the cationic polymerization of vinyl ethers already dates back to 1878 [43], the first report on a controlled polymerization only appeared in the late 1970s by Johnson and Young [44]. They discovered that the



Scheme 8.9 (a) General polymerization mechanism for vinyl ethers and the commonly observed (b) hydrogen abstraction side reaction (X represents the leaving group).

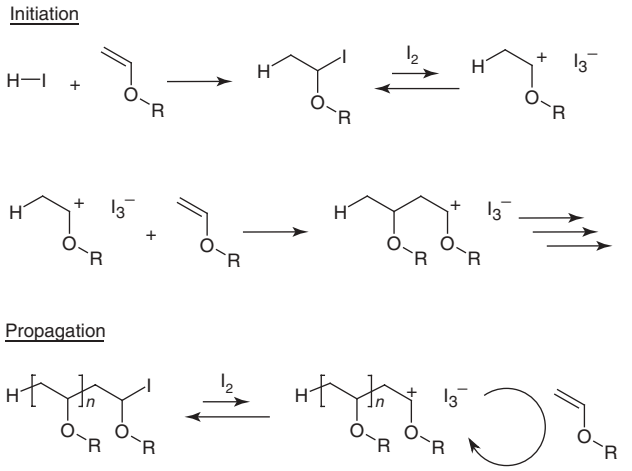


Scheme 8.8 "Living" polymerization of isobutene with a cumyl azide initiator and $AlEt_2Cl$ as Lewis acid activator.

number-average molar mass (M_n) of polymers prepared by the iodine-initiated polymerization of butyl vinyl ether increased on sequential monomer addition after complete monomer consumption. Shortly afterward, Sawamoto and Kennedy reported a "quasi-living" carbocationic polymerization of vinyl ethers by continuous feeding of monomer to an initiator solution, whereby the M_n increased with the amount of added monomer [45]. However, in both these examples the M_n did not correlate to the theoretical value and the polydispersities were rather broad.

In 1984, the first living cationic polymerization of vinyl ethers was reported by Miyamoto et al. [46]. It was found that the polymerization of isobutylvinyl ether (IBVE) in the presence of hydrogen iodide and iodine (equimolar amounts) performed in hexane at $-15\,^{\circ}C$ resulted in a linear increase of M_n with conversion, whereby the amount of hydrogen iodide could be used to control the degree of polymerization. Final proof of the living character of the polymerization was provided by the successful formation of defined block copolymers by sequential monomer addition [47]. Detailed mechanistic and kinetic studies revealed that the polymerization is initiated by the addition of hydrogen iodide to the vinyl ether monomer resulting in the stable covalent α-iodo ether adduct [48]. The added iodine subsequently activates the carbon–iodine bond, leading to the cationic carbenium species. In the early days, a nonionic insertion mechanism was proposed for this hydrogen iodide/iodine-initiated polymerization [10], but nowadays it is generally accepted that there is a continuous equilibration between the "dormant" covalent iodine adduct and the active carbocation as depicted in Scheme 8.10. After this initial development of living polymerization conditions for vinyl ether monomers, various other initiating systems were reported showing similar living polymerization characteristics, whereby the combination of hydrogen iodide and zinc iodide has evolved into one of the most frequently used systems [49]. Nonetheless, a variety of other related cationic polymerization methods have been developed using, for instance, preformed α-chloro or α-bromo ethers as initiators with different zinc halides as activators, whereby the reactivity decreases in the order I > Br ≫ Cl [50].

Besides using preformed α-halide ether initiators, the living polymerization of vinyl ethers can be achieved with carboxylic acid/zinc halide mixtures [51, 52]. The carboxylic acid, such as trifluoro acetic acid, reacts with the vinyl ether resulting in the formation of a covalent adduct. The presence of zinc halide activates the acid bond and mediates the equilibrium between this dormant covalent adduct and the carbenium cation with trifluoroacetate as counterion (Scheme 8.11). When using a stronger Lewis acid, such as $EtAlCl_2$, as activator, the equilibrium is too much shifted to the carbocationic form leading to very fast nonliving polymerization. However, upon addition of



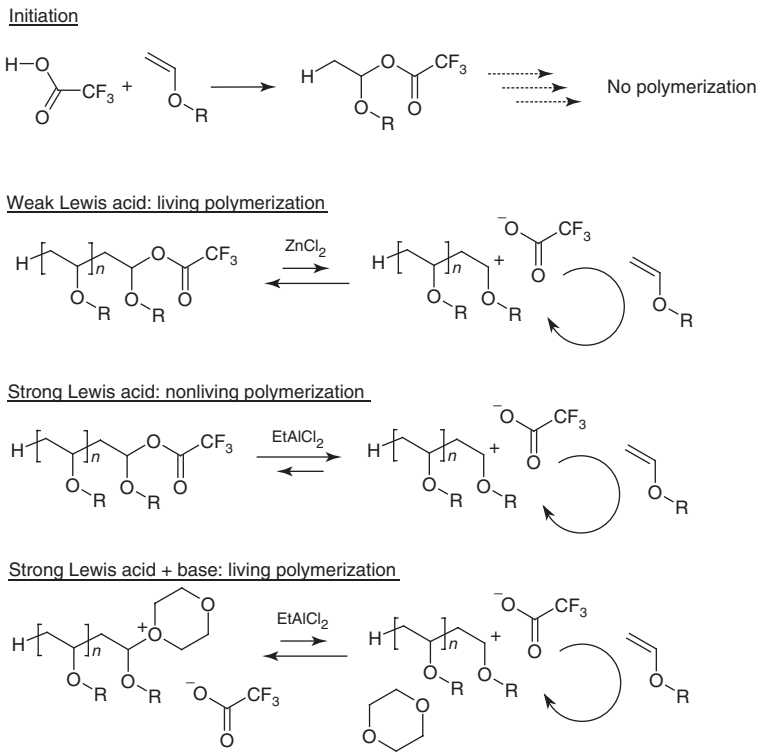
Scheme 8.10 Mechanism for the living cationic polymerization of vinyl ethers with hydrogen iodide and iodine as initiating system.

a base, such as dioxane, the polymerization with $EtAlCl_2$ became living again, which is due to the formation of an oxonium ion that stabilizes the dormant state and, thus, lowers the concentration of carbenium ions (Scheme 8.11).

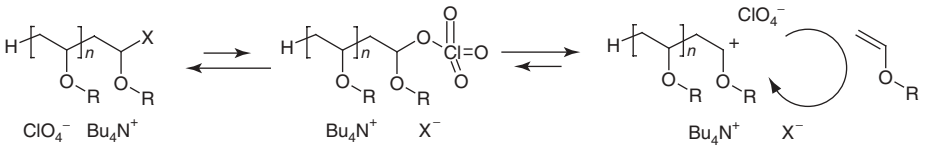
A final method to induce living polymerization of vinyl ethers is based on halide exchange reactions by the addition of a salt. The addition of a tetrabutyl ammonium salt with a nonnucleophilic counteranion, such as perchlorate, to an α-halide ether results in an exchange equilibrium between the halide and the perchlorate. The formed perchlorate adduct is also in equilibrium with the carbocationic species inducing living polymerization of various vinyl ethers as depicted in Scheme 8.12 [53–55]

Similarly, it is possible to transform the nonliving polymerization of vinyl ethers using highly reactive initiators, such as triflic acid, into a living polymerization by the addition of tetrabutyl ammonium iodide [56]. The addition of the halide salt establishes an equilibrium between the active triflate species and the dormant halide species, eventually leading to a similar overall polymerization equilibrium as depicted in Scheme 8.12.

In a recent study by Aoshima, a large variety of metal halides (Fig. 8.3) were screened for the living polymerization of isobutyl vinyl ether initiated by an α-chloro ether [57]. In the absence of added base, only zinc chloride gave rise to a controlled polymerization. By optimization of the base, namely addition of ethyl acetate, dioxane, or tetrahydrofuran, living/controlled polymerization could be achieved for all metal halides, except the metal pentachlorides and metal hexachloride. The polymerizations with $SnCl_4$ and $FeCl_3$ with the appropriate base led to very fast living polymerizations that were finished within seconds and the polymerization of isobutyl vinyl ether with $NbCl_5$



Scheme 8.11 Mechanism of the living polymerization of a vinyl ether with the trifluoroacetic acid using zinc chloride as weak Lewis acid activator or $EtAlCl_2$ as strong Lewis acid as activator, which leads to a living polymerization only in the presence of a base, for example, dioxane.



Scheme 8.12 Activation of dormant halide species by the addition of tetrabutyl ammonium perchlorate salt.

and $TaCl_5$ could be controlled by the addition of tetrabutyl ammonium chloride (Fig. 8.3b).

All previously discussed examples of living cationic polymerization of vinyl ethers were based on homogeneous polymerization media. In 2007, Oashima and coworkers demonstrated the living polymerization of isobutyl vinyl ether in the presence of iron(III) oxide as heterogeneous catalyst and ethyl acetate or dioxane as base [58]. The major advantage of this heterogeneous catalytic system is the easy removal of the metal oxide catalyst. In addition, it was demonstrated that the iron(III) oxide could be reused for at least five times without a decrease in activity.

The development of living cationic polymerization systems for vinyl ethers also enabled the incorporation of functional end groups as well as the control of the polymer architecture. Telechelic polymers have been prepared based on bifunctional initiating systems [59, 50, 60] while multifunctional initiators [61–63] have been utilized for the preparation of star-shaped poly(vinyl ether)s. Larger, but less defined, star-shaped poly(vinyl ether)s have been reported based on the arm-first method; that is, living poly(vinyl ether) chains were transformed into star-shaped polymers by the addition of a bifunctional vinyl ether monomer yielding well-defined star-shaped polymers with 9–44 arms and polydispersity indices below 1.2 [64]. Such star-shaped poly(vinyl ether)s have been used as template for the preparation of gold nanoclusters in combination with a oligoethylene glycol vinyl ether monomer which results in a thermoresponsive poly(vinyl ether) that dissolves in cold water and precipitates upon heating [65]. This hybrid gold nanocluster–polymer system was applied as catalyst for aerobic alcohol oxidation, whereby the polymer phase transition enabled facile isolation of the catalyst upon heating.

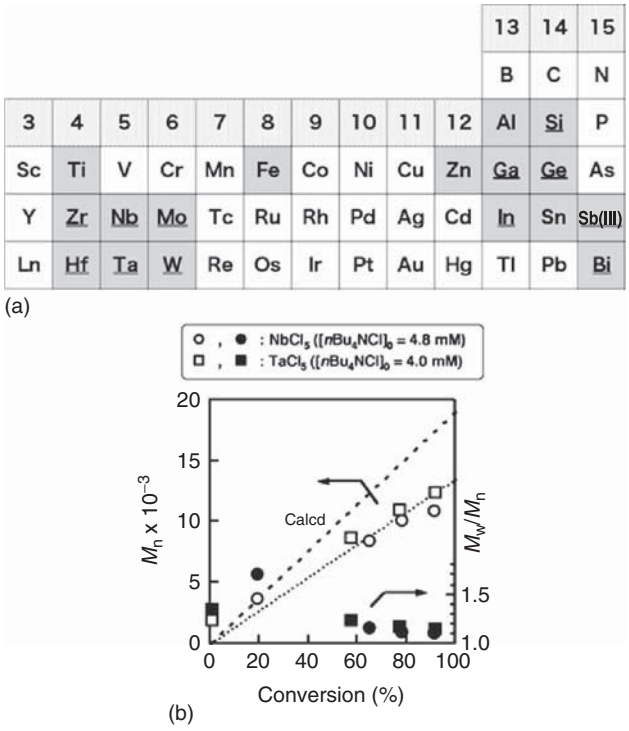
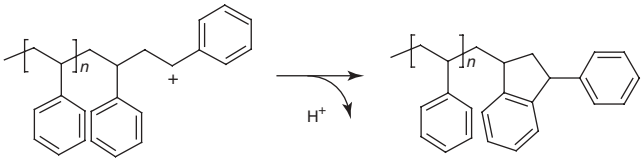


Figure 8.3 (a) All metal elements in gray were screened as metal halides for the living polymerization of vinyl ethers in the presence of added salts and bases. (b) Number-average molar mass (M_n) and polydispersity index (PDI) as function of conversion for the controlled polymerization of isobutyl vinyl ether with $NbCl_5$ and $TaCl_5$ in the presence of tetrabutyl ammonium chloride. *Source*: Reprinted with permission from Kanzawa A, Kanaoka S, Aoshima S. Macromolecules 2009;42:3965–3972 [57]. Copyright 2009 American Chemical Society.

8.2.3 Styrene Monomers

The cationic polymerization of styrene has been known since the 1960s using Lewis acids or strong protic acids as initiators leading to fast, uncontrolled polymerization due to extensive proton transfer reactions to, for example, counteranion, solvent, monomer, or polymer. In addition, chain transfer occurs as a result of an intramolecular Friedel–Craft reaction of the carbocation with the penultimate monomer unit, resulting in an indane chain end and the release of a proton that can reinitiate a new polymer chain as illustrated in Scheme 8.13.



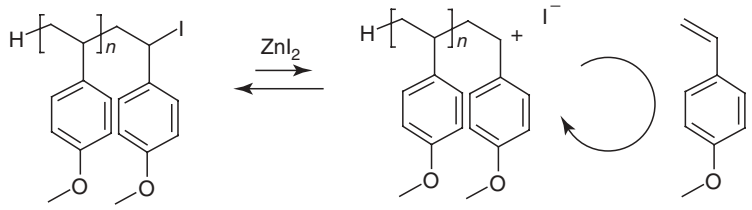
Scheme 8.13 Chain transfer by indane formation during the uncontrolled cationic polymerization of styrene.

The first step toward the development of a living cationic polymerization procedure for styrene was the observation by Pepper that the polymerization of styrene, initiated by anhydrous perchloric acid, stopped at limited conversion when performed below −80 °C [66]. Upon heating, the polymerization was found to continue, which was ascribed to the formation of dormant perchlorate ester end groups at low temperatures, which dissociate into the perchlorate anion and the carbenium ion at elevated temperatures representing the first reported example of an equilibrium between dormant and active chains. The presence of a perchlorate ester end group at each polymer chain was confirmed by the successful formation of block copolymers upon the addition of *N-tert*-butyl aziridine to the dormant polymer chains resulting in living cationic ROP [67]. This latter report was most likely the first ever on the synthesis of block copolymers based on carbocationic polymerization utilizing a sequential monomer addition protocol.

Initially, Gandini and Plesch proposed that the perchloric acid-initiated low temperature polymerization of styrene is based on monomer insertion on the nonionic perchlorate chain ends, which was based on the observation that the polymerization mixture was not conductive [68, 69]. These nonionic polymerizations were referred to as *pseudocationic polymerizations*. However, more detailed investigations by stopped-flow UV–vis spectroscopy revealed the presence of short-lived carbocations indicating that these are the propagating species in the cationic polymerization of styrene [70, 71]. This was also confirmed for the polymerization of styrene with triflic acid for which Matyjaszewski and Sigwalt showed that the covalent triflic ester adduct was unstable even at −78 °C leading to carbocationic propagating species [72].

The carbocationic polymerization of styrene involves secondary benzylic carbenium ions that are stabilized by resonance with the aromatic ring. As such, the presence of electron donating groups, such as alkoxy or alkyl, on the aromatic ring will stabilize the carbenium ion. The first report on controlled/living cationic polymerizations of styrenics involved such stabilized *p*-alkoxystyrene derivatives. Higushimura reported in 1979 that the polymerization of *p*-methoxystyrene contained long-lived propagating species when performed with iodine as initiator [73]. The same group reported the living polymerization of *p*-methoxystyrene with hydrogen iodide/zinc iodide as initiating system at −15 °C in toluene (Scheme 8.14) [74]. The utilization of functional initiators and/or functional end-capping agents was explored for the synthesis of poly (*p*-alkoxystyrene)s with defined end-group functionalities [75].

The living carbocationic polymerization of styrene was reported by Kennedy using 2-chloro-2,4,4-trimethylpentane (TMPCl) with $TiCl_4$ as initiating system in the presence of various electron donors, such as *N,N*-dimethylacetamide



Scheme 8.14 Living carbocationic polymerization of *p*-methoxystyrene using hydrogen iodide and zinc iodide as initiating system in tetrachloromethane.

and hexamethylphosphoramide, and 2,6-di-*tert*-butyl pyridine as proton trap [76]. In the absence of these additives, ill-defined polymers with bimodal molecular weight distributions were obtained. The development of this living carbocationic polymerization method enabled the preparation of linear and three-arm star polystyrene-*b*-poly(isobutene)-*b*-polystyrene triblock copolymers as thermoplastic elastomers [77].

A rather unexpected water- and alcohol-insensitive activator, namely boron trifluoride etherate, was developed by Sawamoto for the living polymerization of *p*-hydroxystyrene in combination with the water adduct of *p*-methoxystyrene as initiator [78]. The polymerizations proceeded even in large excess of water, which is in large contrast with the absolutely dry conditions that are normally required for carbocationic polymerizations. It is proposed that acetonitrile, which is used as polymerization solvent, stabilizes the short-lived carbocationic propagating species. The same polymerization methodology could be applied for the preparation of statistical and block copolymers consisting of *p*-hydroxystyrene and *p*-methoxystyrene [79], as well as for the homopolymerizations of styrene, *p*-chlorostyrene and *p*-methylstyrene in the presence of a proton trap [80].

The controlled polymerization of *p*-methoxystyrene was also demonstrated in aqueous media using the *p*-methoxystyrene HCl adduct as initiator and $Yb(OTf)_3$ as Lewis acid activator [81]. Very recently, the aqueous living cationic suspension polymerization of styrene and methoxystyrene was reported by Ganachaud using the water adduct of *p*-methoxystyrene as initiator and $B(C_6F_5)_3$ as water tolerant Lewis acid activator [82, 83].

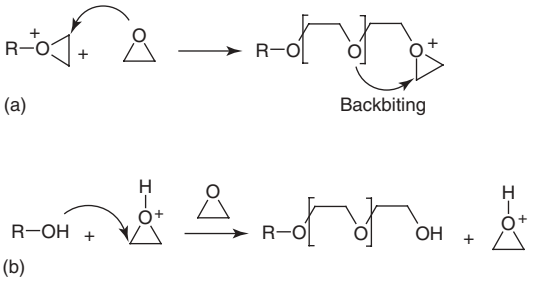
8.3 CATIONIC RING-OPENING POLYMERIZATION

Living cationic ring-opening polymerization (CROP) techniques represent important methods for the polymerization of a wide variety of heterocyclic monomers, such as cyclic ethers, cyclic amines, and cyclic imino ethers [7, 84–87]. The main differences between carbocationic polymerization of vinyl monomers and CROP of heterocyclic monomers arise from the nucleophilic heteroatoms in the latter monomer classes. These heteroatoms undergo cationic ring-opening and are present in the resulting polymer chains where they are prone to undergo chain transfer reactions with the cationic propagating species. So in contrast to the transfer reactions that are induced by the highly reactive carbocations present during cationic vinylic monomer polymerization, the chain transfer reactions that occur during cationic ROP are induced by the similar nucleophilicity of the monomer and the polymer. This section will discuss the living CROP of the most important monomer classes, namely cyclic ethers, cyclic amines, and cyclic imino ethers.

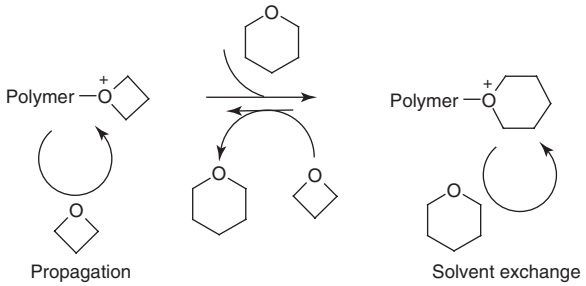
8.3.1 Cyclic Ethers

CROP is only reported for a limited number of cyclic ethers that exhibit enough ring strain to be readily opened. In addition, the rather similar nucleophilicity of the ether moieties in the monomers and the ring-opened polymers together with the reactive cationic oxonium species, often leads to the occurrence of transetherification reactions, complicating the development of living CROP methods. This section will focus on the living CROP of ethylene oxide, oxetane, and tetrahydrofuran.

8.3.1.1 Poly(ethylene oxide) Poly(ethylene oxide), or poly(ethylene glycol), is a popular material for personal, home, and health care applications because of its water solubility in combination with a very low toxicity and the fact that it is not easily recognized by the human immune system [88]. Well-defined poly(ethylene oxide) can be prepared by either living anionic ROP [87–90] or living CROP [87, 91], wherein the anionic polymerization method is mostly used in contemporary research since it yields well-defined polymers in a relatively straightforward manner when carefully purifying all reaction components. In contrast, the CROP of ethylene oxide in standard conditions, that is, an excess of monomer compared to the initiator, results in an uncontrolled polymerization due to the occurrence of backbiting reactions of the cationic propagating species with the polymeric ether moieties resulting in cyclic oligomers. To avoid these backbiting reactions, the CROP of ethylene oxide should be performed



Scheme 8.15 CROP of ethylene oxide via (a) activated chain-end polymerization or (b) activated monomer polymerization.



Scheme 8.16 Living cationic ring-opening polymerization of oxetane using tetrahydropyran as solvent to control polymerization.

via an activated monomer approach instead of a chain-end activation approach [87, 91]. This activated monomer polymerization procedure requires an excess of hydroxyl end groups in relation to the monomer and, thus, involves continuous feeding of the monomer to keep the monomer concentration very low (Scheme 8.15).

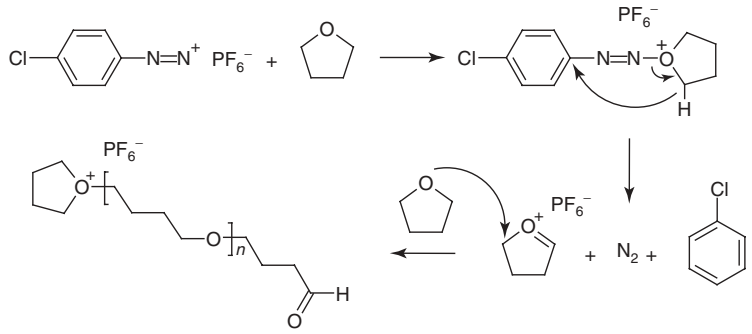
8.3.1.2 Poly(oxetane) The uncontrolled CROP of oxetanes, or 1,3-propylene oxide, is a commonly applied polymerization method for the fixation of coatings by crosslinking. In contrast to these widespread applications of oxetanes in coatings, only a few recent examples of the living CROP of oxetanes have been reported that are based on reversible deactivation of the living chain end by exchange with a nucleophilic nonpolymerizable solvent, such as dioxane or tetrahydropyran [92, 93]. The large excess of the solvent will induce addition of this cyclic ether onto the living polymer chain end, leading to a stable oxonium ion that does not react with the polymeric ether moieties and, thus, prevents chain transfer reactions. Continuous exchange of the oxonium end group leads mostly to solvent exchange reactions. When the oxonium solvent adduct is exchanged with oxetane, the higher reactivity enables the ring-opening of the subsequent oxetane unit leading to polymerization. This proposed polymerization mechanism is depicted in Scheme 8.16. Well-defined poly(oxetane)s could be prepared in dioxane (M_n up to 150,000 g/mol; polydispersity below 1.3), although incorporation of the dioxane into the polymers was observed above 50% monomer conversion because of activation by copolymerization. The lower nucleophilicity of tetrahydropyran could prevent the incorporation of the solvent, but a relatively slow exchange between the oxetane and tetrahydropyran adducts led to polydispersity indices of 1.4–1.5.

8.3.1.3 Poly(tetrahydrofuran) The cyclic ether monomer that has been studied in most detail with regard to living CROP is tetrahydrofuran [94]. As a result of its slightly higher nucleophilicity compared to the polymeric ether bonds, in combination with less sterical hindrance, it is relatively straightforward to develop a living polymerization procedure since the propagating oxonium species do not readily attack the polymer. The first living CROP of tetrahydrofuran was reported by Dreyfuss and Dreyfuss using (*p*-chloro)benzenediazonium hexafluorophosphate as initiator [95, 96]. Detailed mechanistic investigations revealed that the chlorophenyl cation abstracts a hydrogen from tetrahydrofuran and the resulting oxonium ion initiates the polymerization leading to an aldehyde functionality at the beginning of the polymer chains as depicted in Scheme 8.17.

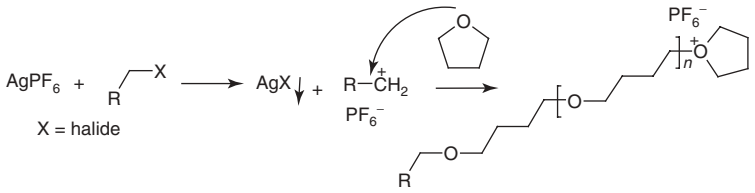
Initiation of the living CROP of tetrahydrofuran with organic halides was first reported by Thompson [97]. Both the alkyl halide and silver hexafluorophosphate were added to initiate the polymerization, whereby halide exchange results in precipitation of the silver halide salt under the formation of the carbocationic hexafluorophosphate adduct that initiates the polymerization (Scheme 8.18). This organohalide initiation method provides direct control over the polymer end groups by variation of the halide initiator, as was demonstrated using, for example, bifunctional organohalide initiators [97, 98], or initiators carrying initiating groups for controlled radical polymerizations providing direct access to poly(tetrahydrofuran) containing block copolymers [99].

In contrast to these initial reports on the living CROP of tetrahydrofuran which were performed without additional solvents, Penczek and coworkers demonstrated that the solvent plays an important role in the cationic ROP of tetrahydrofuran since it controls the proximity and stability of the ion pair at the living chain end [100, 101]. The polymerization rate increases in more polar solvents because of stabilization of the ion pair, whereby it was demonstrated that the methyl-triflate-initiated CROP of tetrahydrofuran involves an equilibrium between the cationic propagating oxonium species and the covalent triflic acid adduct, which can be shifted by the solvent choice as depicted in Scheme 8.19. Nonetheless, as a result of the much higher reactivity of the cationic propagating species, the polymerization rate is almost exclusively determined by the concentration of oxonium ions.

For the preparation of functional poly(tetrahydrofuran), a variety of other triflic esters have been prepared starting



Scheme 8.17 Mechanism for the *p*-chlorobenzenediazonium hexafluorophosphate-initiated living cationic ring-opening polymerization of tetrahydrofuran.

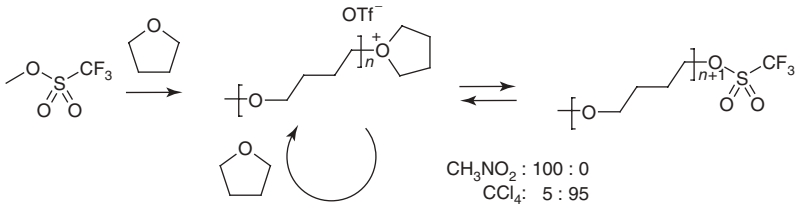


Scheme 8.18 Mechanism for the living cationic ring-opening polymerization of tetrahydrofuran initiated by the addition of both an organic halide and silver(I) hexafluorophosphate.

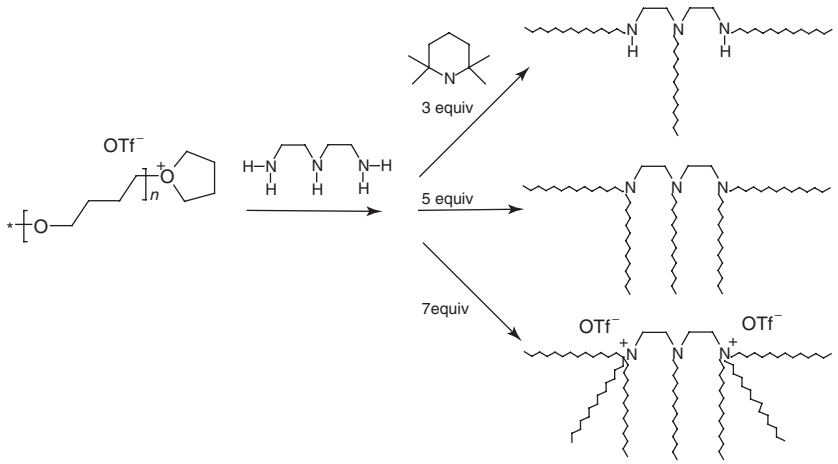
from the corresponding alcohols by reaction with triflic anhydride in the presence of 2,6-di-*tert*-butylpyridine as nonnucleophilic proton trap [102, 103]. Nonactivated aliphatic triflic esters resulted in slow initiation of the CROP, while the activated triflic esters of allyl alcohol and benzyl alcohol precursors afforded fast initiation, linear first-order kinetics, and poly(tetrahydrofuran) with narrow molar mass distributions. This approach has been extended to the preparation of well-defined three-arm star poly(tetrahydrofuran) using the triflic ester of 1,3,5-tris(hydroxymethyl)benzene as initiator [103].

In addition to the introduction of functional groups during initiation, termination of the living chain ends by the addition of a nucleophile has been exploited. Most commonly, water is added as terminating agent, resulting in the direct formation of a hydroxyl chain-end functionality. In addition, a wide range of amine nucleophiles can be utilized as end-capping agents, including primary, secondary, tertiary amines as well as less reactive aromatic amines [104–106]. It is important to note that termination with primary amines leads to the formation of a polymeric secondary amine that can also terminate a living chain end, resulting in a polymeric tertiary amine that can react with a third living polymer chain potentially leading to star-shaped polymers. Nonetheless, this subsequent termination of living polymer chains with primary amines is partially obstructed by the release of triflic acid which protonates the formed secondary amines [106]. The multiple end-capping possibilities of primary amines with living poly(tetrahydrofuran) chains was exploited by Goethals for the preparation of star-shaped polymers [107]. The living CROP of tetrahydrofuran was terminated by adding diethylene triamine as end-capping agent together with 2,2,6,6-tetramethylpiperidine to trap the released triflic acid. The number of polymer arms of the resulting star-shaped poly(tetrahydrofuran) could be controlled to be 3, 5, or 7 by varying the amount of proton trap that was added as depicted in Scheme 8.20. The solution and melt viscosity of the star-shaped poly(tetrahydrofuran) was significantly lower compared to the linear analogs because of reduced chain entanglements. Combination of this end-capping approach with methacrylate- or allyl-functionalized triflic ester initiators yielded star-shaped poly(tetrahydrofuran) bearing reactive double bonds at the periphery, which were successfully utilized for the preparation of crosslinked polymer networks [108, 109].

Upon termination of the living CROP of tetrahydrofuran with (strained) cyclic tertiary amines, such as 1,3,3-trimethylazetidine, *N*-phenyl-pyrrollidine, or *N*-phenyl-piperidine, the reactivity of the cationic chain end is significantly reduced making it insensitive to water while it still can react with stronger nucleophiles, such as deprotonated carboxylic acids [110–112], which has been exploited for the introduction of chain-end functionalities as well as for the formation of star-shaped poly(tetrahydrofuran) and poly(tetrahydrofuran) graft copolymers by reaction with poly(acrylic acid) sodium salt [113]. More recently, Tezuka demonstrated the formation of a wide range of



Scheme 8.19 Schematic representation of the methyl-triflate-initiated CROP of tetrahydrofuran comprising equilibration between cationic and covalent propagating species. The ratio of the cationic versus covalent propagating in different solvents is also indicated.



Scheme 8.20 Synthesis of three, five-, and seven-armed star-shaped poly(tetrahydrofuran) by end-capping with diethylene triamine in the presence of different amounts of 2,2,6,6-tetramethyl piperidine proton trap.

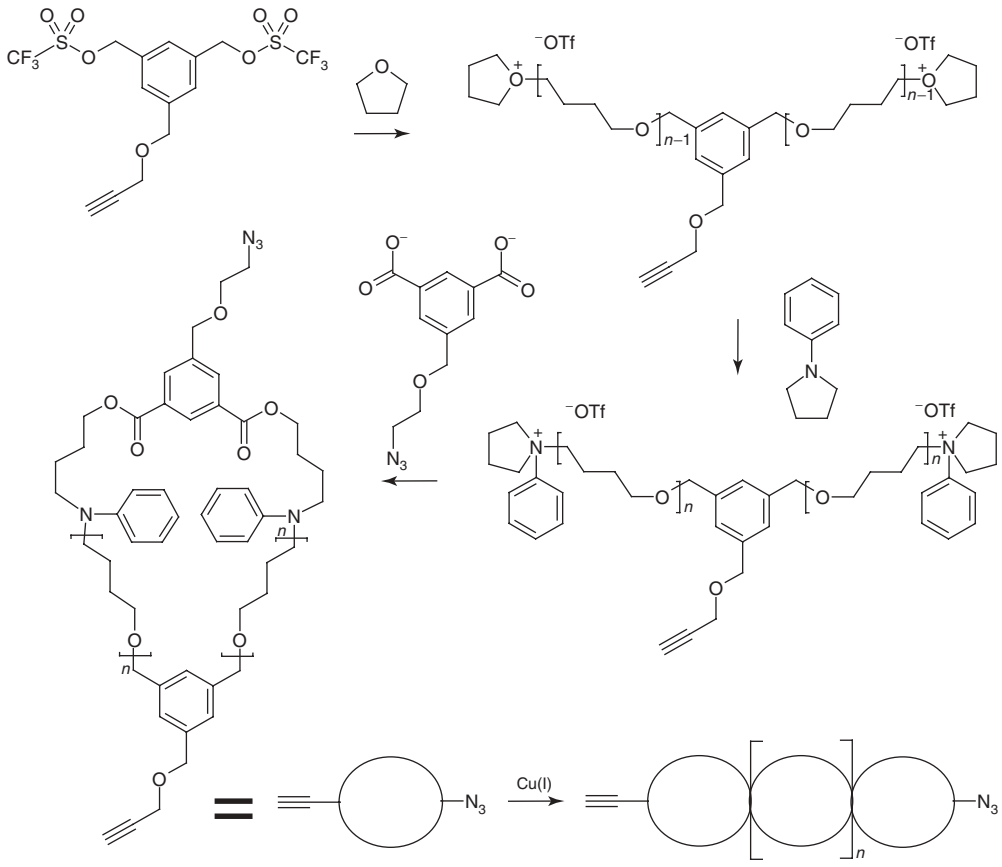
multicyclic polymer structures based on the combination of functional groups carrying bifunctional triflic ester initiators, *N*-phenyl-pyrrolidine end-capping, followed by cyclization with a functional group carrying bifunctional acids and coupling of these cyclic poly(tetrahydrofuran)s utilizing click chemistry methods [114]. As a representative example, the synthesis of poly(cyclic poly(tetrahydrofuran)) is schematically depicted in Scheme 8.21.

Besides first moderating the oxonium end-group activity by reaction with cyclic tertiary amines followed by termination, the living CROP of tetrahydrofuran can be also directly terminated by the addition of carboxylic acid sodium salts [99], dithiocarbamic acid sodium salts [115], or sodium alkoxides [116]. However, these direct functionalization approaches are more sensitive to traces of water or other impurities and do not allow extensive manipulation of the living polymer chains.

In contrast to these beautiful examples of poly(tetrahydrofuran) chain-end modification, the majority of studies that utilize poly(tetrahydrofuran) make use of the commercially available methyl triflate or triflic anhydride [117] initiators in combination with water as terminating agent, resulting in mono- or bis-hydroxy-functionalized poly(tetrahydrofuran). These hydroxyl-functionalized polymers can be further used in a variety of different coupling and modification reactions. Poly(tetrahydrofuran) is a soft material with a glass transition temperature of $-86\,^{\circ}C$ and has been frequently used as soft block in thermoplastic elastomers [118–120]. The relatively straightforward access to well-defined poly(tetrahydrofuran)s by living CROP also stimulated their application in supramolecular polymers by incorporation of end groups capable of hydrogen bonding [121, 122] or metal–ligand complexation [123–125].

8.3.2 Cyclic Amines

Cyclic amines represent another class of monomers that can be polymerized by CROP, whereby various polymer properties can be obtained by variation of the ring-size as well as the substituents on both the carbon and nitrogen atom. Three- and four-membered cyclic amines, aziridines and azetidines, possess high ring strain and can undergo CROP, while larger cyclic amines do not have sufficient ring strain to undergo CROP. Similar to the CROP of cyclic ethers, the nucleophilicity of the amine groups in the monomers and polymers are both rather

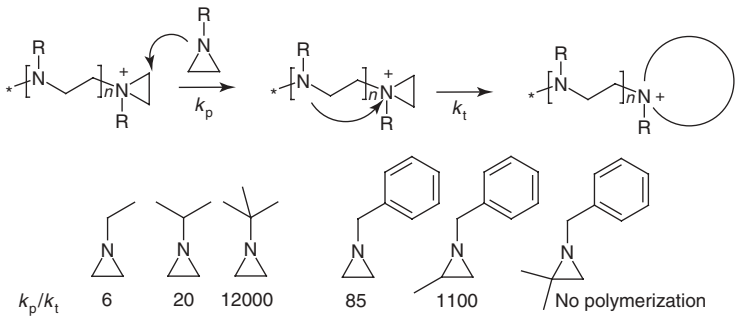


Scheme 8.21 Schematic representation of the synthesis of poly(cyclic poly(tetrahydrofuran)), bottom right, utilizing a bifunctional alkyne-modified initiator for the living CROP followed by end-capping with *N*-phenyl-pyrrolidine to moderate the end-group reactivity. Subsequent end-group modification with a bifunctional acid modified with an azide moiety yields the cyclic poly(tetrahydrofuran) comprising both alkyne and azide functionalities, which is subsequently polymerized by cycloaddition in the presence of copper(I).

high, facilitating chain transfer and/or termination reactions and, thus, complicating the development of living CROP methods. In this section, the CROP of aziridines and azetidines will be discussed.

8.3.2.1 Aziridines Ethylenimine is the simplest aziridine and its CROP is already known since 1941 [126]. Currently, poly(ethyleneimine) is still produced on an industrial scale via CROP. However, the CROP of ethylenimine, that is, unsubstituted aziridine, produces a highly branched poly(ethylenimine) because of the occurrence of proton transfer reactions, chain transfer reactions as well as various termination reactions resulting in a polymer that contains a mixture of primary, secondary, and tertiary amine groups. This extensive occurrence of transfer reactions is caused by the high nucleophilicity of the secondary amine groups in the polymer that strongly compete with the monomer. The CROP of 2-methylaziridine and 2-phenylaziridine have also been reported, but are even more complicated than the polymerization of ethylenimine because of the occurrence of the previously discussed transfer and termination reactions in combination with variations in tacticity as well as the presence of head-to-tail, tail-to-tail and head-to-head diads [127, 128].

In comparison to the previously discussed monomers, the polymerization of N-substituted aziridines is easier to control since the side reactions by proton transfer are eliminated because of the absence of primary and secondary amines. Nonetheless, termination by nucleophilic attack of the cationic propagating chain end into polymeric tertiary amines results in the formation of unreactive quaternary ammonium groups, that is, termination. As a result, the polymerization of N-substituted aziridines usually stops at limited conversion as was first demonstrated for *N*-methylaziridine by Jones [129]. Detailed evaluation of the polymerization kinetics as well as the evolution of molar mass during the polymerization revealed that termination mainly occurs via intramolecular backbiting

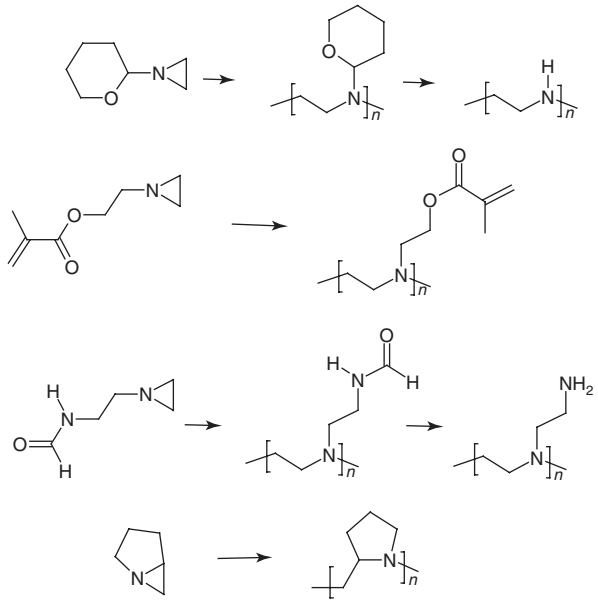


Scheme 8.22 Schematic representation of the CROP of N-substituted aziridines and the most prominent intramolecular termination reaction. At the bottom, the k_p/k_t ratio for several monomers is given as a measure for the livingness of the polymerization (performed in CH_2Cl_2 using Et_3OBF_4 as initiator at 20 °C).

yielding a stabile nonstrained cyclic polymer end group. The ratio of the polymerization rate constant (k_p) over the termination rate constant (k_t) can be regarded as a measure for the livingness of the polymerization of N-substituted aziridines (Scheme 8.22) [85]. By changing the N-substituent from ethyl to isopropyl and tertbutyl, the k_p/k_t ratio significantly increases, indicating that termination is more strongly suppressed by the steric bulkiness of the monomer than the polymerization, which can be understood by the fact that the polymeric amines are surrounded by multiple, flexible substituents while the end group and monomer both carry one substituent that is constrained by the cyclic aziridine structure [130]. Similarly, the introduction of a methylene substituent on the carbon atom of *N*-benzyl-aziridine significantly increases the k_p/k_t ratio while introducing two substituents on the same carbon atom completely suppresses the polymerization [85, 130, 131].

Even though termination cannot be completely eliminated for the polymerization of tertbutylaziridine, the termination rate is much slower than the propagation rate resulting in a defined end group at near-quantitative conversions, which together with the good control over the molar mass distribution are the characteristics of a controlled polymerization [132]. Since termination reactions are suppressed during the polymerization of *N-tert*-butylaziridine, the living cationic polymer chains can be terminated by the addition of a nucleophile to introduce a wide range of end-group functionalities [133, 134] as well as for the preparation of block and graft copolymer structures when using polymeric nucleophiles [133, 135].

Besides the most frequently studied N-substituted aziridine, *N-tert*-butylaziridine, a number of functional poly (N-substituted aziridine)s has been reported based on *N*-tetrahydropyranylaziridine, 2-(1-aziridinyl)ethyl methacrylate, *N*-(ethylformamide)aziridine, and the bicyclic 1-aza-[1,3,0]-bicyclohexane as depicted in Scheme 8.23.



Scheme 8.23 Structures of less common N-substituted aziridines as precursors for functional polymers. From top to bottom: *N*-tetrahydropyranylaziridine, 2-(1-aziridinyl)ethyl methacrylate, *N*-(ethylformamide)aziridine, and the bicyclic 1-aza-[1,3,0]-bicyclohexane.

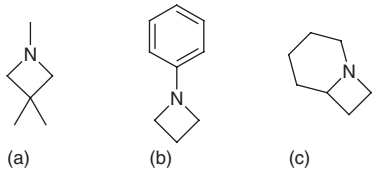
The CROP of *N*-tetrahydropyranylaziridine results in the tetrahydropyran-protected linear poly(ethylenimine) and, thus, provides straightforward access to linear poly(ethylenimine) by acidic removal of the tetrahydropyran groups (Scheme 8.23) [136]. As discussed previously, linear poly(ethylenimine) cannot be prepared by simply polymerizing ethylenimine because of transfer reactions resulting in branched polymers. Poly(ethylenimine)s with polymerizable methacrylate side groups have been reported based on the CROP of 2-(1-aziridinyl)ethyl methacrylate (Scheme 8.23) [137]. Subsequent radical polymerization of the methacrylate moieties results in densely crosslinked

polymer networks. Poly(*N*-(2-aminoethyl)aziridine) has been prepared by CROP of the corresponding formamide derivative since the presence of a nucleophilic amino group during the CROP would result in termination reactions [138]. Subsequent hydrolysis of the formamide groups resulted in the amino-functionalized poly(ethylenimine) as depicted in Scheme 8.23. A final example of a functional poly(aziridine) is based on the polymerization of the bicyclic 1-aza-[1,3,0]-bicyclohexane monomer resulting in a chiral polymer with a cyclic tertiary amine in the backbone (Scheme 8.23) [139, 140].

8.3.2.2 Azetidines The CROP of azetidines without the N-substituent is very similar to the CROP of ethylenimine as discussed in the previous section. As such, the CROP of azetidine is accompanied by a large number of hydrogen transfer, chain transfer, and termination reactions resulting in the formation of branched poly(propylenimine) comprising a mixture of primary, secondary, and tertiary amines [141].

The introduction of an N-substituent to the azetidine ring avoids the proton transfer reactions resulting in a polymerization that can be simply described by initiation, polymerization, and termination. Especially, the termination might give rise to branching and uncontrolled polymerizations when the living cationic chain end reacts with polymeric amines yielding a quaternary ammonium branching point. The CROP of three N-substituted azetidine monomers has been studied in detail, namely 1,3,3-trimethylazetidine, *N*-phenylazetidine, and 1-azabicyclo[4.2.0]octane (conidine) as shown in Scheme 8.24.

Kinetic investigations of the CROP of 1,3,3-trimethylazetidine with triethyloxonium tetrafluoroborate as initiator revealed that the polymerization proceeded in a living manner [142, 143]. In contrast to the living polymerization of 1,3,3-trimethylazetidine, significant termination reactions by attack of the living chain end onto polymeric amines were observed for the CROP of 1-methylazetidine, leading to branches or cyclic end groups (see Scheme 8.22) resulting from intermolecular and intramolecular termination, respectively [144]. This striking difference between the CROP of 1-methylazetidine and 1,3,3-trimethylazetidine clearly demonstrates the importance of the two methyl groups attached to the polymer backbone, which apparently induce sufficient steric hindrance to obstruct the reaction between the azetidinium propagating species with the polymeric amines.



Scheme 8.24 Structure of the most commonly studied azetidine monomers: (a) 1,3,3-trimethylazetidine, (b) *N*-phenylazetidine, and (c) 1-azabicyclo[4.2.0]octane.

Similarly, the polymerization of *N*-phenylazetidine with methyl triflate as initiator shows a relatively controlled polymerization, although branching due to predominantly intermolecular termination does occur as demonstrated by the relatively low k_p/k_t ratio of 30 at 30 °C [145].

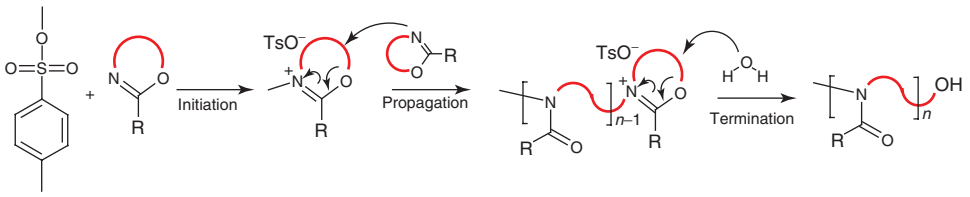
The bicyclic azetidine monomer 1-azabicyclo[4.2.0] octane can be polymerized in a living manner using the proton acid or alkylhalide adducts of the monomer as initiator, as demonstrated by the constant concentration of active species as well as the linear increase of the degree of polymerization with conversion [146, 147]. In addition, 1-azabicyclo[4.2.0]octane is a chiral monomer, and, by polymerization of an enantiomerically pure monomer, main-chain chiral polymers were obtained [148].

8.3.3 Cyclic Imino Ethers

In contrast to the previously discussed cationic ROPs, the nucleophilicity of the cyclic imino ether monomers is much higher compared to the resulting poly(cyclic imino ether)s. This decrease in nucleophilicity is due to the isomerization of the imino ether moiety into an amide during the CROP as depicted in Scheme 8.25. As a result, the CROP of a wide range of cyclic imino ethers can be performed in a living manner since chain transfer to polymer side reactions are less likely to happen. Moreover, the R-group attached to the 2-position of the monomer determines the polyamide side chains and strongly influences the polymer properties.

The CROP of 2-oxazoline and 2-oxazine cyclic imino ethers was first reported in 1965 by Litt in a patent application [149]. Shortly thereafter, the CROP of various 2-oxazolines and a range of cationic initiating systems was demonstrated by four independent research groups [150–153] and the first scientific report on the CROP of 2-oxazines polymerization also appeared in 1967 [154]. The CROP of 2-oxazolines bearing chiral 4- and 5-substituents on the ring was first reported in 1974 [155, 156]. The following will focus on the living CROP of 2-oxazolines since this is the most extensively studied class of cyclic imino ethers. For an overview of the polymerization of larger cyclic imino ethers as well as 4- and 5-substituted 2-oxazoline monomers, the reader is referred to a recent review article [157].

Poly(2-oxazoline)s are attractive materials because a wide range of different monomers can be polymerized by living CROP, whereby the polymer properties can be significantly altered by changing the substituent on the 2-position of the 2-oxazoline ring. The importance of this side chain on the resulting polymer properties are evident

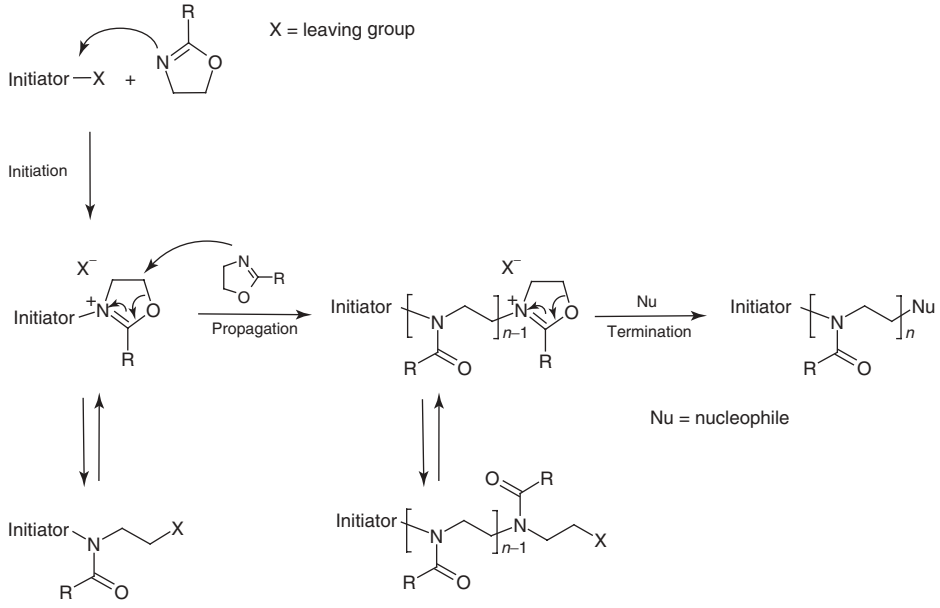


Scheme 8.25 Schematic representation of the methyl-tosylate-initiated CROP of cyclic imino ethers indicating the isomerization from an imino ether to an amide moiety during polymerization as well as the R functionality of the monomer that determines the polymer side-chain functionality.

from the water solubility of poly(2-methyl-2-oxazoline), the lower critical solution temperature (LCST) behavior of poly(2-ethyl-2-oxazoline) [158, 159], and the different analogues of poly(2-propyl-2-oxazoline) [160–162], while larger aliphatic or aromatic side chains result in hydrophobic polymers. In addition, poly(2-methyl-2-oxazoline) and poly(2-ethyl-2-oxazoline) are biocompatible and are not recognized by the immune system of living species similar to poly(ethylene oxide) [88, 163, 164]. In addition, 2-oxazolines with saturated and/or unsaturated fatty acid side chains have been prepared and polymerized by living CROP [165].

Under appropriate conditions, mostly using alkyl halides, triflates, or tosylates as initiator, the CROP of 2-oxazolines proceeds via a "living" mechanism [84, 86]. In such an ideal "living" polymerization, all polymer chains are initiated at the same time by nucleophilic attack of the imino ether onto an electrophilic initiator. Similar to the previously discussed cationic polymerizations, the CROP of 2-oxazolines can proceed via cationic or covalent propagating species or an equilibrium between these species, as depicted in Scheme 8.26. The living CROP proceeds via nucleophilic attack of the monomer onto the C5 of the oxazolinium species, resulting in ring-opening of the oxazolinium while the newly attached monomer will be transferred into the new oxazolinium chain end. This monomer addition continues until all monomer is consumed or until a nucleophilic terminating agent is introduced into the polymerization mixture.

The type of propagating species is mainly determined by the nucleophilicity of the monomer and basicity of the leaving group of the initiator, whereby covalent propagating species are present when the basicity of the counterion is higher than the nucleophilicity of the monomer and cationic propagating species are present if the basicity of the counterion is lower than the monomer nucleophilicity. The most nucleophilic monomer, 2-methyl-2-oxazoline, polymerizes via cationic propagating species with all counterions except



Scheme 8.26 Schematic representation of the living CROP of 2-oxazolines including the equilibrium between covalent and cationic propagating species.

chloride [86, 166, 167]. In contrast, the least nucleophilic 2-perfluoralkyl-2-oxazoline monomers polymerize only via cationic propagating species with the least basic triflate counterions [86, 168]. The living CROP of the majority of monomers with intermediate nucleophilicity, such as 2-ethyl-2-oxazoline [166, 167, 169, 170], 2-unsubstituted-2-oxazoline [86, 171] and 2-phenyl-2-oxazoline [86, 166, 172], are based on an equilibrium between covalent and cationic propagating species which is determined by the basicity of the counterion and is strongly affected by the solvent polarity. The solvent stabilization effect on the ion pair proximity has been illustrated by the use of ionic liquids as extremely polar solvents, leading to a fourfold acceleration of the methyltosylate-initiated polymerization of 2-ethyl-2-oxazoline compared to using acetonitrile as solvent, despite the fact that both polymerizations proceed via cationic propagating species [173].

The large variation in polymerization rates among the various 2-oxazoline monomers has been exploited for the preparation of quasi-diblock copolymers, namely, gradient copolymers with a narrow and steep monomer gradient, by statistical copolymerization of selected monomer combinations exhibiting large differences in reactivity. Such a one-pot quasi-diblock copolymer synthesis was first demonstrated for the statistical copolymerization of 2-phenyl-2-oxazoline and a much less reactive 2-perfluoroalkyl-2-oxazoline [174]. This "living" CROP (in nitromethane at 120 °C initiated by methyl *p*-nitrobenzenesulfonate) revealed complete consumption of the 2-phenyl-2-oxazoline after 2 min with only minor incorporation of the fluorinated monomer. Continuation of the polymerization for another 40 h led to full conversion of the fluorinated monomer. The final polymer had a narrow molar mass distribution, which, together with the monomer conversion profile, demonstrated the one-pot formation of a quasi-diblock copolymer. More recently, the one-pot statistical copolymerizations of 2-phenyl-2-oxazoline with the more nucleophilic aliphatically substituted 2-methyl-2-oxazoline, 2-ethyl-2-oxazoline, or 2-nonyl-2-oxazoline were reported to result in quasi-diblock copolymers, whereby, first, the aliphatic monomer is incorporated, followed by slow incorporation of the 2-phenyl-2-oxazoline [175, 176]. The monomer distribution along the polymer chain, which is calculated on the basis of the individual monomer conversions during the copolymerization, for statistical quasi-diblock copolymers consisting of 2-nonyl-2-oxazoline and 2-phenyl-2-oxazoline is shown in Figure 8.4.

The livingness of the CROP of 2-oxazolines allows the incorporation of chain-end functionalities using functional electrophilic initiators as well as functional nucleophilic terminating agents. Examples of reported functional initiators include allyl- [177], propargyl [178], and phtalimido [179] (as precursor for amines) functionalized tosylates. In addition, the use of multifunctional initiators has been utilized for the preparation of star-shaped poly(2-oxazoline)s with various core structures [180–183].

Besides functional initiators, a wide range of functional terminating agents have been utilized for the preparation of functional poly(2-oxazoline)s, including deprotonated carboxylic acids [184, 185], amines [185, 186], and deprotonated thiols (Scheme 8.27) [187]. The termination with primary amines can be complicated by the formation of secondary amines that can react with a second polymer chain after proton transfer to the unreacted primary amines.

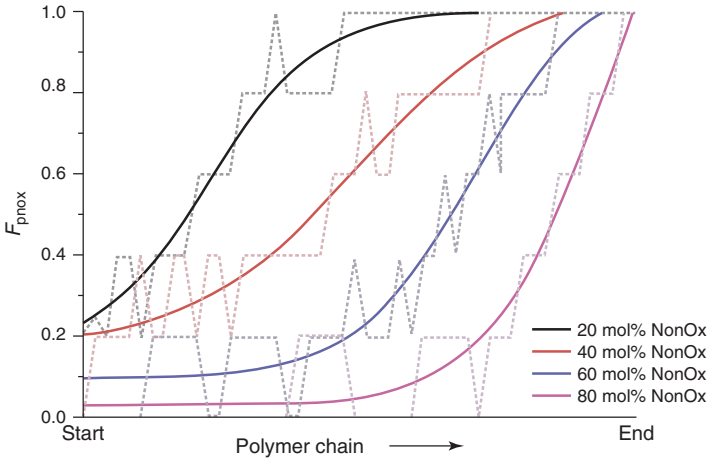
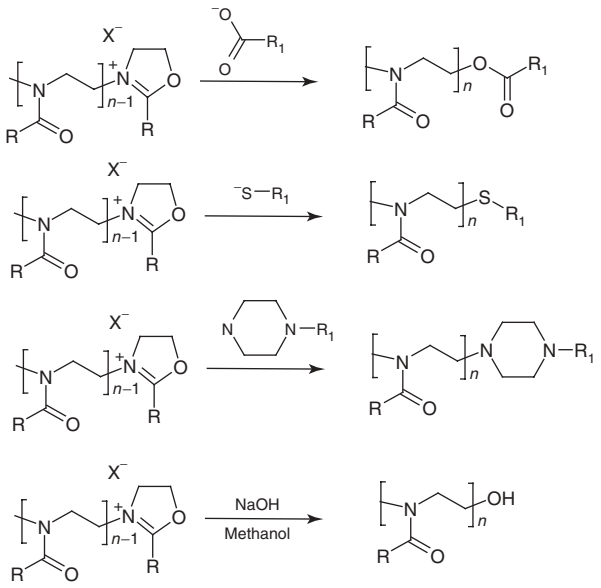


Figure 8.4 Monomer distribution along the polymer chain for statistical copolymers of 2-nonyl-2-oxazoline (NonOx) and 2-phenyl-2-oxazoline (PhOx). *Source*: Reprinted with permission Lambermont-Thijs HML, Jochems MJ, Hoogenboom R, Schubert US. J Polym Sci A Polym Chem 2009;47:6433 [176]. Copyright 2009 John Wiley and Sons, Inc. (*See insert for the color representation of the figure*.)



Scheme 8.27 Schematic representation of the functionalization of poly(2-oxazoline)s using nucleophilic terminating agents.

Therefore, the use of secondary amines might be preferable since the higher basicity of the formed tertiary amine suppresses proton transfer to the secondary amines. Piperidine has been identified as an ideal terminating agent for the living poly(2-oxazoline) chains, resulting in fast (less than 10 min) and quantitative termination [188]. Besides termination of the living chains with piperidine, a variety of monofunctionalized piperazines have been employed to introduce functional groups to the chain ends of poly(2-oxazoline)s (Scheme 8.27) [189–191]. The use of tertiary amines as terminating agents provides cationically charged end groups [185, 188], which have been demonstrated to result in antimicrobial poly(2-oxazoline)s [192]. Moreover, the introduction of a hydroxyl end group can be performed by quenching the polymerization with methanolic sodium hydroxide (Scheme 8.27) [86].

Finally, the living CROP of 2-oxazolines provides direct access to well-defined diblock copolymers by sequential monomer addition, that is, addition of a second monomer after full conversion of the first monomer [193, 194]. Further monomer addition after the second and third monomer has been demonstrated to result in defined triblock [195, 196] and tetrablock copoly(2-oxazoline)s [197].

8.4 SUMMARY AND PROSPECTS

Despite the fast development and versatility of controlled radical polymerization methods for a variety of vinyl monomers, there is still a need for cationic polymerization methods for certain important monomer classes, in particular isobutene and vinyl ethers, which cannot be polymerized in a controlled manner using radical procedures. Poly(isobutene) is an attractive soft polymeric material for applications in, for example, thermoplastic elastomers and recently also as a biomaterial [198]. Poly(vinyl ether)s represent a versatile class of polymers with tunable properties based on the variation of the ether side chain and high hydrolytic stability, especially when compared to poly(meth)acrylates. The living CROP of mainly tetrahydrofuran and 2-oxazolines provides direct access to well-defined polymers, wherein both the initiation and termination steps provide the possibility to introduce a wide variety of functional groups. Poly(tetrahydrofuran) is a popular soft polymeric material for use as soft block in, for example, thermoplastic elastomers. The properties of poly(2-oxazoline)s can be easily tailored for certain applications by variation of the polymer side chain. This versatility of poly(2-oxazoline)s in combination with the biocompatibility, stealth behavior, and thermoresponsive behavior has led to a renewed interest in poly(2-oxazoline)s in recent years.

Therefore, it is expected that both living/controlled carbocationic polymerization and living CROP of these monomers will remain popular methods for the construction of defined macromolecular architectures for a variety of applications.

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