People's Democratic Republic of Algeria
Ministry of Higher Education and Scientific Research
Ibn Khaldoun University - Tiaret

Faculty of Materials Sciences
Chemistry Department

Course Handout

Control of Polymerization Reactions

Duration:[30 h Lectures + 15 h Tutorials]

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Preface

The course Control of Polymerization Reactions has been designed to provide an in-depth understanding of the fundamental principles governing the synthesis and behavior of polymers. It explores the various mechanisms of polymerization and the key parameters that influence the kinetics, molecular weight, and architecture of macromolecules.

In this course, particular emphasis is placed on the strategies used to control polymerization processes. Students will study the main types of polymerizations including free radical, ionic, coordination, and controlled/living polymerizations and examine how reaction conditions, initiators, catalysts, temperature, and solvent choice affect the structure and properties of the resulting polymers. The course also discusses recent advances in the field, such as reversible-deactivation radical polymerization (RDRP) techniques, which allow the synthesis of polymers with precise architectures and narrow molecular weight distributions.

In addition to theoretical concepts, the course integrates practical and experimental aspects, enabling students to connect reaction mechanisms with laboratory practice. Through examples and case studies, they will learn how to design, analyze, and optimize polymerization reactions to achieve targeted functional materials.

This course is intended for Master’s students in Organic Chemistry and macromolecular chemistry. It aims to strengthen their understanding of polymer chemistry and prepare them for research or industrial work in polymer synthesis, materials science, and macromolecular engineering. The knowledge gained will serve as a foundation for advanced studies and innovative applications in modern polymer technology.

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Introduction

The control of polymerization reactions represents one of the most significant challenges in modern polymer chemistry, as it directly determines the molecular characteristics and final properties of polymeric materials. Among the different polymerization mechanisms, radicaland ionic polymerizations are two major approaches for the synthesis of high-performance polymers. Both processes involve the successive addition of monomer units to a growing active center, yet they differ fundamentally in the nature of their active species and in their sensitivity to reaction conditions.

Radical polymerization is widely recognized for its versatility and robustness. It can be applied to a broad range of monomers and is relatively insensitive to impurities, making it suitable for large-scale industrial production. However, classical radical polymerization is inherently difficult to control due to the transient and highly reactive nature of free radicals. Random initiation and termination events lead to polymers with broad molecular weight distributionsand poorly defined architectures. To overcome these limitations, controlled or living radical polymerization (CRP) techniquessuch as Atom Transfer Radical Polymerization (ATRP), Reversible Addition-Fragmentation Chain Transfer (RAFT), and Nitroxide-Mediated Polymerization (NMP) have been developed. These methods achieve precise control over chain growth by maintaining a dynamic equilibrium between active and dormant species, minimizing irreversible termination and enabling the synthesis of polymers with predictable molecular weights and narrow dispersities.

In contrast,ionic polymerization, which includes anionic and cationic mechanisms, allows for an even higher degree of control when conducted under strictly anhydrous and impurity-free conditions. In these systems, the active centers (carbanions or carbocations) remain active throughout the polymerization, resulting in living polymers with no inherent termination reactions. This enables the synthesis of polymers with extremely narrow molecular weight distributions and complex architectures, such as block and graft copolymers. However, ionic polymerizations are much more sensitive to moisture, temperature, and impurities than radical systems, which limits their industrial applicability.

The control of polymerization reactions, whether radical or ionic, is crucial for designing materials with tailored properties such as mechanical strength, thermal stability, biodegradability, and responsiveness to external stimuli. Controlled processes enable the preparation of polymers for advanced applications in biomedical engineering, nanotechnology, coatings, and smart materials. By mastering initiation efficiency, propagation kinetics, and termination behavior, polymer chemists can now design macromolecules with structures and functions approaching those of natural biopolymers.

In summary, while radical polymerization remains the most industrially accessible technique due to its robustness and simplicity, ionic polymerization provides unmatched precision in molecular design. The ongoing development of controlled and living polymerization methods continues to bridge the gap between these two approaches, offering powerful tools for the creation of next-generation functional materials.

Radical polymerization

Introduction

Radical polymerization represents one of the most important methods for the synthesis of polymers with a wide range of molecular structures and industrial applications. It is characterized by its simplicity, versatility, and ability to proceed under relatively mild conditions while being tolerant to impurities and functional groups. This process has been widely employed in the manufacture of everyday materials such as plastics, coatings, adhesives, and resins. Typical examples include polymers derived from vinyl monomers, such as poly(methyl methacrylate), polystyrene, and polyacrylamide, which together constitute a large proportion of the world's synthetic polymer production.

One of the major advantages of radical polymerization lies in its broad applicability to various monomers and its adaptability to different reaction media, including bulk, solution, suspension, and emulsion systems. The kinetics of radical polymerization depend strongly on factors such as the initiator type, monomer concentration, temperature, and the viscosity of the reaction medium. The overall rate of polymerization and the molecular weight distribution of the resulting polymers can be controlled by optimizing these parameters. However, conventional radical polymerization often leads to polymers with broad molecular weight distributions due to the random nature of radical termination processes.

Description of Radical Polymerization

Radical polymerization is a chain-growth polymerization process in which the active centers of growing polymer chains are free radicals. These radicals are highly reactive species that contain an unpaired electron, capable of initiating and propagating the addition of monomer units containing double bonds, typically vinyl or acrylate monomers.

The overall mechanism of radical polymerization involves three main stages: initiation, propagation, and termination.

During initiation, radicals are generated from the decomposition of an initiator. such as benzoyl peroxide or azobisisobutyronitrile under the effect of heat, light, or redox reactions. These radicals attack the double bond of monomer molecules, forming new radical centers on the growing chain. In the propagation step, the radical adds successively to additional monomer units, causing the polymer chain to grow rapidly. Finally, in the termination step, two active chains combine or disproportionate, stopping the growth process.

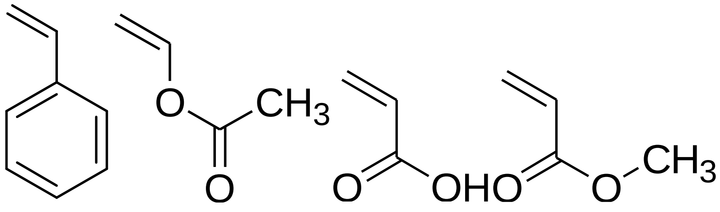
Monomers:

Radical polymerization involves monomers that contain carbon–carbon double bonds (vinyl groups) capable of reacting with free radicals.

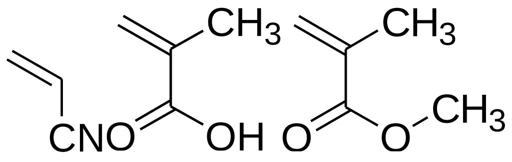
Common monomers include:

- Vinyl monomers: ethylene, vinyl chloride (VC), vinyl acetate (VAc)
- Acrylic and methacrylic monomers: methyl acrylate (MA), methyl methacrylate (MMA), acrylonitrile (AN), acrylamide
- Styrenic monomers: styrene, α-methylstyrene, substituted styrenes
- Dienes: butadiene, isoprene (can lead to cross-linking or elastomers)

Monomers containing electron-withdrawing groups (–COOR, –CN, –$CONH_2$, –Cl) polymerize particularly well by radical mechanisms.



Styrene vinyl acetate acrylic acid methyl acrylate



Acrylonitrile methacrylic acid methyl methacrylate

Figure: vinylic monomers**.**

Reaction Conditions:

Radical polymerization can be carried out under various conditions depending on the desired molecular weight and medium:

Table: Types of radical polymerization.

Mode	Example	Temperature(°C)	Remarks
bulk	Styrene, MMA	50-120	Fast, but heat control difficult
Solution	Styrene in toluene	50-80	Easier temperature control
Suspension	PVC	40–70	Good heat removal
Emulsion	Acrylates	30-80	Fast, produces fine latex particles

Mechanistic Steps

Initiation: The initiation step is the first and essential stage of radical polymerization. It involves the generation of free radicals capable of attacking the monomer's double bond to form an active growing chain.

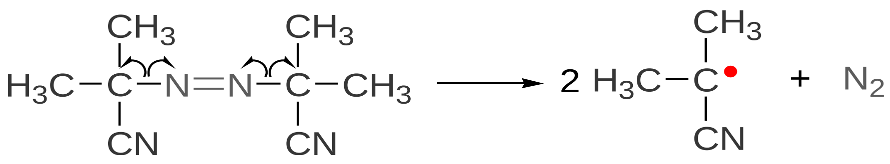
Types of Initiation in Radical Polymerization: There are several types of initiation, depending on how radicals are produced:

- **Thermal Initiation:** Radicals are generated by the thermal decompositionof an initiator under heat.

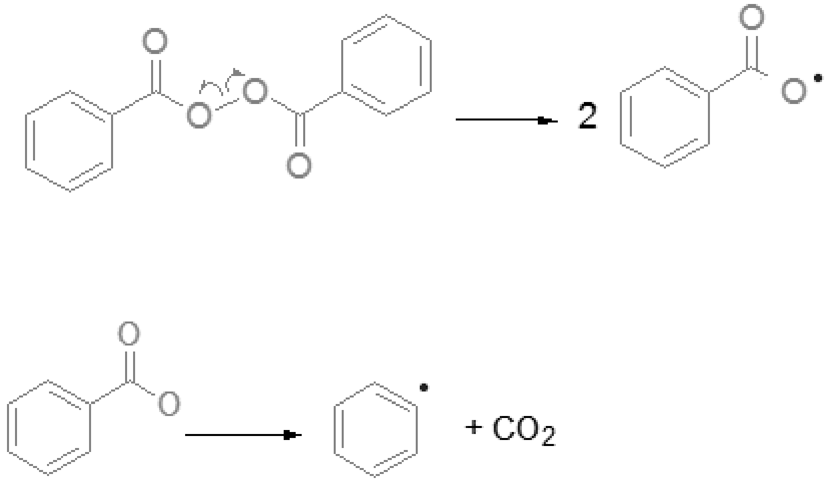
This is the most common initiation method in radical polymerization. The most Typical initiators are:

- Benzoyl peroxide (BPO)
- Azo-bis(isobutyronitrile) (AIBN)
- Dicumyl peroxide

- Decomposition of Azo-bis(isobutyronitrile) (AIBN)



- Decomposition of Benzoyl peroxide (BPO)



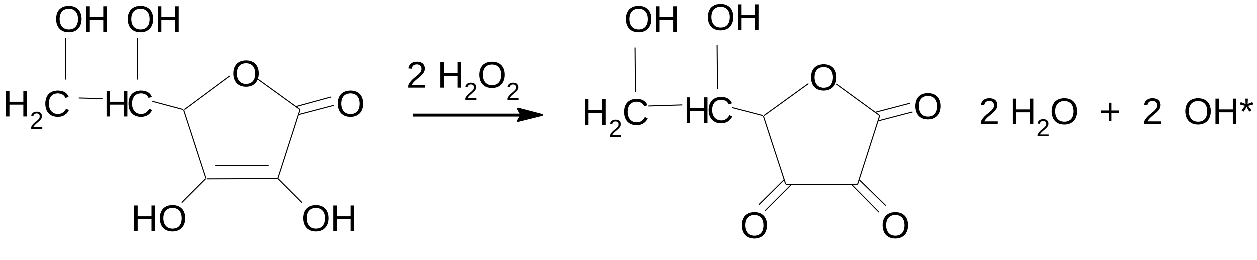
➢ **Redox Initiation:** Radicals are formed by oxidation–reduction (redox) reactions at low temperatures.This type is widely used in emulsion and aqueous polymerizations. The Typical redox systemsare:

- Hydrogen peroxide / ferrous ion (H_2O_2/Fe^{2+})
- Persulfate / bisulfite ($S_2O_8^{2-}/HSO_3^{-}$)

Fenton salt:

$$H_2O_2 + Fe^{2+} \longrightarrow OH^* + OH^- + Fe^{3+}$$

Hydrogen peroxide/ ascorbic acid:

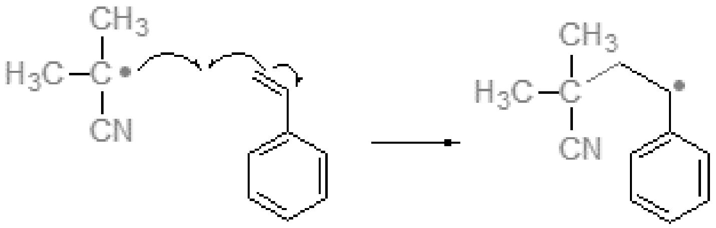


- **Photochemical Initiation:**Radicals are produced by absorption of light (UV or visible) by a photoinitiator that undergoes homolytic cleavage or electron transfer. The Typical initiators are:
  - Benzoin ethers
  - Benzophenone
  - Camphorquinone

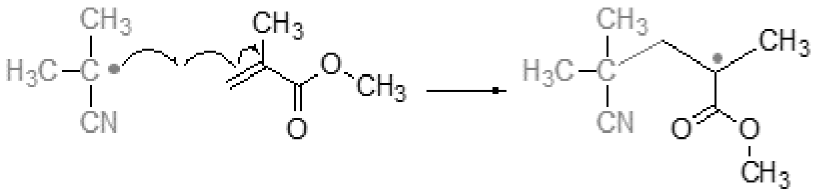
- **Radiation Initiation:**High-energy radiation (γ-rays, X-rays, or electron beams) directly splits chemical bonds to form radicals in monomers or added sensitizers.
- **Plasma or Mechanical Initiation** (less common): Radicals can also be generated by plasma discharge or ultrasound (sonochemical) energy, used in special cases or advanced polymerization systems.

The initiator molecule undergoes homolytic cleavage of a covalent bond, resulting in the formation of two radicals, each bearing an unpaired electron. These radicals are highly reactive and serve as the starting points for the polymerization process. For example, thermal initiators such as benzoyl peroxide or AIBN decompose upon heating to yield benzoyloxy or cyanoisopropyl radicals, respectively. These primary radicals rapidly react with the π bond of a monomer molecule (such as styrene or methyl methacrylate), forming the first active radical of the growing polymer chain. This moment marks the true beginning of the chain reaction, as the radical site is now transferred to the monomer unit, ready to propagate through successive additions of new monomer molecules.

Initiation of styrene

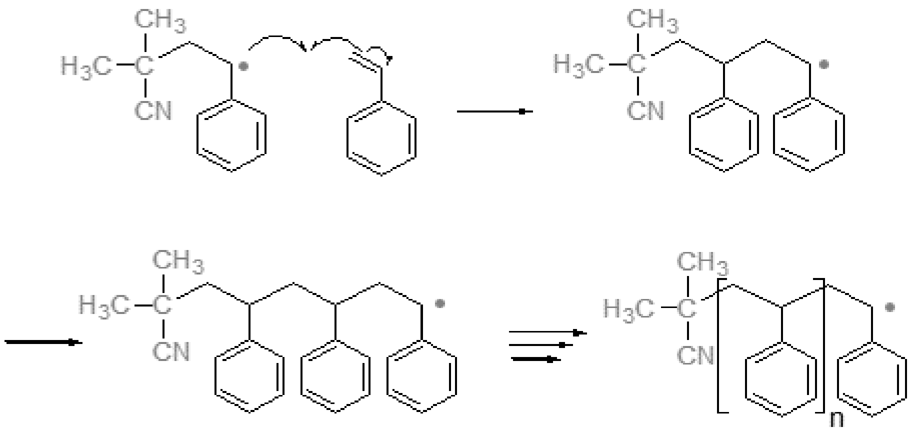


Initiation of methyl methacrylate

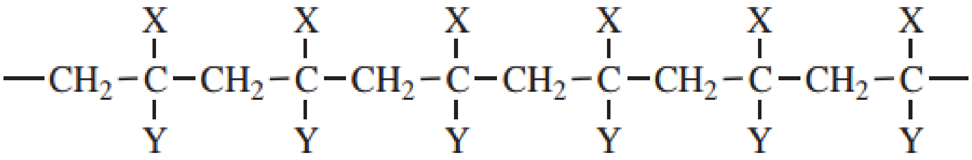


Propagation: The active radical adds successively to monomer units:

There are two possible points of attachment on monosubstituted (XH) or 1,1-disubstitutedmonomers for a propagating radicalon either carbon 1 or carbon 2:

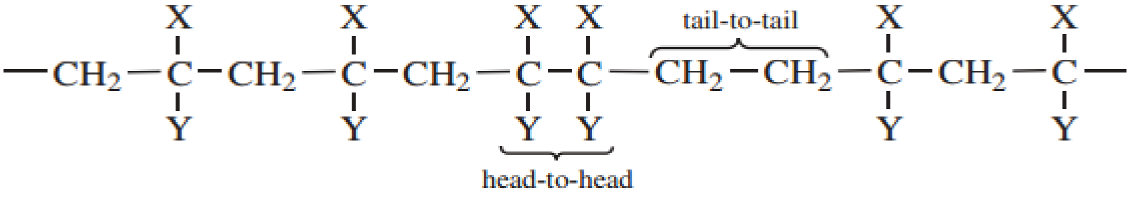


If each successive addition of monomer molecules to the propagating radical occurs in thesame manner, the final polymer product will have an arrangement of monomer units in which the substituents are on alternate carbon atoms:



$$-CH_2-\underset{Y}{\overset{X}{C}}-CH_2-\underset{Y}{\overset{X}{C}}-CH_2-\underset{Y}{\overset{X}{C}}-CH_2-\underset{Y}{\overset{X}{C}}-CH_2-\underset{Y}{\overset{X}{C}}-CH_2-\underset{Y}{\overset{X}{C}}-$$

This type of arrangement (III) is usually referred to as a head-to-tail(H-T) or 1,3-placement of monomer units. An inversion of this mode of addition by the polymer chain propagating alternately via propagation reactionswould lead to a polymer structure with a 1,2-placement of substituents at one or more places in the final polymer chain. 1,2- placement is usually referred to ashead-to-head(H-H) placement.

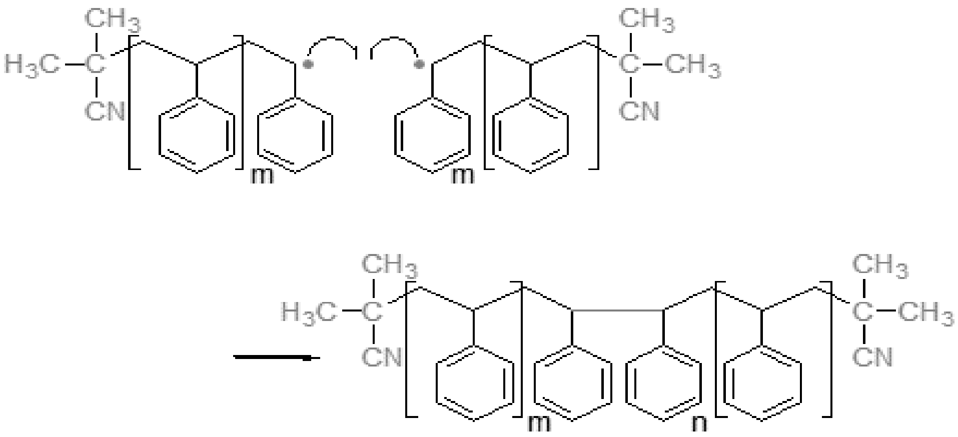


Termination:

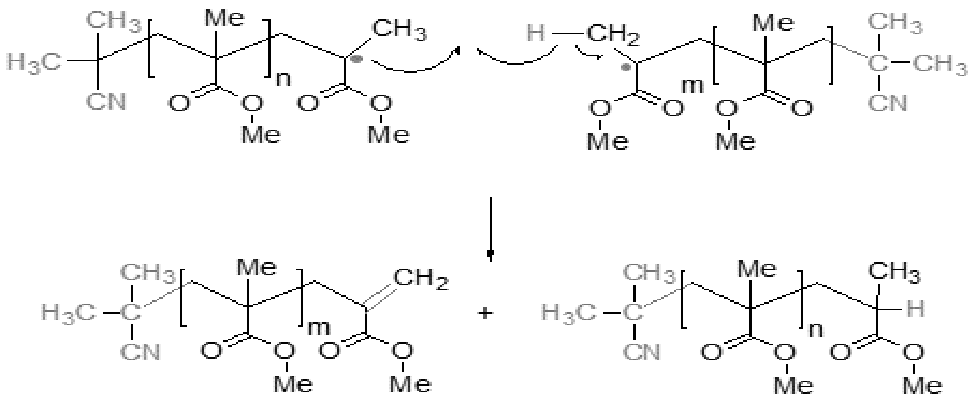
At some point, the propagating polymer chain stops growing and terminates. Termination with the annihilation of the radical centers occurs by bimolecular reaction between radicals. Two radicals react with each other by combination(coupling) or, more rarely, by disproportionation, in which a hydrogen radical that is beta to one radical center is transferred to another radical center. This results in the formation of two polymer molecules one saturated and one unsaturated:

Termination can also occur by a combination of coupling and disproportionation. The two different modes of termination can be represented in general terms by:

* Combination of coupling



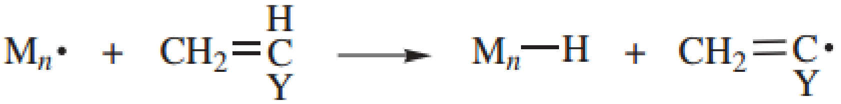
* Disproportionation



Chain Transfer Reactions

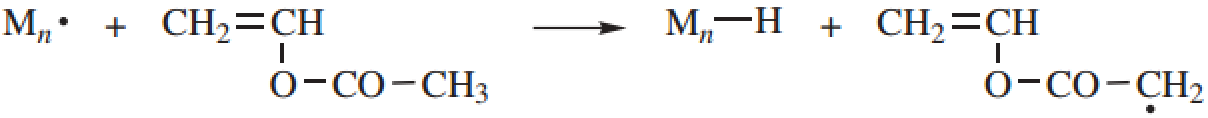
The growing radical transfers its activity to another species (solvent, monomer, chain-transfer agent), generating a new radical and stopping the current chain:

Monomer transfer: The monomer chain-transfer constants are generally small for most monomers. Chain transfer tomonomer places the upper limit to the polymer molecular weight that can be obtained, assuming the absence of all other transfer reactions.



$$M_n\cdot + CH_2{=}\underset{Y}{\overset{H}{C}} \longrightarrow M_n{-}H + CH_2{=}\underset{Y}{C}\cdot$$

Involves breaking the strong vinyl C-H bond. The largest monomer transfer constants are generally observed when the propagating radicals have very high reactivities, for example, ethylene, vinyl acetate, and vinyl chloride. Chain transfer to monomer for vinyl acetate had been attributed to transfer from the acetoxy methyl group



$$M_n\cdot + CH_2{=}\underset{O-CO-CH_3}{CH} \longrightarrow M_n{-}H + CH_2{=}\underset{O-CO-\dot{C}H_2}{CH}$$

Initiator transfer: The transfer with azonitriles, probably occurs by the displacement reaction:

$$M_n\cdot + RN{=}NR \longrightarrow M_n{-}R + N_2 + R\cdot$$

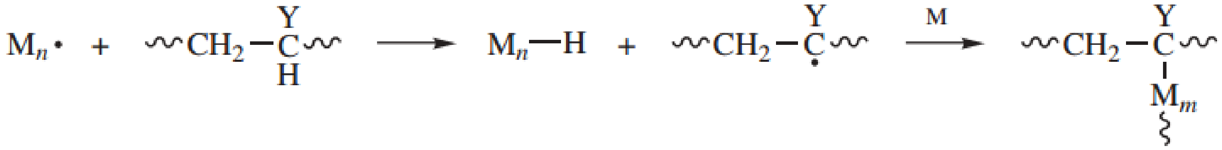
Many peroxides have significant chain-transfer constants. Dialkyl and diacyl peroxides undergo transfer by

$$M_n\cdot + RO{-}OR \longrightarrow M_n{-}OR + RO\cdot$$

where R=alkyl or acyl. The acyl peroxides have higher transfer constants than the alkyl peroxides, due to the weaker O-O bond of the former. The hydroperoxides are usually the strongest transfer agents among the initiators. Transfer probably involves hydrogen atom

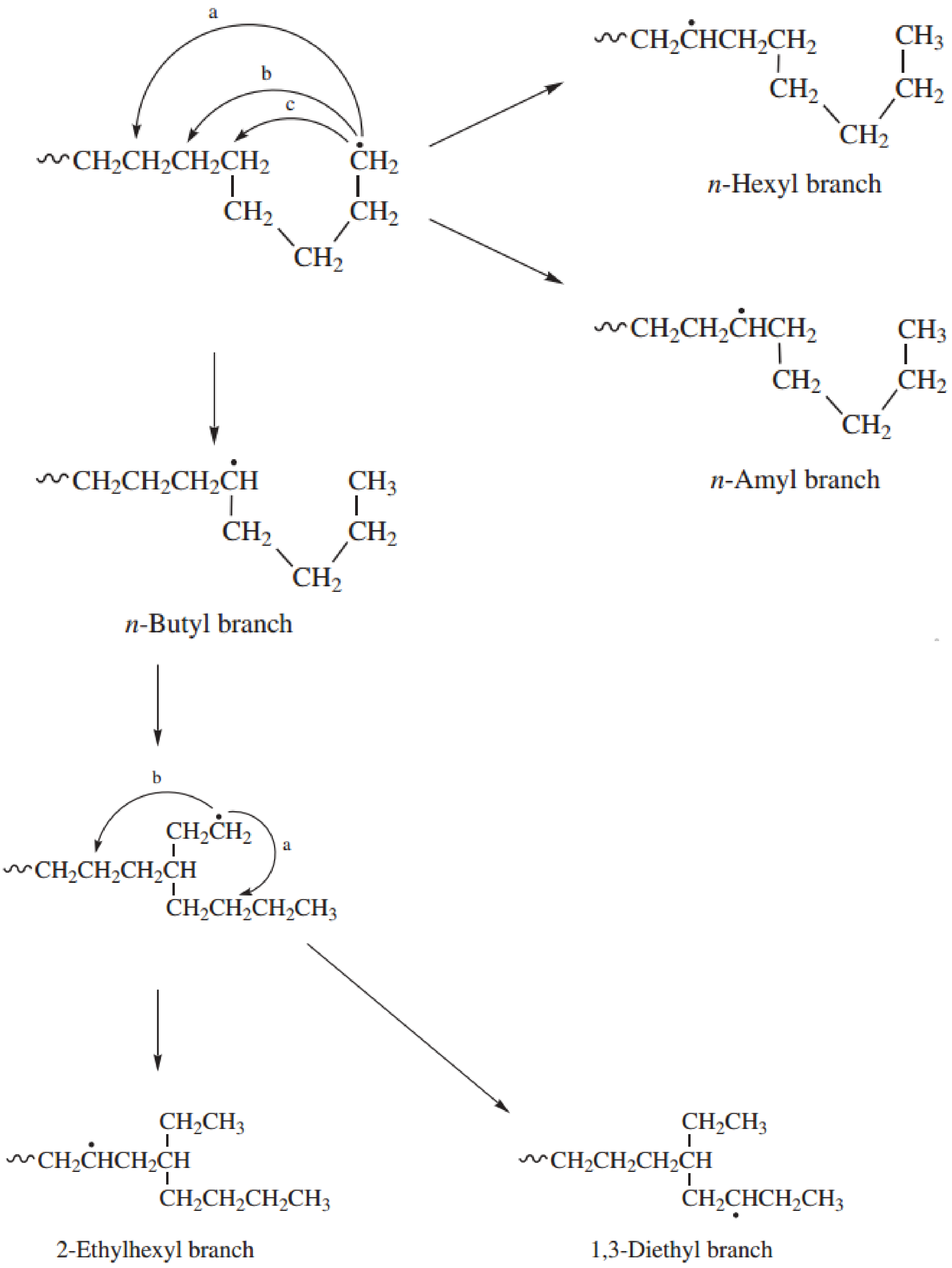
$$M_n\cdot + ROO{-}H \longrightarrow M_n{-}H + ROO\cdot$$

Chain Transfer to Polymer: Transfer to polymer results in the formation of a radical site on a polymer chain. Thepolymerization of monomer at this site leads to the production of a branched polymer, forexample:

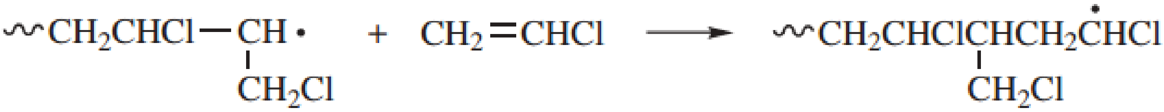


$$M_n\cdot + \sim CH_2{-}\overset{Y}{\underset{H}{C}}\sim \longrightarrow M_n{-}H + \sim CH_2{-}\overset{Y}{\underset{\cdot}{C}}\sim \xrightarrow{M} \sim CH_2{-}\overset{Y}{\underset{\underset{\wr}{M_m}}{C}}\sim$$

An accepted mechanism for the formation of short branching in polyethylene involves a backbiting intramolecular transfer reaction in which the propagating radical abstracts hydrogens from the fifth, sixth, and seventh methylene groups from the radical end. The resulting radicals propagate with monomer to form n-hexyl, n-amyl, and n-butyl branches, respectively. The general predominance of n-butyl branches is ascribed to the fact that it is formed through a 6-membered transition state (consisting of the five carbons and the hydrogen being abstracted). Ethyl branches arise from radical undergoing a second intramolecular transfer reaction after the addition of one ethylene molecule prior to further propagation, leading to 1,3-diethyl and 2-ethylhexyl branches:


a
b
c
n-Hexyl branch
n-Amyl branch
n-Butyl branch
b
a
2-Ethylhexyl branch
1,3-Diethyl branch

Short branching has also been verified in poly(vinyl acetate), poly(vinyl chloride), and various polyacrylates. Branching in poly(vinyl acetate) and polyacrylates involve the intramolecular backbiting mechanism as in polyethylene:



$$\sim CH_2CHCl-\underset{\displaystyle CH_2Cl}{CH\cdot} + CH_2{=}CHCl \longrightarrow \sim CH_2CHCl\underset{\displaystyle CH_2Cl}{C}HCH_2\dot{C}HCl$$

Kinetic Expressions

Rate of initiation: The initiation reaction in polymerization is composed of two steps, In most polymerizations, the second step (the addition of the primary radical to monomer) is much faster than the first step. The homolysis of the initiator is the rate-determining step in the initiation sequence, and the rate of initiation is then given by:

$$I \xrightarrow{k_d} 2R\cdot$$

$$R\cdot + M \xrightarrow{k_i} M_1\cdot$$

$$\frac{d[R*]}{dt} = 2\ k_i\ [I]$$

$$Ri = 2\ f\ k_i[I]$$

where [I] is the concentration of the initiator and f is the initiator efficiency. The initiator efficiency is defined as the fraction of the radicals produced in the homolysis reaction that initiate polymer chains. The value off is usually less than unity due to wastage reactions.

Rate of propagation: The successive additions may be represented by

$$M_1\cdot + M \xrightarrow{k_p} M_2\cdot$$

$$M_2\cdot + M \xrightarrow{k_p} M_3\cdot$$

$$M_3\cdot + M \xrightarrow{k_p} M_4\cdot$$

etc., etc.

In general

$$M_n\cdot + M \xrightarrow{k_p} M_{n+1}\cdot$$

Where kp is the rate constant for propagation. Propagation with growth of the chain to high polymer proportions takes place very rapidly. The rate of polymerization is given by:

$$Rp = -\frac{d[M]}{dt} = kp\,[M][M\cdot]$$

Rate of termination: Termination can also occur by a combination of coupling and disproportionation. The twodifferent modes of termination can be represented in general terms by

$$M_n\cdot + M_m\cdot \xrightarrow{k_{tc}} M_{n+m}$$

$$M_n\cdot + M_m\cdot \xrightarrow{k_{td}} M_n + M_m$$

Where k_{tc} and k_{td} are the rate constants for termination by coupling and disproportionation, respectively. One can also express the termination step by

$$M_n\cdot + M_m\cdot \xrightarrow{k_t} \text{dead polymer}$$

The rate of termination is given by :

$$Rt = -\frac{d[M.]}{dt} = 2\,kt\,[M\cdot]^2$$

Steady-state approximation:

During a radical polymerization, the concentration of free radicals increases rapidly at the beginning of the reaction and then reaches an almost constant value over time. This situation is known as the steady-state condition.

This assumption is based on the idea that the rate of radical formation (initiation) is equal to the rate of radical disappearance (termination or combination). Although radicals are highly reactive and have a very short lifetime, their overall concentration remains essentially constant after a short induction period.

Mathematically, this condition can be expressed as:

$$Ri = Rt$$

where:

(Ri) is the rate of initiation (formation of radicals),

(Rt) is the rate of termination (disappearance of radicals).

From this relation, the average radical concentration can be expressed as:

$$[M\bullet] = kp \sqrt{2\, f\ \frac{kd\,[I]}{kt}}$$

The quasi-steady-state assumption greatly simplifies the kinetic analysis of radical polymerization because it allows the overall rate of polymerization to be related to the square root of the initiation rate, as shown by:

$$Rp = kp\,[M][M\bullet] = kp\,[M] \sqrt{2\, f\ \frac{kd\,[I]}{kt}}$$

While neglecting the initiator concentration,

$$K = kp \sqrt{2\, f\ \frac{kd}{kt}} \text{ and } Rp = K\,[M]$$

$$\frac{-d\,[M]}{[M]} = K\,dt$$

The variation of the monomer concentration will give by:

$$[M]_t = [M]_0\, e^{-K},$$

the result can be presented by the shown curve.

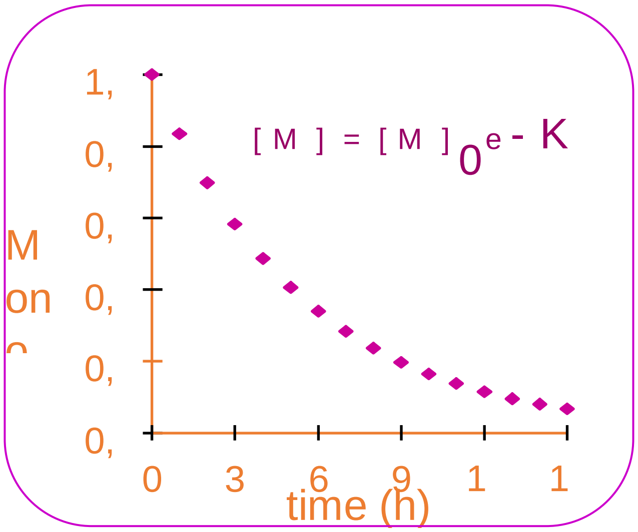


Figure: variation of monomer concentration as function of time

Kinetic Chain Length (ν)

The kinetic chain length is the average number of monomer molecules polymerized per radical produced:

$$\nu = \frac{Rp}{Ri}$$

Mode of Termination

The number-average degree of polymerization Xn, defined as the average number of monomer molecules contained in a polymer molecule, is related to the kinetic chain length. If the propagating radicals terminate by coupling, a dead polymer molecule is composed of two kinetic chain lengths and

$$\overline{X}_n = 2\nu$$

For termination by disproportionation, the kinetic chain length is synonymous with the number-average degree of polymerization

$$\overline{X}_n = \nu$$

The number-average molecular weight of a polymer is given by

$$\overline{M}_n = M_o \overline{X}_n$$

Where Mo is the molecular weight of the monomer.

The mode of termination is experimentally determined from the observation of the number of initiator fragments per polymer molecule. This requires the analysis of the molecular weight of a polymer sample as well as the total number of initiator fragments contained in that sample. Termination by coupling results in two initiator fragments per polymer molecule, while disproportionation results in one initiator fragment per polymer molecule. The fractions of propagating chains, a and (1-a), respectively, which undergo termination by coupling and disproportionation can be related to b, the average number of initiator fragments per polymer molecule. For a reaction system composed of n propagating chains,coupling yields an initiator fragments and an/2 polymer molecules, while disproportionation yields (1-a)ninitiator fragments and (1-a)npolymer molecules. The average numberof initiator fragments perpolymer molecule, defined as the total initiator fragments dividedby the total number of polymer molecules, is given as

$$b = \frac{an + (1-a)n}{an/2 + (1-a)n} = \frac{2}{2-a}$$

from which the fractions of coupling and disproportionation are obtained as

$$a = \frac{2b-2}{b}$$

$$1 - a = \frac{2-b}{b}$$

The kinetic chain length is inversely dependent on the radical concentration or the polymerization rate. This is of great practical significanceany attempt to increase the polymerization rate by increasing the radical concentration comes at the expense of producing smaller polymer molecules. The kinetic chain length at constant polymerization rate is a characteristic of the particular monomer and independent of the method of initiation.

The general relationship between the degree of polymerization and the kinetic chain length is

$$\overline{X}_n = b\nu = \frac{2\nu}{(2-a)}$$

CONTROLLED/"LIVING" FREE RADICAL POLYMERIZATIONS

Introduction:

Although radical polymerization is easy to perform and allows rapid polymer formation, it is traditionally difficult to control. Random initiation and termination events often lead to polymers with broad molecular weight distributions and poorly defined structures. To overcome this limitation, controlled or living radical polymerization (CRP) techniques have been developed, enabling better control over molecular weight, architecture, and functionality.

Today, radical polymerization remains one of the most important techniques for the synthesis of synthetic polymers, providing materials for applications ranging from plastics and coatings to biomedical and nanotechnological systems.

Ideally, a living system leads to a polymer with a number-average degree of polymerization (DPn) predetermined by the ratio of the concentration of monomer consumed at time t to the initial initiator concentration (DPn = $\Delta[M]t$ / $[A]_0$). The chain polydispersity then approaches a Poisson distribution (DPI ≈ 1 + 1/DPn). Experimentally, the controlled nature of a system is assessed by monitoring the polymerization kinetics, as well as the evolution of molar masses and polydispersity indices as a function of conversion. The characteristic behaviors observed during various polymerizations.

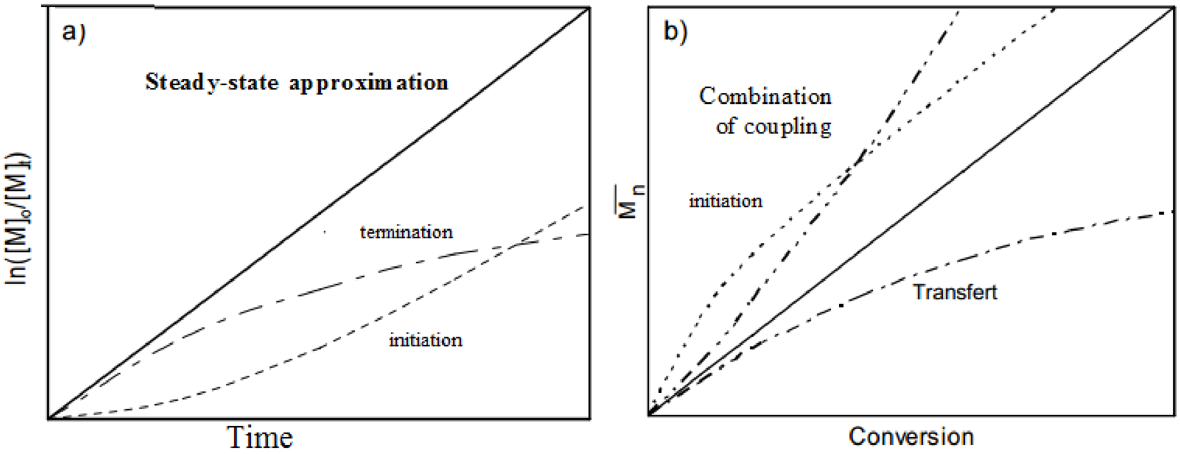


Figure: Schematic effect of termination, slow initiation, and chain transfer to the monomer on (a) the kinetics of a controlled polymerization and (b) on the evolution of Mn.

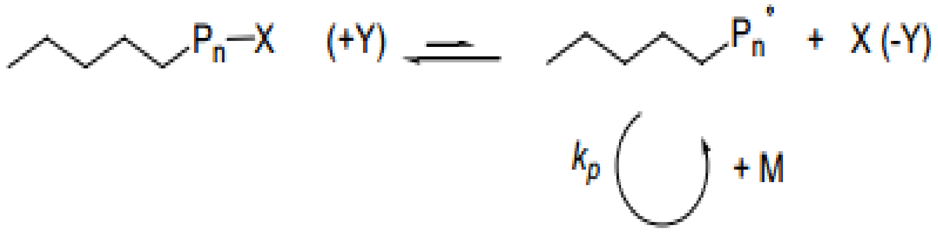
A controlled system exhibits several characteristics:

- A linear evolution of ln([M]$_0$/[M]t) with time is observed (where [M]$_0$ and [M]t represents the initial and instantaneous monomer concentrations, respectively, if the reaction is first order with respect to monomer concentration. This behavior reflects a constant concentration of active centers (quasi-steady state), which is observed in living and controlled polymerizations. An acceleration of monomer consumption or the presence of an inhibition period indicates slow initiation, whereas a decrease in the polymerization rate is a sign of a reduction in the concentration of active centers caused by termination reactions. Chain-transfer steps have no effect on the kinetics, since the concentration of active species is conserved.
- A linear increase of Mn with conversion indicates a constant number of chains. Molar masses lower than the theoretical values reflect the presence of chain-transfer reactions, whereas a higher Mn indicates slow initiation or chain coupling by radical termination through recombination.
- The polydispersity index should decrease with conversion for systems exhibiting instantaneous initiation and rapid exchange between dormant and active species. Conversely, the index increases when the contribution of termination and transfer reactions becomes too significant.
- The functionality of the chain ends is not affected by slow initiation or slow exchange processes. However, it is altered when termination and transfer reactions become predominant.

Principle of CRP:

The successes achieved in controlling carbocationic polymerizations have paved the way for new radical systems. In both cases, the control mechanism is based on establishing an equilibrium or exchange between propagating species and dormant covalent chains that can revert to the active state. This concept has been widely adopted in radical polymerization to achieve controlled growth.

The principle of Controlled Radical Polymerization (CRP) involves introducing into the reaction medium an entity capable of temporarily trapping the propagating macromolecular chains, according to the mechanism described below:



The following table compares various parameters of conventional radical polymerization and controlled radical polymerization.

Table: Difference between conventional polymerization and CRP

	conventionnel polymerization	**CRP**
Temperature (°C)	60	60-120
initiation	slow	Fast
Chain's state	dead	dormant
[P°] (mole/L)	10^{-7} – 10^{-9}	10^{-8} – 10^{-9}
[P°] (mole/L)	10^{-7} – 10^{-9}	10^{-2} – 10^{-3}
Total Life time of Radical	<1 second	>1hour

It should be noted that in conventional radical polymerization, experimental conditions (such as slow initiation) are chosen so that the concentration of active chains remains low. In controlled radical polymerization (CRP), the chains created within a short period by the initiator are immediately trapped, leaving only a very small concentration of polymer radicals (P°) in the medium. Ultimately, the radical concentrations in both systems are comparable.

Conventional free radical polymerization techniques are inherently limited in their ability to synthesize resins with well-defined architectural and structural parameters. Free radical processes have been recently developed which allow for both control over molar masses and for complex architectures. Such processes combine both radical techniques with living supports, permitting reversible termination of propagating radicals. In particular, three controlled free radical polymerizations have been well investigated.

Each of these techniques is briefly presented below and all are based upon early work involving the use of initiator-transfer-agent-terminators to control irreversible chain termination of classical free radical process.

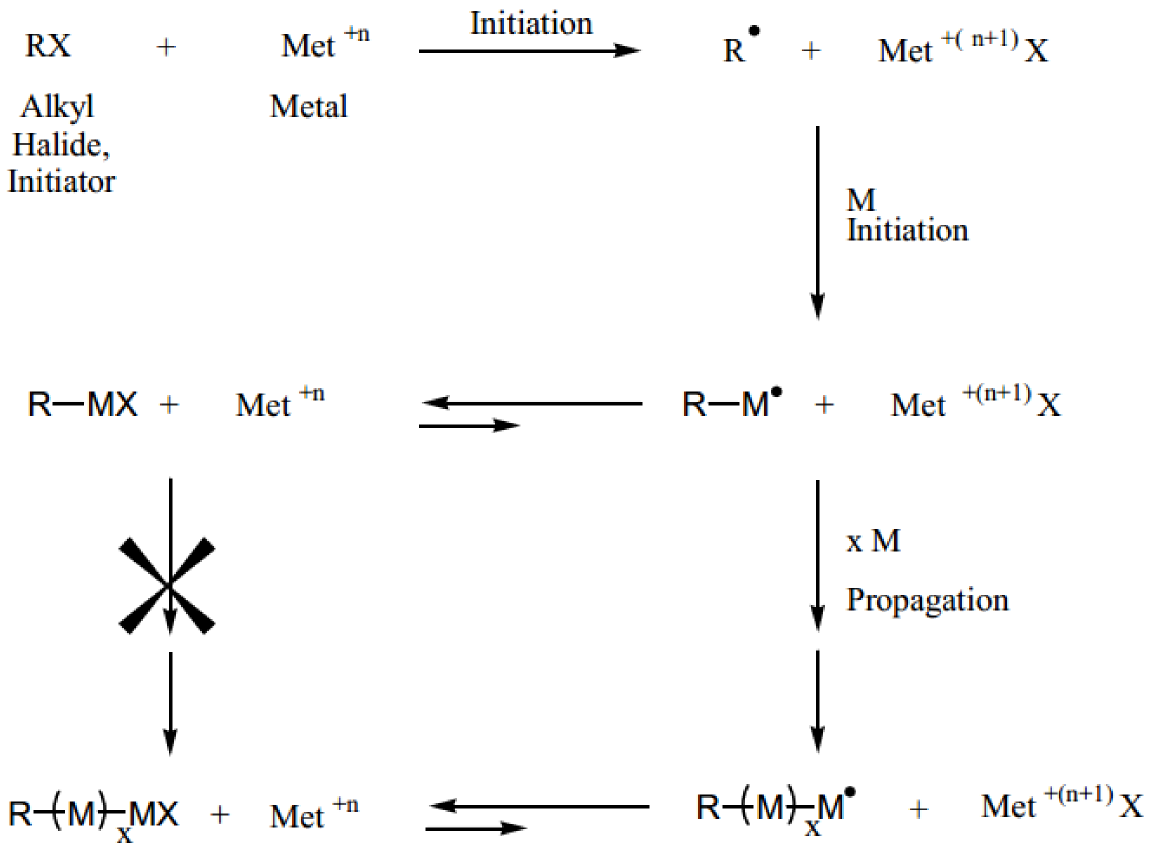
Methyl acrylate oligomers were synthesized through the reversible capping of growing radical chains by a stable free radical. Although the significance of this process was not fully recognized at the timepartly due to the challenges associated with extending this method to polyacrylatesthe reversible capping of active chains represented the first mechanism among three general approaches to controlled or "living" radical polymerization.

Atom Transfer Radical Polymerization:

Atom Transfer Radical Polymerization (ATRP) is one of the most powerful and widely used methods of controlled/living radical polymerization. Developed in the mid-1990s by Krzysztof Matyjaszewski et al, ATRP enables the synthesis of polymers with well-defined molecular weights, narrow molecular weight distributions, and precisely controlled architecturessuch as block, graft, and star polymers.

The ATRP process is based on a reversible redox equilibrium between an active radical species and a dormant alkyl halide. The reaction is typically catalyzed by a transition metal complex(usually copper) in a lower oxidation state.

A first method for controlling radical polymerization involves the use of a catalytic amount of a copper(I) coordination complex, which can reversibly abstract a halide from the polymer chain end. This enables a switching mechanism between a dormant state and an active, propagating state.



Reversible addition-fragmentation chain transfer (RAFT)

RAFT polymerization is a type of controlled/living radical polymerization that allows the preparation of polymers with controlled molecular weights and narrow molecular weight distributions.

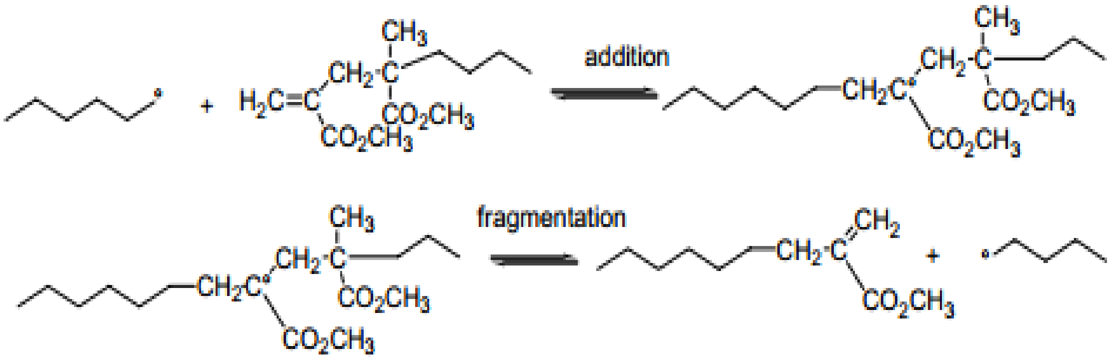
This method uses a special compound called a RAFT agent. The RAFT agent helps control the growth of polymer chains by a reversible addition–fragmentation mechanism, keeping most of the chains dormant while only a few are active at a time.

The reaction starts with a normal radical initiator (like AIBN), which forms free radicals that add to the monomer. These radicals then react with the RAFT agent, forming an intermediate that can break apart to start new polymer chains. This continuous exchange keeps all the chains growing evenly.

RAFT polymerization works with many types of monomers (acrylates, methacrylates, styrene, acrylonitrile, etc.) and can be carried out in solution, bulk, or emulsion. It allows the synthesis of block copolymers, star polymers, and other complex architectures.

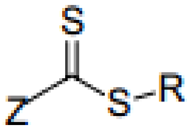
- **RAFT with PMMA**

An approach, known as reversible addition-fragmentation chain transfer (RAFT), was used with macromonomers bearing a double bond based on methacrylates for the synthesis of PMMA-b-poly(meth)acrylate block copolymers. The polydispersity indices remain relatively high, on the order of 1.3.



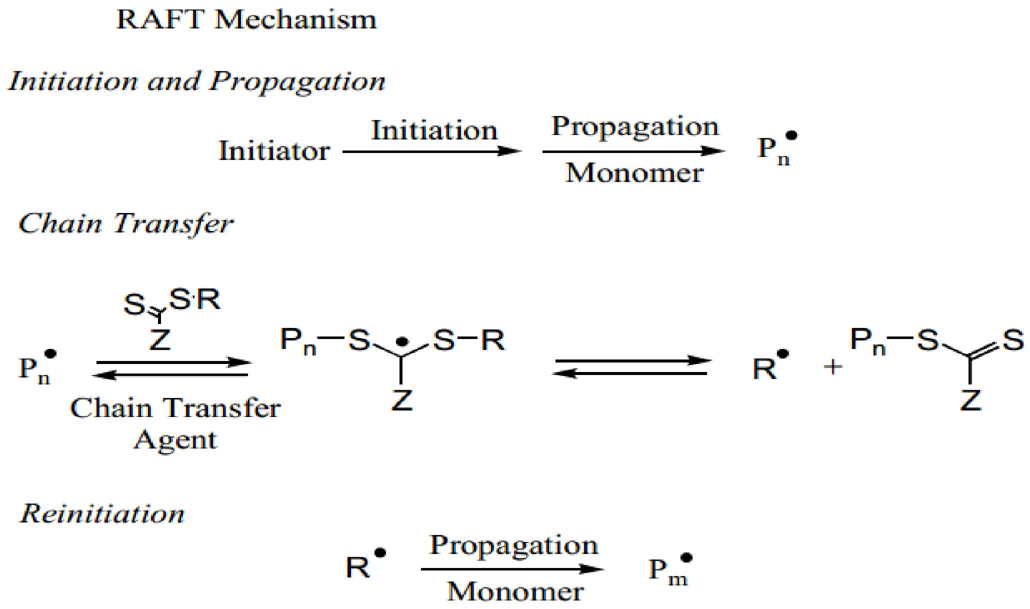
- **RAFT with Dithio compounds**

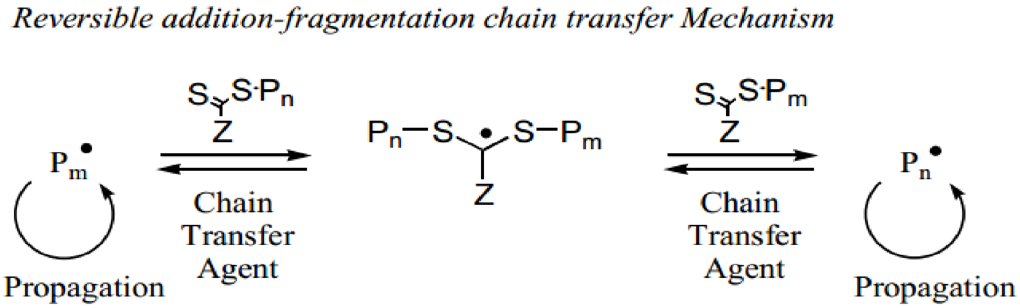
More recently, the concept of reversible addition–fragmentation chain transfer has been applied by the same author with greater success. Indeed, it appears that a molecule bearing a thiocarbonylthio entity (S = C–S) (Scheme 8) is considerably more effective for this type of mechanism. Four types of thiocarbonylthio agents are distinguished: dithioesters (Z = alkyl, aryl), trithiocarbonates (Z = thioalkyl), xanthates (Z = alkoxy) and dithiocarbamates (Z = N-alkyl).



Transfer agent dithiocarbonylthio

Similar to the previous methods, the rapid transition between dormant and active chain ends allows the polymerization to exhibit controlled or "living" characteristics (see Scheme 4).

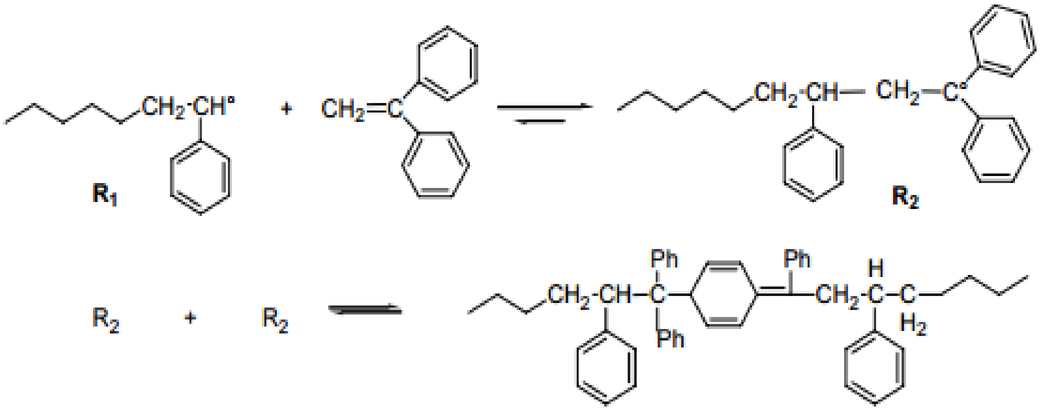




The polymerization is carried out simply by adding a chain-transfer agent to a conventional radical-polymerization mixture. Radicals generated during the initiation step add to the C═S double bond of the transfer agent. The intermediate radical species thus formed undergoes fragmentation to yield a polymer-bearing RAFT agent and a new radical capable of rapidly re-initiating other chains. Thereafter, the degenerative transfer mechanism establishes a dynamic equilibrium between propagating and dormant chains. In order for the fraction of dead chains to be low, it is necessary that the number of radicals generated by the initiator (I°) is negligible compared to those created by the R° radical from the transfer agent. Thus, one must have [I] ≪≪ [At], where At is the transfer agent, and the target molar masses are then calculated relative to the concentration of the transfer agent. At the end of the reaction, the majority of chains carry the dithiocarbonylthio end-group and are capable of re-activation for further chain extension. Well-defined block copolymers with narrow molecular-weight distributions (PDI < 1.1) have thus been prepared.

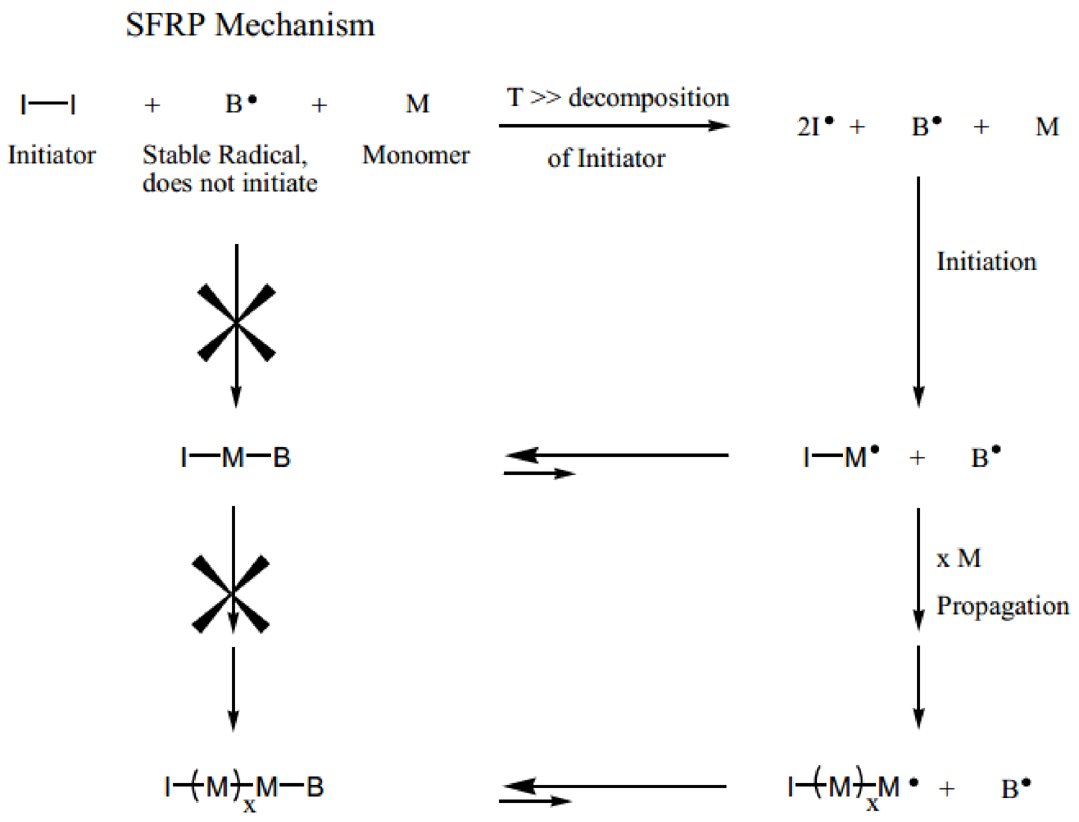
- **RAFT with diphenylethylene (DPE)**

Very recently, adding a small amount (ca. 0.3 mol % relative to monomer) of 1,1-diphenylethylene (DPE) during a radical polymerization resulted in a certain degree of molecular-weight control, with polydispersity indices around 1.7 for reaction temperatures between 70 and 110 °C. Block copolymers such as PMMA-b-PS as well as amphiphilic block copolymers (e.g., PS-b-P(N-vinylpyrrolidone)) have been obtained. The process is chiefly applied to polymer synthesis in dispersion or grafting. Mechanistic investigations revealed an exchange between dormant and active species in the presence of DPE, and equilibria between these species have been proposed.



Stable Free Radical Polymerization

The principle of reversible homolytic cleavage of a dormant chain end, generating both a stable free radical and an active radical site, was later applied to the polymerization of styrene and subsequently to acrylates catalyzed by cobalt porphyrin alkyl complexes. More recently, this strategy has been extended to a wide range of monomers through the use of monomer-specific initiators. This approach became known as “Stable Free Radical Polymerization” (SFRP).



The modern era of CRP began with using 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) to polymerize styrene. During this polymerization, TEMPO was used as a stable free radical (SFR), allowing the temporary deactivation of growing radical chains.

Stable free radical polymerization (SFRP) involves the use of stable radicals such as nitroxides (**nitroxide-mediated polymerization, NMP**), iniferters (initiator–transfer agent–terminator), free radicals derived from triazolinyl, (arylazo)oxides, borinates, and verdazyls. The use of certain transition metals such as Mo, Os, Fe, and Co can also be mentioned.

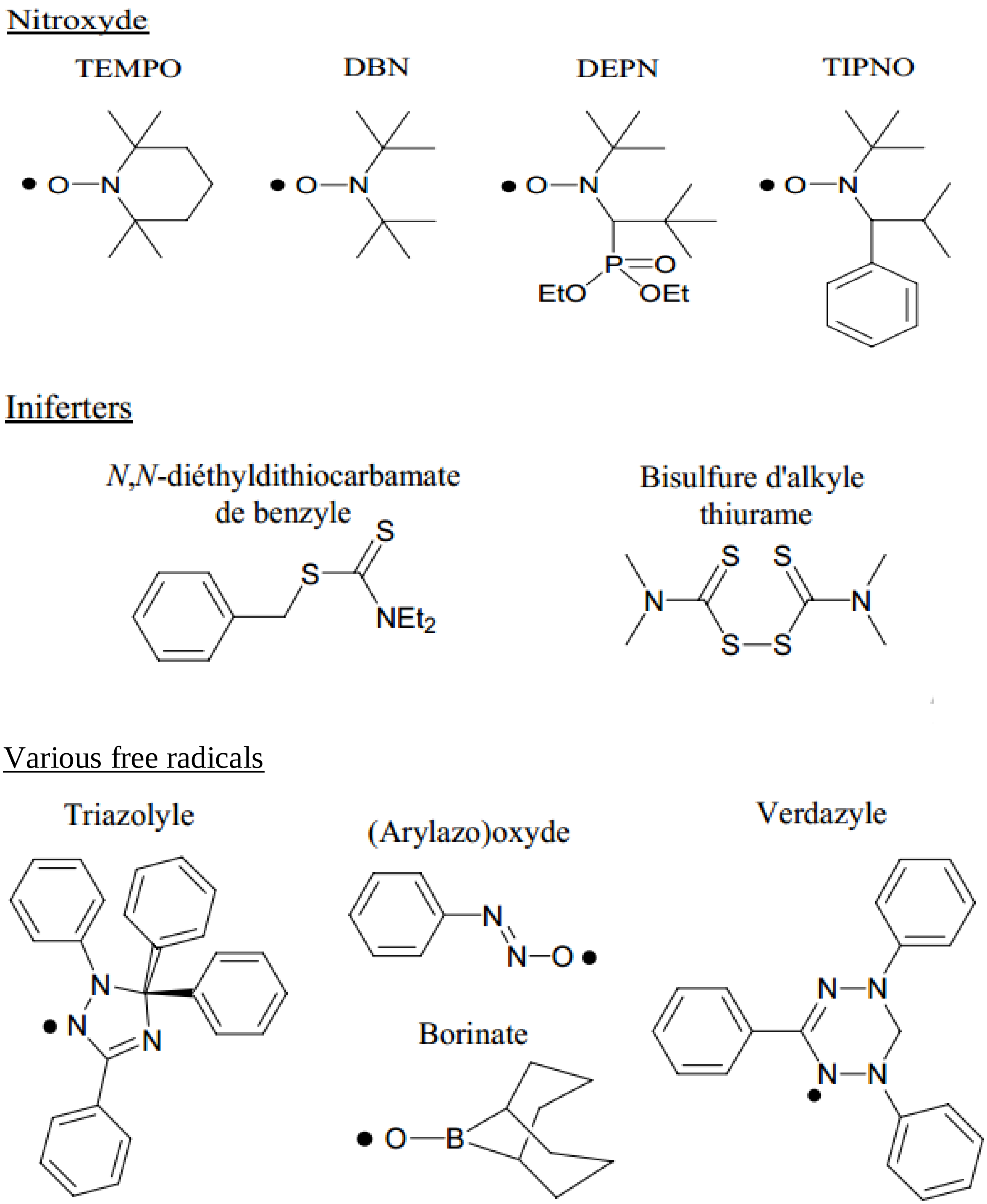
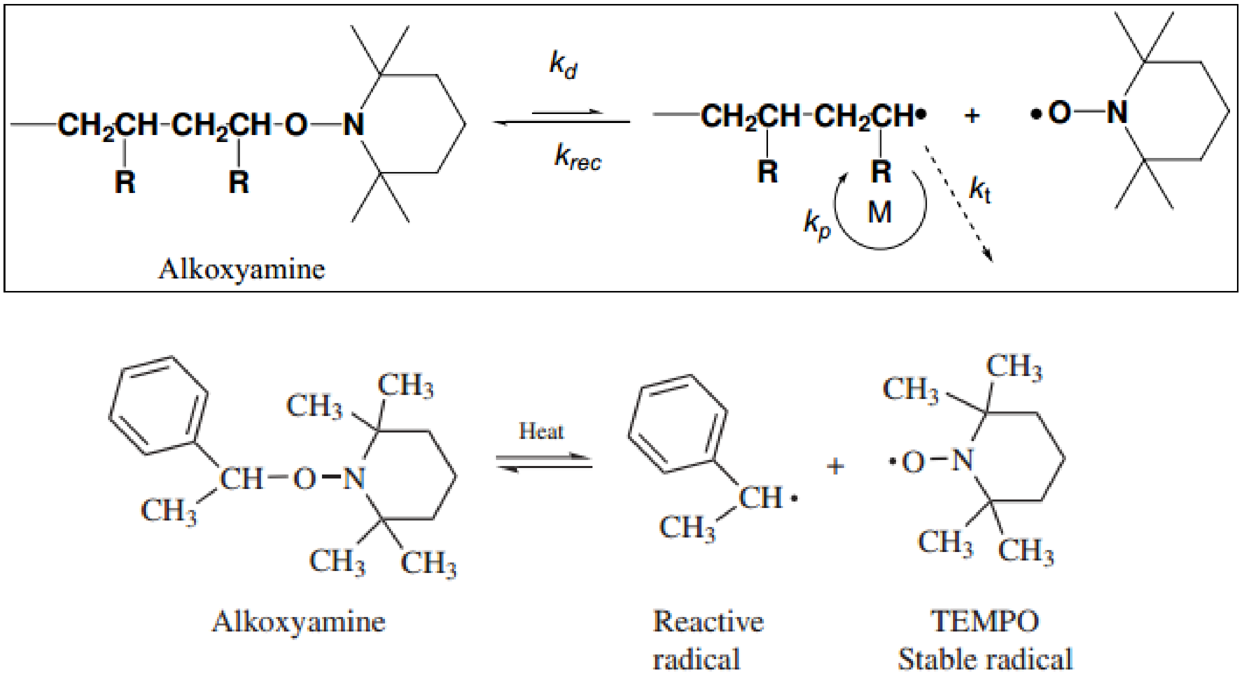


Figure: Examples of nitroxides, iniferters, and various free radicals used as SFRs.

Nitroxide-Mediated polymerization:

Control in NMP, the most common SFRP technique, is achieved through a dynamic equilibrium between the dormant alkoxyamine species and the propagating free radical. In order to efficiently carry out the polymerization, the stable free radical (for example, TEMPO) must not react with itself, initiate polymerization, or participate in side reactions such as β-hydrogen abstraction.

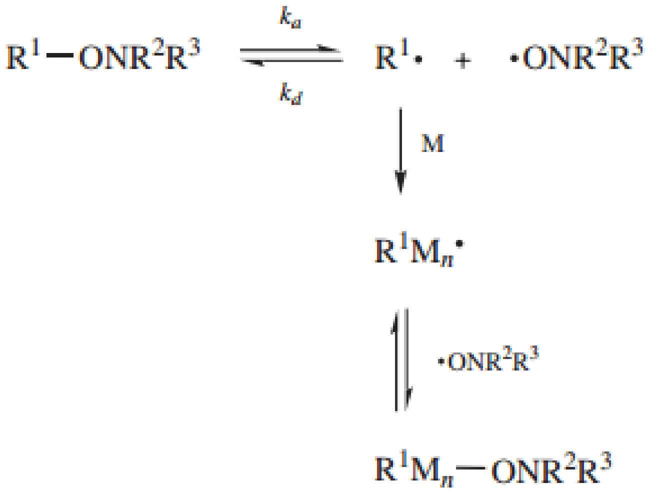
The C–O bond of the alkoxyamine is relatively strong. Consequently, the equilibrium constant ($K_{e}q$) of an NMP process (the ratio of the kinetic constants of dissociation, kd, and recombination, k_rec) is generally low. For example, $K_{e}q$ is close to 1.5×10^{-11} M in the case of bulk styrene polymerization at 120 °C.



Scheme: equilibrium reactions of NMP

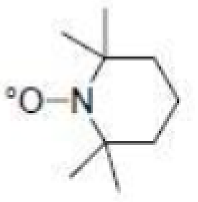
NMP systems using TEMPO are effective in the case of styrene and its derivatives. However, they are unsuitable for the polymerization of acrylates and several other monomers, since the equilibrium is then shifted too strongly toward the dormant species. The polymerization can be accelerated if the TEMPO concentration is reduced. This can be achieved, for example, through the slow self-destruction of TEMPO by the gradual addition of additives or radicals. Such self-destruction is observed spontaneously during the thermally initiated, self-initiated polymerization of styrene.

The reactive radical initiates polymerization while the stable radical mediates the reactionby reacting with propagating radicals to lower their concentration. The overall processis analogous to ATRP. The nitroxide radical, although unreactive withitself, reacts rapidly with thepropagating radical to decrease the concentration of propagatingradicals sufficiently that conventional bimolecular termination is negligible. The propagatingradical concentration is much lower than that of the dormant species; specifically,Kis small,and this results in living radical polymerization with control of molecular weight and molecular weight distribution. The general characteristics of ATRP applyto NMP, that is, reaction variables control polymerization rate, molecular weight, and PDI inthe same way.

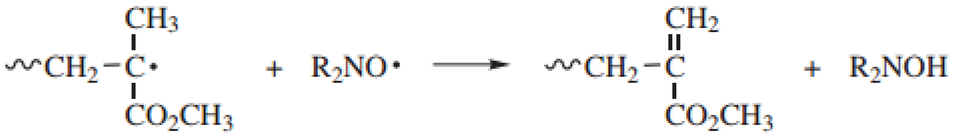


NMP with TEMPO generally requires higher temperatures (125–145°C) and longer reaction times (1–3 days) compared to ATRP, and only styrene and 4-vinylpyridine polymerizations proceed with good control of molecular weight and polydispersity. Narrow molecularweight distributions with PDI below 1.1–1.2 are difficult to achieve with other monomers.

The sluggishness of TEMPO systems is ascribed toKvalues being too low.Kvalues arelower than in ATRP. Various techniques have been used to increase Rp. Adding a conventional initiator with a long half-life (slowly decomposing) to continuously generate reactiveradicals throughout the reaction works well. Another technique is the addition of anacylating agents to reduce the concentration of nitroxide radicals via their acylation. Self-initiation in styrene polymerization also enhancesthe reaction rate. Polystyrene was prepared in the presence of 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO). It was well defined at high molar masses in the range of 20,000 to 30,000 g/mol, with a polydispersity index of 1.2.



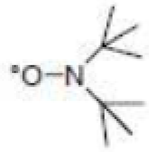
Scheme: 2,2,6,6-tétramethylpiperidine-1-oxyle (TEMPO)



$$\sim\!\!\sim CH_2-\underset{CO_2CH_3}{\overset{CH_3}{C}}\cdot \quad + \quad R_2NO\cdot \longrightarrow \sim\!\!\sim CH_2-\underset{CO_2CH_3}{\overset{CH_2}{\overset{\|}{C}}} \quad + \quad R_2NOH$$

Scheme: The equilibrium between the propagating chains and the dormant chains

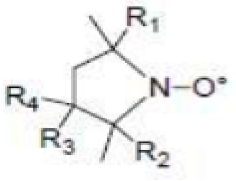
Di-tert-butyl nitroxide (DBN). It was synthesized well-defined polystyrenes at 80–100 °C in the presence of DBN, reaching molar masses of up to 70,000 g/mol with a polydispersity index of 1.2. Since the C–ON bond is more labile than that of TEMPO, DBN could be used to polymerize tert-butyl acrylate up to molar masses of 10,000 g/mol.



Scheme:di-*tert*-butyl nitroxide (DBN).

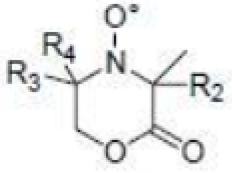
Five-membered cyclic compounds were synthesized, and the efficiency of different Proxyl derivatives was investigated. Depending on the nature of the substituents on the ring, the polymerization rates are either higher (for example, $R_1 = R_2 = \text{Ph}$, $R_3 = R_4 = \text{H}$) or lower ($R_1 =$

$R_2 = R_3 = R_4 = H$) than those observed in the presence of TEMPO. While molar mass control is maintained with styrene, a significant broadening of the molecular weight distribution is observed at the beginning of the polymerization (Ip = 2.2).



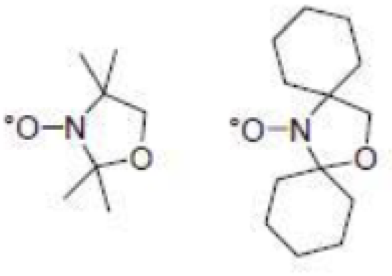
Scheme: Proxyl and its derivatives.

Five-membered cyclic nitroxides, known as "morphones," were obtained by incorporating an ester function into the ring. These molecules are capable of controlling the polymerization of n-butyl acrylate. Although the polymerization rate is relatively fast, the synthesized samples are not well defined (Ip = 1.7).



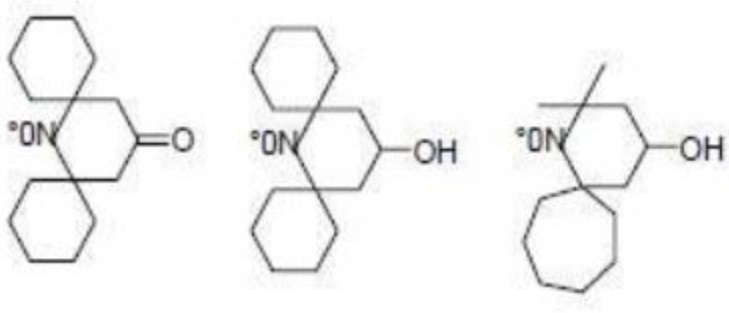
Scheme: Morphones

A new type of cyclic nitroxides was developed with the aim of polymerizing styrene at lower temperatures than those required with TEMPO (110 °C), in order to minimize the contribution from thermal self-initiation. The first nitroxide prevents styrene polymerization from occurring due to an excessively strong C–ON bond, whereas in the case of the second, the polymerization rate is governed by the self-initiation of styrene.



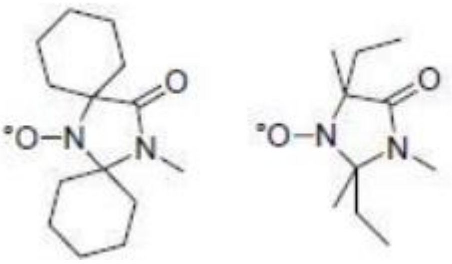
Scheme: nitroxides proposed by Yamada.

Nakaruma proposed other nitroxides with a spiro structure. Their efficiency appears to be more promising, as polystyrenes with molar masses reaching 100,000 g/mol and polydispersity indices of around 1.15 were synthesized at temperatures ranging from 70 to 110 °C.



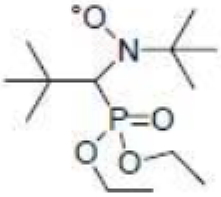
Scheme: nitroxides proposed by Nakaruma.

Imidazolidinones were tested in NMP (nitroxide-mediated polymerization). These nitroxides were found to control the polymerization of styrene at rates faster than those observed in the presence of TEMPO. They were used in the polymerization of tert-butyl acrylate, stopping the reaction at 40% conversion. For methyl methacrylate polymerization at 90 °C, chain growth hardly exceeded 20–30% conversion, with polydispersity indices ranging from 1.4 to 1.7.



Scheme: Imidazolidinones

SG1 proved to be effective in controlling the polymerization of styrene and n-butyl acrylate at 123 °C within reasonable reaction times (around 3 hours).

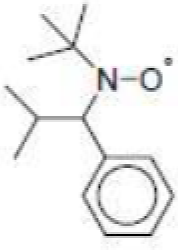


Scheme:N-tert-butyl-1-diethylphosphono-2,2-dimethylpropyl nitroxyde (SG1)

The use of a difunctional dialkoxyamine SG1 enabled the controlled synthesis of triblock copolymers (poly(styrene-b-n-butyl acrylate-b-styrene)) with a polydispersity index of 1.4.

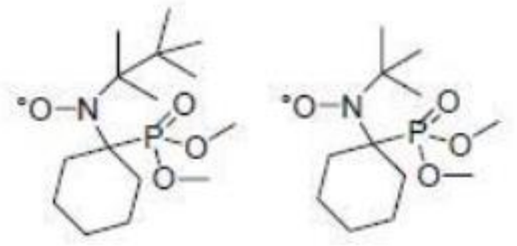
Scheme: a difunctional dialkoxyamine SG1

TIPNO proved to be “universally” effective in NMP. Although the polymerization times are relatively long (on the order of 10 hours), this nitroxide can reliably be used to control the polymerization of styrene at 123 °C with a polydispersity index of around 1.1, as well as the polymerization of n-butyl acrylate in the presence of a slight excess of free nitroxide (5 mol%).The range of monomers that can be polymerized in a controlled manner in the presence of TIPNO has expanded to include acrylamides, acrylonitrile, and 1,3-dienes such as isoprene and 1,3-butadiene. Well-defined block copolymers such as PABu-b-PS, poly(isoprene)-based copolymers, star-shaped architectures, and statistical copolymers like poly(styrene-co-maleic anhydride) have been successfully synthesized.



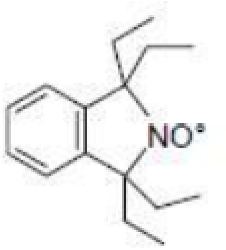
Scheme:2,2,5-Trimethyl-4-phenyl-3-azahexane-3-oxy(TIPNO).

The nitroxide proposed by Catala was developed for the purpose of polymerizing styrene at low temperatures (90 °C). This nitroxide enables molar masses of up to 160,000 g/mol with a polydispersity index of 1.6.



Scheme : Nitroxide proposed by Catala

The polymerization of styrene in its presence shows a linear increase in molar mass up to 50,000 g/mol at 80% conversion and 110 °C. The resulting molecular weight distribution is relatively narrow (Ip = 1.1–1.2).



Scheme: 1,1,3,3-tetraethylisoindoline-2-oxylnitroxide (TEISO).

IONIC POLYMERIZATION

Introduction:

The active center in this type of polymerization is positive or negative ions, known as carbonium or carbanion respectively.The ionic polymerization differs from free radical polymerization by that:

1- The system of polymerization is heterogeneous because the initiators are always inorganic materials.

2- Very high rate of reaction and very high Mwt polymer.

3- Presence of co catalyst beside the initiator or the catalyst. The co catalyst form ion pair as a counter ion with the growing ion. The propagation step is the insertion of the monomer between the ion pair to form a new active center.

Cationic polymerization

Cationic polymerization is a chain-growth polymerization mechanism in which the active center is a positively charged species (a carbocation). This type of polymerization is especially important for monomers that can stabilize a positive charge through electron-donating groups.It is widely used to produce polymers such as:

- Polyisobutylene
- Poly(vinyl ethers)
- Certain styrenic polymers

Monomers Suitable for Cationic Polymerization

Not all monomers can undergo cationic polymerization. Suitable monomers must be able to stabilize a carbocation intermediate.Common monomer types

- Isobutylene
- Vinyl ethers (–OR substituent)
- Styrene and substituted styrene
- Dienes (under specific conditions)

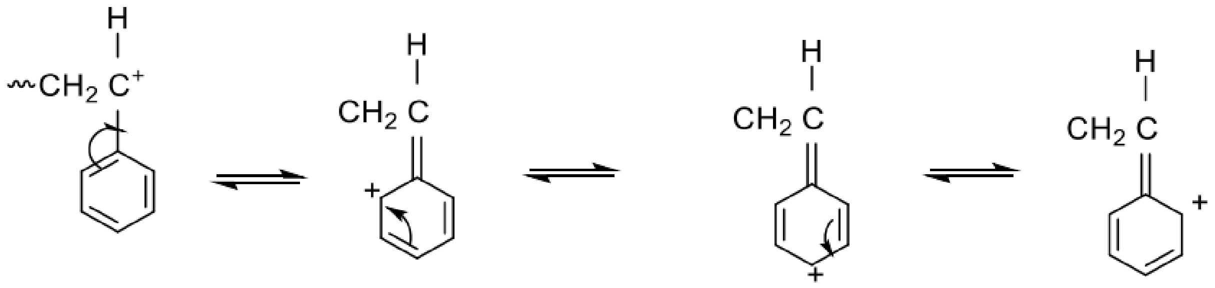
Effect of substituents

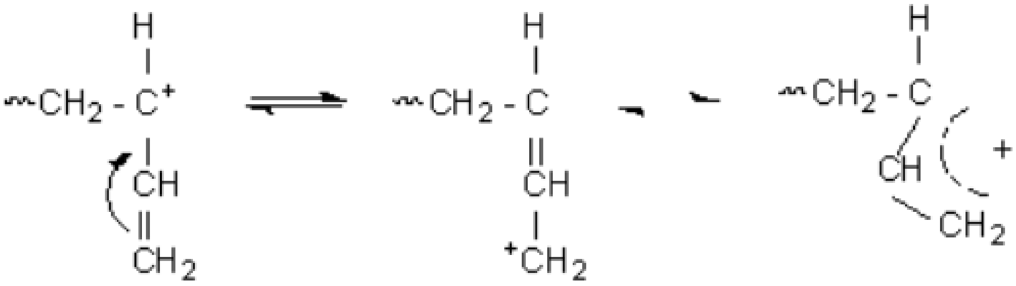
- Electron-donating groups (EDG) → increase reactivity; Examples: $-CH_3$, –OR, –Ar
- Electron-withdrawing groups (EWG) → decrease or inhibit polymerization; Examples: –CN, –COOR

The active center in this type of polymerization most be positive ion. These positive centers may be on carbon atom or other atoms like nitrogen or oxygen or sulfur asbelow:

$R_3C^+H_3C^+R_3S^+R_3O^+$
carbenium carbonium sulfonium oxonium

These positive ions are kinetically unstable. The presence of neighbor denoting group like OR, SRphenyl, or N_2R increase the stability of the ions through resonance (delocalization) or inductive effect.





Mechanism

Initiation step

There are many types of initiators can be used as below:

- Organic salt that can supply stable carbenium ions: like CH_3CO^+, ClO_4or $[(C_6H_5)_3C]^+[ClO_4]^-$which can be dissociate in polar solvent to positive and negative ions:

$$[(C_6H_5)_3C]^+ [ClO_4]^- \longrightarrow (C_6H_5)_3C^+ + ClO_4^-$$

- **Lewis's acids:** like $AlCl_3$, BF_3, $SnCl_4$, $TiCl_4$

This catalyst must be ionized before attack with the monomers

$$2AlCl_3 \rightarrow AlCl_2^+ + AlCl_4^-$$

$$2BF_3 \rightarrow BF_2^+ + BF_4^-$$

These initiators are used to initiate the polymerization at low temperature and to get high Mw. polymers.

Co catalyst must be used with this type of initiator like water, ether, or some alkyl halide. The co catalyst form complex with the initiator (ion pair)

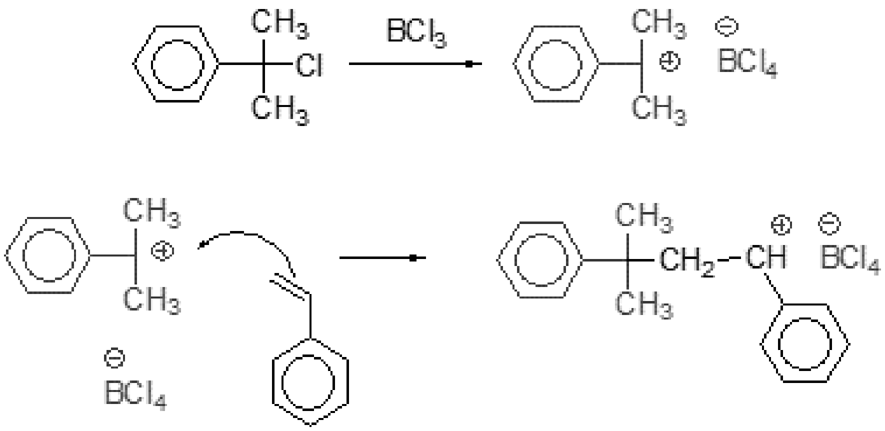
$$H_2O + TiCl_4 \rightleftharpoons H^+ TiCl_4OH^-$$

$$HCl + TiCl_4 \rightleftharpoons H^+ TiCl_5^-$$

The proton was added to the monomer and the negative ion stay behind the new positive active center.

It was noticed that isobutylene did not polymerize in presence of dry BF_3, but polymerized directly in presence of some drops of water with BF_3.

Another co-catalyst can give a carbocation



Propagation:

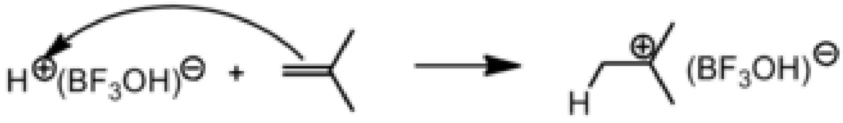
The propagation step in cationic polymerization involves the addition of monomer units to an active cationic site on the growing polymer chain. During this step, the monomerreacts with the cationic center, leading to the formation of a new cationic site at the end of the polymer chain. This new cationic site then reacts with another butadiene monomer, continuing the chain growth.

In the case of butadiene, the propagation typically occurs by alternating the addition of monomers in a head-to-tail fashion, although some regioselectivity can occur depending on the reaction conditions. As the polymerization progresses, the chain grows longer, and the active cationic site remains at the end of the polymer, continuing to propagate the polymer chain.

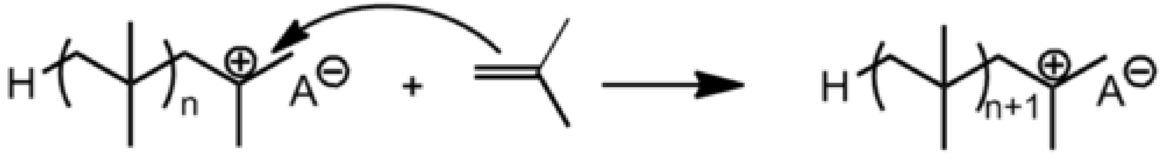
This process is typically facilitated by the presence of a suitable cationic initiator, and is highly sensitive to temperature and solvent conditions, which can affect the polymer's molecular weight and structure.

Initiation of butadiene

$$BF_3 + H_2O \rightleftharpoons H^{\oplus}(BF_3OH)^{\ominus}$$



Propagation step



Effect of temperature:

The temperature of the reaction has an effect on the rate of propagation. The overall activationenergy for the polymerization (E) is based upon the activation energies for the initiation (Ei), propagation (Ep), and termination (Et)steps:

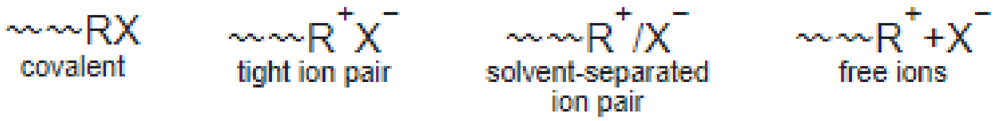
$$E = Ei + Ep - Et$$

Generally, Et is larger than the sum of Ei and Ep, meaning the overall activation energy isnegative. When this is the case, a decrease in temperature leads to an increase in the rate of propagation. The converse is true when the overall activation energy is positive.

Chain length is also affected by temperature. Low reaction temperatures, in the range of 170–190 K, are preferred for producing longer chains. This comes as a result of the activation energy for termination and other side reactions being larger than the activation energy for propagation. As the temperature is raised, the energy barrier for the termination reaction is overcome, causing shorter chains to be produced during the polymerization process.

Effect of solvent and counterion

The solvent and the counterion (the gegen ion) have a significant effect on the rate of propagation. The counterion and the carbenium ion can have different associations according to intimate ion pair theory; ranging from a covalent bond, tight ion pair (unseparated), solvent-separated ion pair (partially separated), and free ions (completely dissociated).

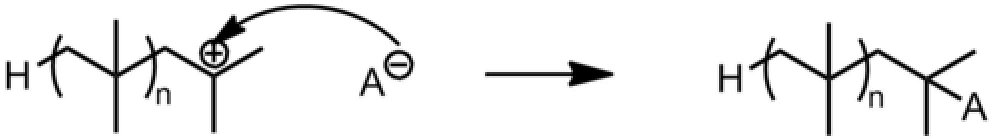


Scheme: Range of associations between carbenium ion (R+) and gegen ion (X-)

The association is strongest as a covalent bond and weakest when the pair exists as free ions. In cationic polymerization, the ions tend to be in equilibrium between an ion pair (either tight or solvent-separated) and free ions. The more polar the solvent used in the reaction, the better the solvation and separation of the ions. Since free ions are more reactive than ion pairs, the rate of propagation is faster in more polar solvents. The size of the counterion is also a factor. A smaller counterion, with a higher charge density, will have stronger electrostatic interactions with the carbenium ion than will a larger counterion which has a lower charge density. Further, a smaller counterion is more easily solvated by a polar solvent than a counterion with low charge density. The result is increased propagation rate with increased solvating capability of the solvent.

Termination

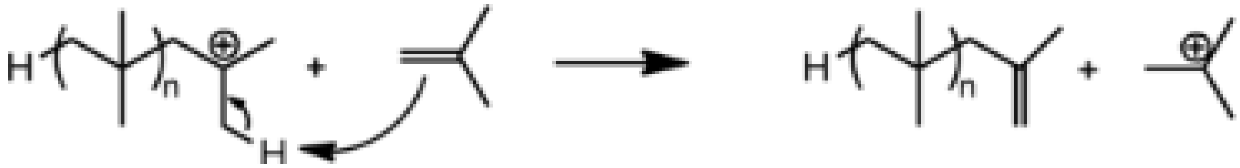
Termination generally occurs by unimolecular rearrangement with the counterion. In this process, an anionic fragment of the counterion combines with the propagating chain end. This not only inactivates the growing chain, but it also terminates the kinetic chain by reducing the concentration of the initiator-coinitiator complex.



Chain transfer

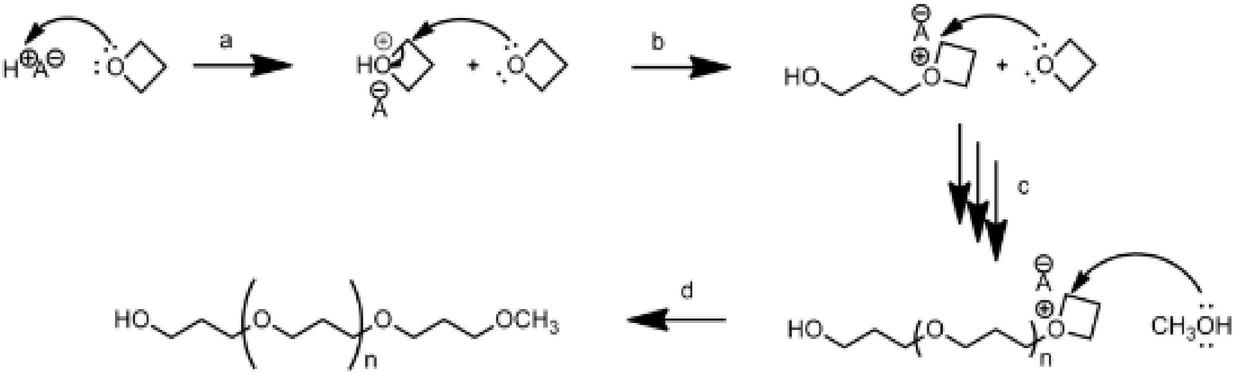
Chain transfer can take place in two ways. One method of chain transfer is hydrogen abstraction from the active chain end to the counterion. In this process, the growing chain is terminated, but the initiator-coinitiator complex is regenerated to initiate more chains.

The second method involves hydrogen abstraction from the active chain end to the monomer. This terminates the growing chain and also forms a new active carbenium ion-counterion complex which can continue to propagate, thus keeping the kinetic chain intact.



Cationic ring-opening polymerization

Cationic ring-opening polymerization follows the same mechanistic steps of initiation, propagation, and termination. However, in this polymerization reaction, the monomer units are cyclic in comparison to the resulting polymer chains which are linear. The linear polymers produced can have low ceiling temperatures, hence end-capping of the polymer chains is often necessary to prevent depolymerization.



Scheme: Cationic ring-opening polymerization of oxetane involving (a and b) initiation, (c) propagation, and (d) termination with methanol

Kinetics:

The rate of propagation and the degree of polymerization can be determined from an analysis of the kinetics of the polymerization. The reaction equations for initiation, propagation, termination, and chain transfer can be written in a general form:

$$I^+ + M \xrightarrow{k_i} M^+$$
$$M^+ + M \xrightarrow{k_p} M^+$$
$$M^+ \xrightarrow{k_t} M$$
$$M^+ + M \xrightarrow{k_{tr}} M + M^+$$

In which I^+ is the initiator, M is the monomer, M^+ is the propagating center, and k_i, k_p, k_t, and k_{tr} are the rate constants for initiation, propagation, termination, and chain transfer, respectively. For simplicity, counterions are not shown in the above reaction equations and only chain transfer to monomer is considered. The resulting rate equations are as follows, where brackets denote concentrations:

$$Ri = k_i[I^+]\,[M]$$

$$Rp= k_p\,[M][M^+]$$

$$Rt = k_t\,[M^+]$$

$$Rtr = k_{tr}[M^+][M]$$

At the steady state Ri =Rt

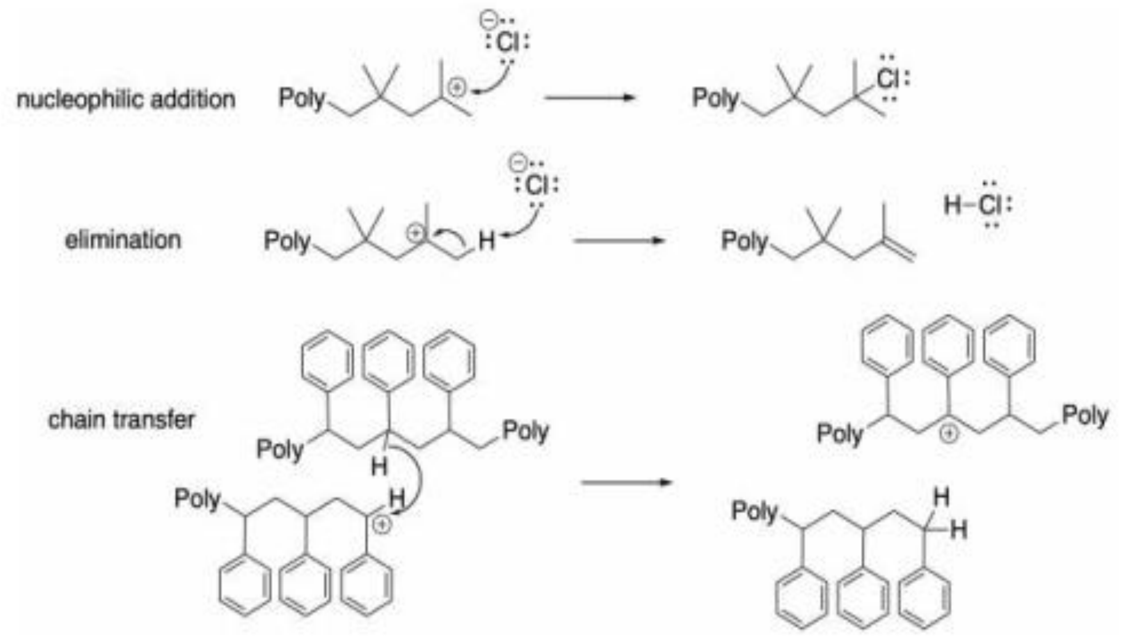
$$[M^+]= (\,k_i[I^+]\,[M])/\,k_t$$

Living Cationic polymerization

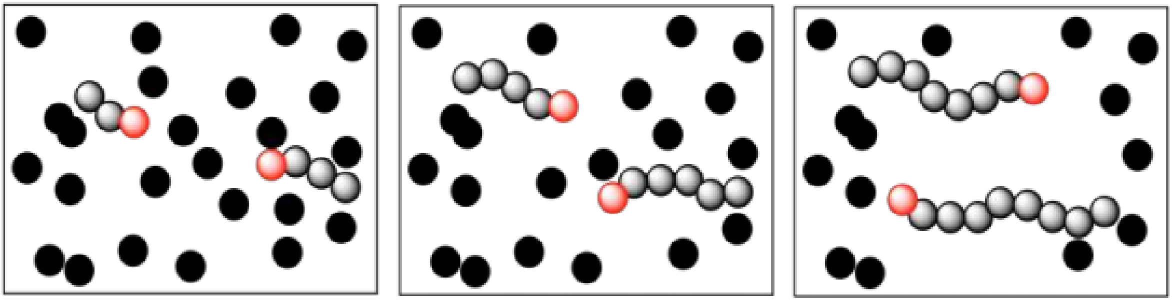
Description

Taking the example of the alkene's polymerization:

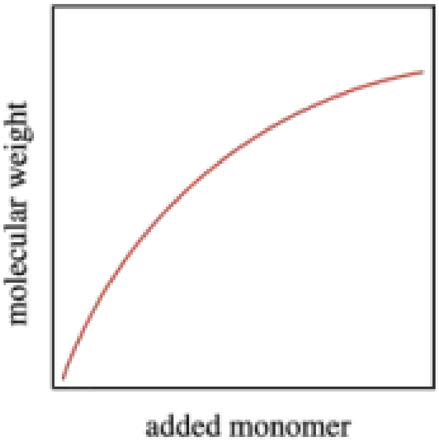
Alkenes are a common polymer feedstock, used to make a range of very familiar plastics in everyday use. Because their propertiesdepend strongly on their molecular weights and molecular weight distributions, it is very important to be able to control the growthof these long-chain polymers from their alkene monomers. Termination events, such as combination of the cation with anucleophile, elimination, or chain transfer, all contribute to a widening disperity between chains that have undergone these eventsand those that continue to grow.



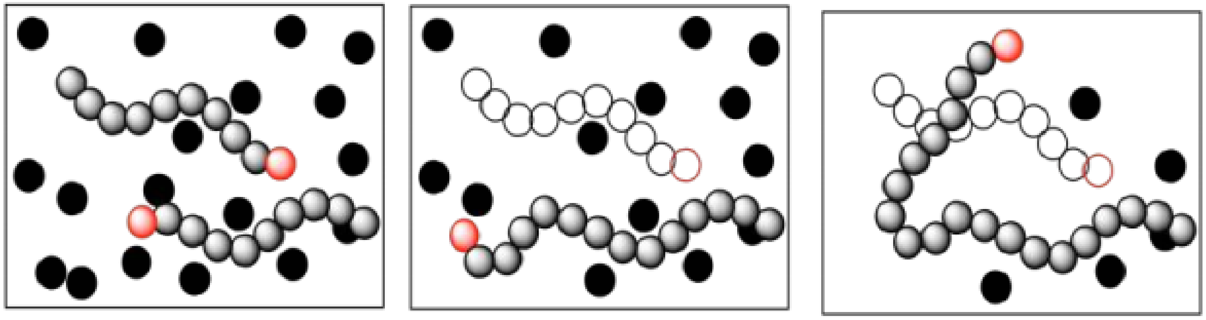
In any polymerization, as in any other reaction, we are dealing with thousands of reactions involving thousands of differentmolecules all happening at the same time. Several reactive chains growing in tandem would be expected to grow at similar rates,and ultimately, they would reach similar degrees of polymerization. That means they would all have the same number of monomersincorporated into the final polymer chain and so theywould all have similar molecular weight.



What happens when one of these growing chains undergoes some kind of termination event? Chain death, as this problem iscommonly called, has a couple of direct consequences. Obviously, the chain that stopped growing does not keep up with the others,so its molecular weight is lower than the rest. That fact alone might lead us to believe the average molecular weight would be lower than we had expected in this polymerization. If we added more and more polymer to the polymerization overtime, we wouldn'texpect the molecular weight to keep increasing, becausetheiractive sites keep getting quenched.



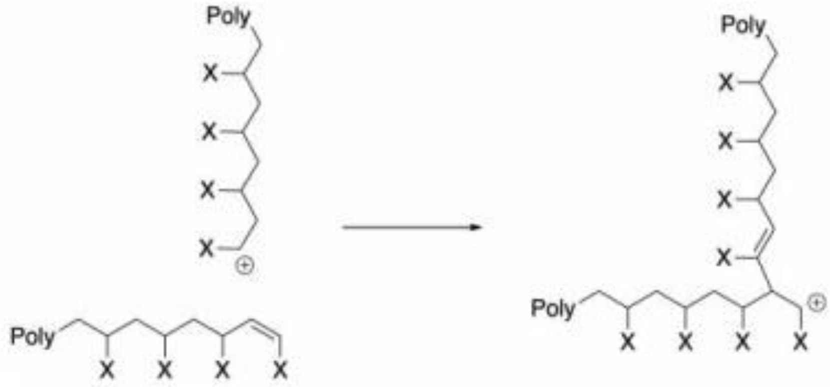
More subtly, that growing chain had been slated to enchain a certain number of monomers, some of which are still left in thesystem when it dies. What happens to them? Of course, the other growing chains will each get some extra monomers. That meansthe dispersity problem gets even worse; one chain stops growing and is shorter than anticipated, but others gobble up the extramonomers and become longer than anticipated. Dispersity, the distribution of molecular weights, gets wider.



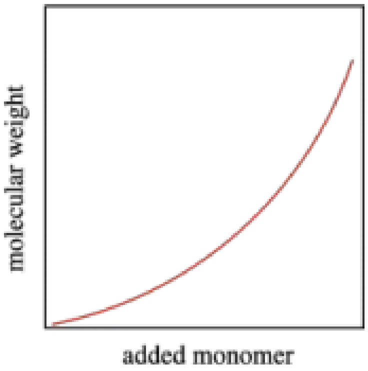
chain death

widening dispersity

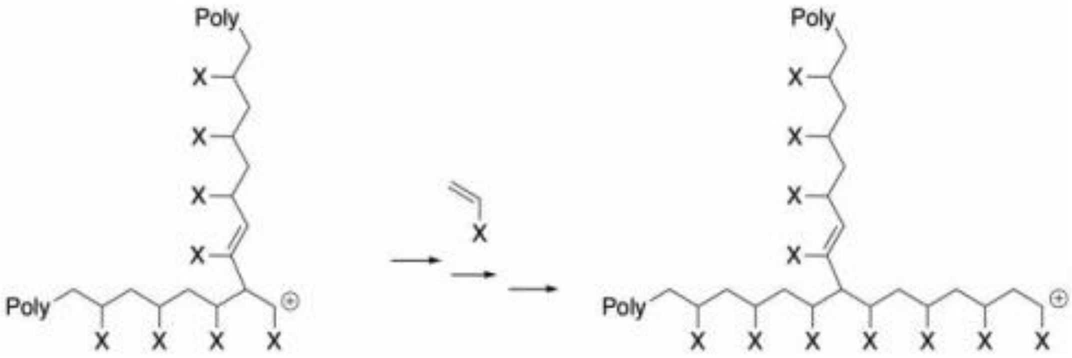
The problem can be even worse when a termination occurs through elimination, resulting in the formation of a new alkene.Because that new alkene is already found at the end of a polymer chain, when it combines with a cationic chain end the polymermolecular weight effectively doubles.



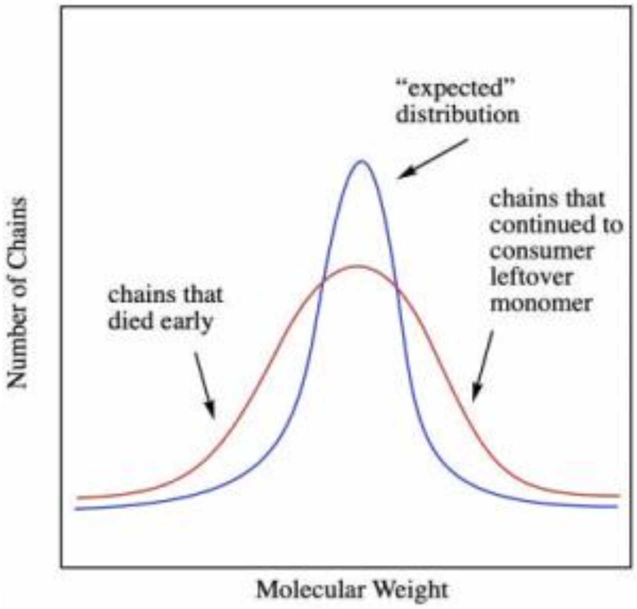
In other words, although we would reasonably expect molecular weight to stop increasing as chains die, resulting in lowermolecular weight than expected, the opposite can also happen. We can observe an increase in molecular weight, because the chainsthat are left are consuming all of the monomer, becoming much bigger, and occasionally two chains are combining to dramaticallyincrease molecular weight. Molecular weight increase is proceeding in an uncontrolled and somewhat unpredictable way.



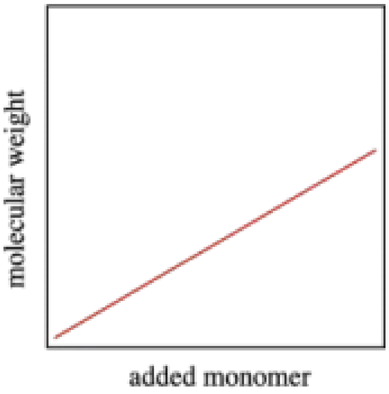
Furthermore, the reaction of a cationic growing chain with a macroalkene results in a sudden shift in polymer morphology. Insteadof a straight chain, we now have a dramatically branched polymer. That change in morphology has a severe impact of polymerproperties.



All of these factors mean that the distribution of molecular weights gets broader when chain reactions undergo unexpectedtermination. The term for the width of molecular weight distribution is dispersity (D), sometimes called polydispersity index (PDI).In the graph below, the red line describes a sample from a polymerization that was not as well controlled asthe one described bythe blue line. There are a lot more polymer chains that are both longer and shorter than the average.



In an ideal polymerization, growing chains wouldn't dieunexpectedly. They would continue to grow, and we could easily predicthow long each chain would become based on how much monomer and initiator we added. Each initiator molecule would start onegrowing chain, and each growing chain would enchain its portion of the monomers. The molecular weight would be predictedeasily because the polymer chains would grow linearly withadded monomer. A polymerization in which there is a linearrelationship between added monomer and molecular weight, even as the molecular weight becomes very high, iscalled a "livingpolymerization".



A second feature of living polymerization is that dispersity (or PDI) stays relatively constant throughout the course of a reaction.Because there are no chain terminations, the reactivechains all continue to grow at the same pace, and the polymers that result areof uniform molecular weight.

In order to achieve a living cationic polymerization, we would have to prevent unwanted terminations steps. There are a variety ofsystems that accomplish this goal, but they share some common features. Essentially, these methods intentionally allow anucleophile to combine with the cationic chain end, but use a Lewis acid to reactivate the resulting compound and regenerate thegrowing chain end.

Like other cationic polymerizations, these processescould be initiated by addition of a protic acid toan alkene to generate a cation.That initial cation would then begin reacting with the nucleophilic alkenes around it, generating subsequent cations that sustain achain reaction. In practice, it's instead very common to add an ionizable compound, such as a tertiary alkyl halide, along with aLewis acid co-initiator. The Lewis acid promotes ionization of the initiator, forming a cation.

Once that cation has formed, regardless of how it got there, it can begin to react with the monomers around it. The chain reactionwill continue, consuming more and more monomers, resulting in a longer growing chain with higher molecular weight.

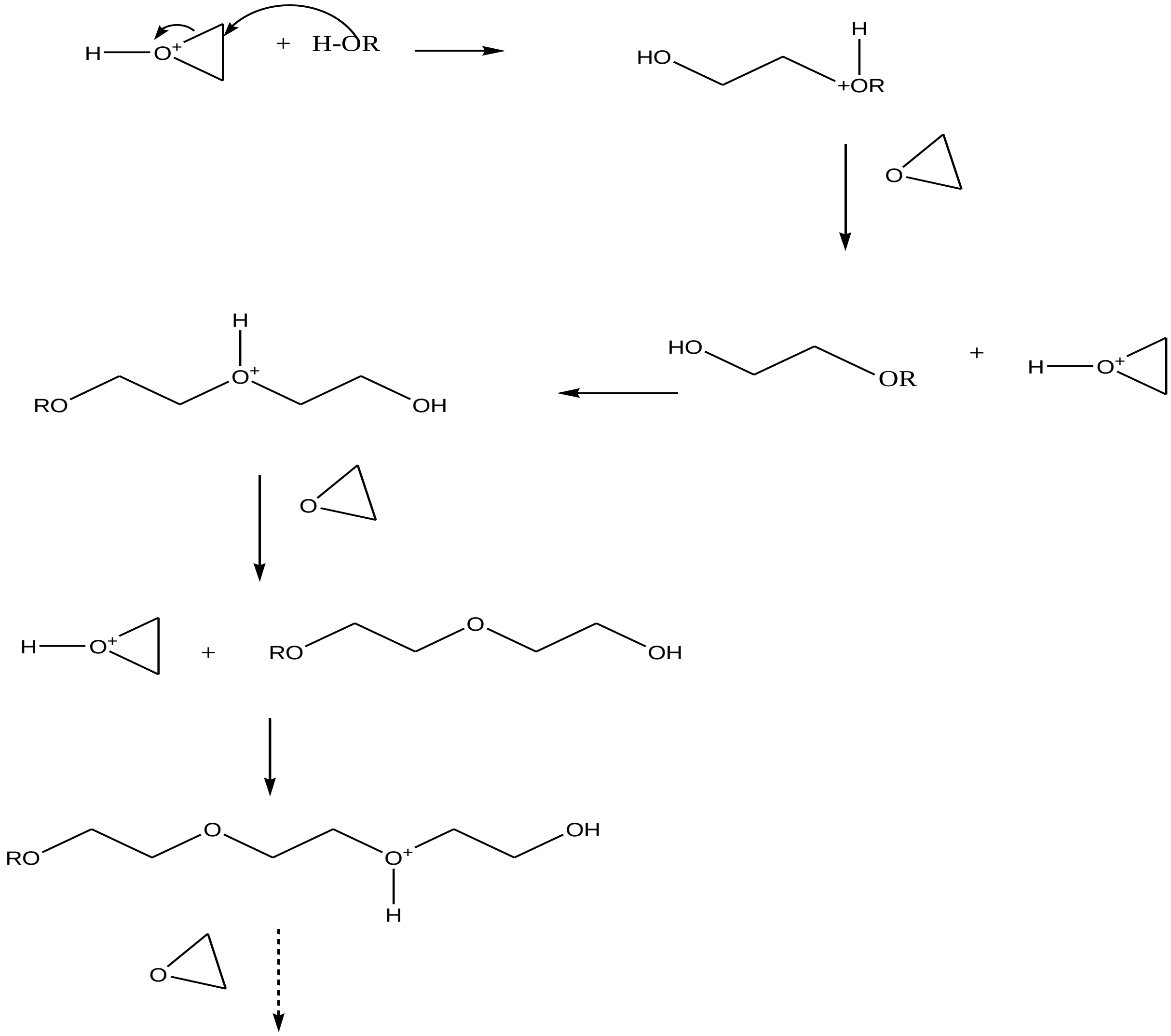
Lewis acid-base adducts always form reversibly, however. Atsome point, the adduct can give back to the cationicchain end thesame anionic group that it once extracted from the initiator. The chain stops growing, because it no longer contains a reactive site.

However, just as the Lewis acid once extracted an anionic group from the initiator, it can extract it from this polymer chain. Whenit does, the cationic chain end will start reacting with more monomers, and the chain will grow again.

Living cationic polymerization depends on an equilibrium between a reactive, growing phase and an unreactive, dormant phase.There is an inherent trade-off here. The concentration of reactive cationic chain ends is lowered because a large fraction of thechains is always dormant. That low concentration of cations means there is less opportunity for chain termination events; that'shelpful in keeping dispersity low. On the other hand, that low concentration of cations also means the polymer grows much moreslowly than it would otherwise.

Control by monomer activation

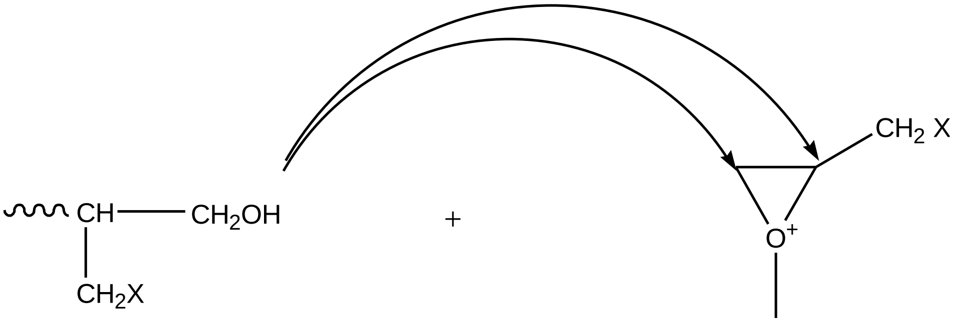
This involves a Bronsted acid in the presence of an alcohol or polyol and leads to a significant reduction in the formation of macrocycles.



Scheme: control of the polymerization of ethylene oxide by monomer activation.

The proton generated in the reaction medium complexes with the oxygen of the epoxide group, forming an oxonium ion, which activates the epoxide ring. The alcohol then attacks the activated monomer.Initiation results from the addition of the activated monomer to the hydroxyl group of the alcohol.Propagation continues by successive addition of the protonated monomer to the hydroxyl group of the growing chain.

The above mechanism applies to ethylene oxide but becomes more complex in the case of substituted monomers.Certain additions may be favored over others.



Example of polymerization:

In this table, we present different polymerizations:

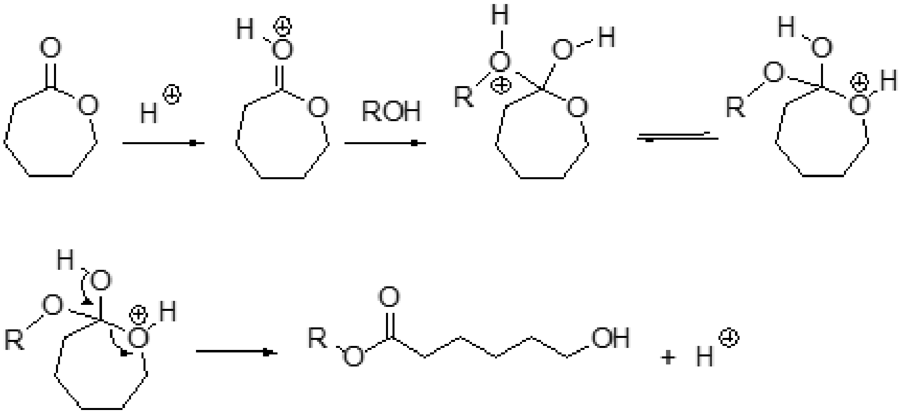
Monomer	Initiator	Alcohol	T (°C)	Mn	DPI
Propylene oxyde	$B(C_6F_5)_3$	Methanol	23	2300	1.28
Propylene oxyde	$B(C_6F_5)_3$	1,4 butanidiol	23	2800	1.25
Epichloridrin	$SnCl_4$	1,4 butanidiol	30	2100	1,41
Epichloridrin	BF_3(EtOH)	1,4 butanidiol	65	1200	1.20

For propylene oxide, using methanol as the alcohol gives a number-average molar mass (Mn) of 2,300 g/mol with a PDI of 1.28, while using 1,4-butanediol slightly increases (Mn) to 2,800 g/mol and reduces the PDI to 1.25. This indicates that the bifunctional 1,4-butanediol allows slightly higher molar mass and a narrower molecular weight distribution, likely due to better control over polymer growth.

For epichlorohydrin, the choice of initiator has a strong influence on the polymerization. With $SnCl_4$, the polymer reaches (Mn = 2,100) g/mol and PDI = 1.41, whereas with $BF_3 \cdot EtOH$, (Mn) is lower at 1,200 g/mol but with improved control (PDI = 1.20). This suggests that $BF_3 \cdot EtOH$ acts as a milder or more selective initiator compared to $SnCl_4$.

Temperature also plays a role, as epichlorohydrin polymerizations are conducted at higher temperatures (30–65 °C) than those of propylene oxide (23 °C). However, the lower PDI obtained with $BF_3 \cdot EtOH$ at 65 °C shows that the initiator choice has a greater effect on polymer control than temperature alone.

Overall, the results indicate that the combination of alcohol type and initiator strongly affects both the molar mass and the distribution, with diols and milder Lewis acids generally giving better control.



Scheme: Control of caprolactone by monomer activation

Anionic polymerization

Principle and Mechanism

Anionic polymerization generally occurs through three main steps: initiation, propagation, and termination (which may be absent in living systems). Anionic polymerization occurs when a negatively charged active center (carbanion) propagates through successive additions of monomer molecules.

The polymerizability of a monomer in this type of polymerization depends largely on the stability of the carbanion formed during propagation and the electronic nature of the substituentsattached to the double bond.

Monomers that contain electron-withdrawing groups (EWG) conjugated with the double bond are particularly suitable for anionic polymerization.

These groups stabilize the negative charge of the growing chain through resonance and inductive effects, lowering the energy of the transition state and favoring propagation.

Typical examples include:

- Acrylonitrile ($CH_2=CH–CN$)
- Methyl methacrylate ($CH_2=C(CH_3)COOCH_3$)
- Styrene ($CH_2=CH–C_6H_5$) (under controlled conditions)
- Butadiene ($CH_2=CH–CH=CH_2$) and isoprene

On the other hand, monomers containing electron-donating groups (EDG) such as alkyl or alkoxy substituents tend to destabilize the carbanion, making them unsuitable for anionic polymerization.

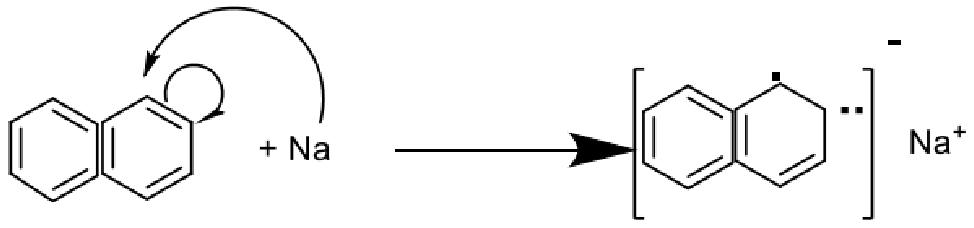
The general trend of polymerizability in anionic polymerization can be summarized as follows:

Monomers with strong electron-withdrawing substituents are highly reactive, while those with electron-donating substituents are either poorly reactive or inert.

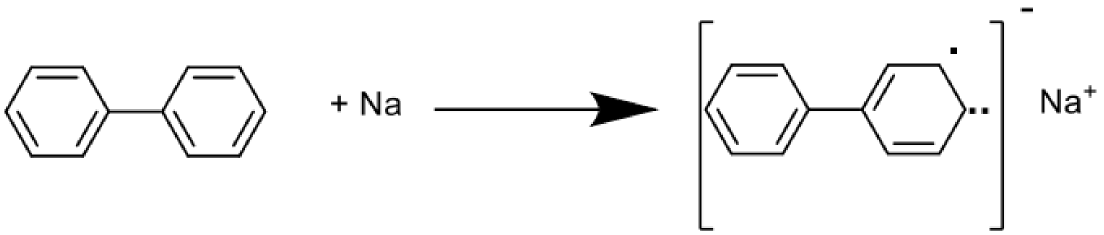
Control of reaction conditions particularly: solvent polarity, temperature, and absence of protic impurities is also essential, since anionic polymerization is extremely sensitive to traces of moisture and oxygen.

Initiation: The process begins when an anionic initiator, such as an alkali metal (Li, Na, K), an organolithium compound (e.g., n-butyllithium), or an alkali metal amide, reacts with a monomer containing an electron-withdrawing group. The initiator donates an electron or an anionic fragment to the monomer, generating a carbanion at the end of the polymer chain. They can:

a) Alkali metals, like sodium which start the reaction by transfer the electron from the metal to the monomer. Before this step there is the co-catalyst like naphthalene, anthracene or biphenyl, whereby the electron transfer to them from the metal to form aromatic free radical anion.

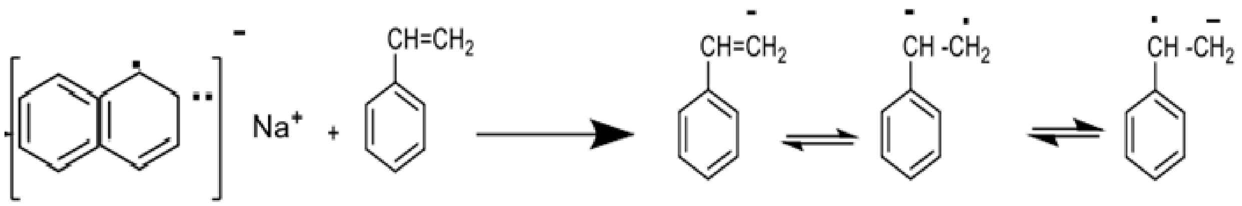


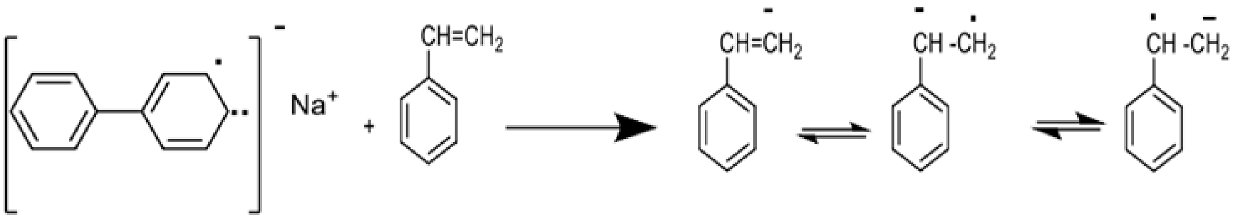
sodium naphthalene



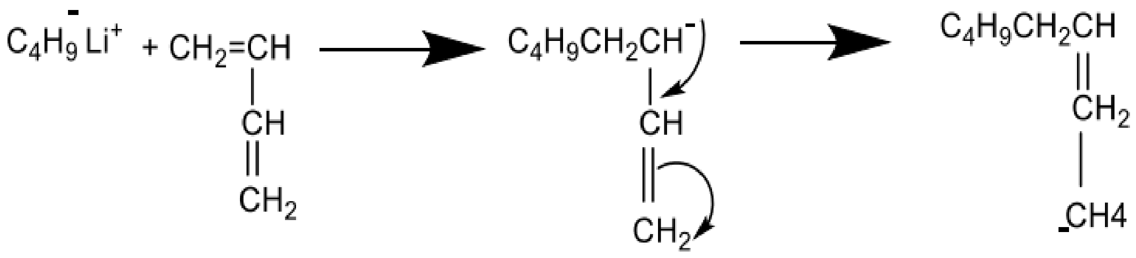
sodium biphenyl

The electron transfer from the free radical anion to the monomer.



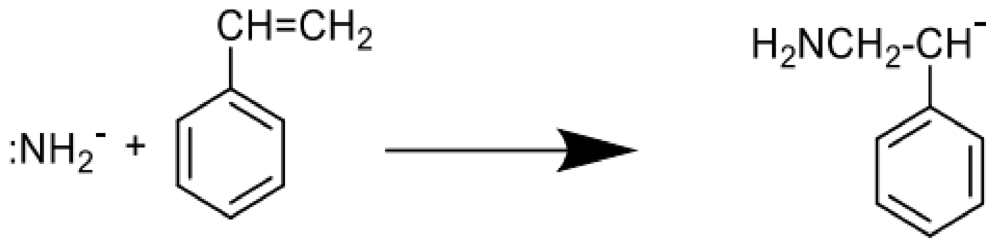


b) Metal alkyls, like Butyl lithium or triphenyl methyl sodium



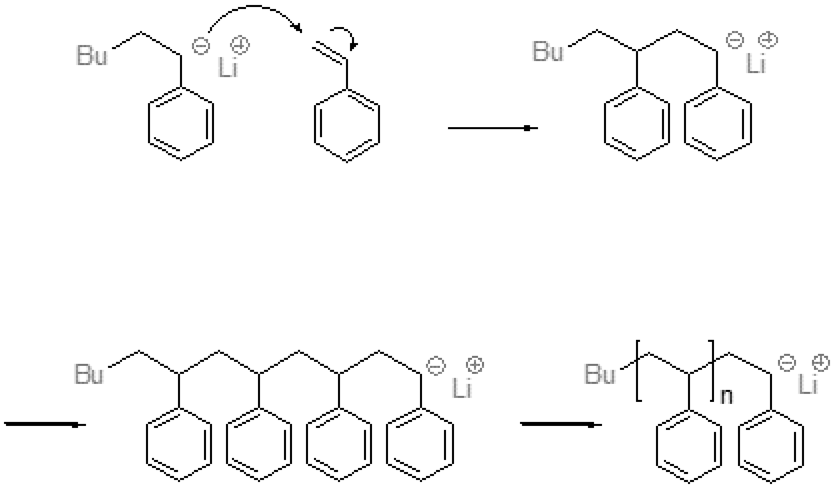
c) Metal amide, like sodium amide or potassium amide

$$KNH_2 \rightleftharpoons K^+ + :NH_2^-$$

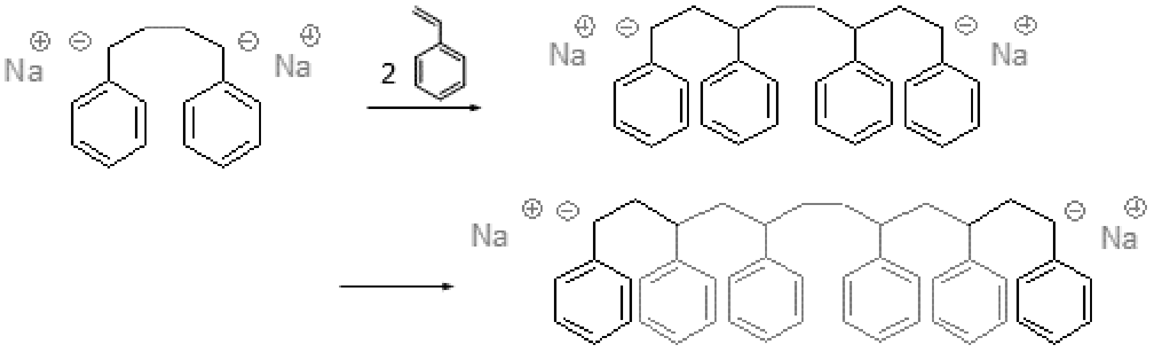


Propagation:

The carbanion formed in the initiation step adds to successive monomer molecules, extending the polymer chain:



Scheme:chain propagation with Bu-Li initiator



Scheme:chain propagation with naphthalene sodium initiator

Because the carbanionic center remains highly reactive, the chain continues to grow as lo.ng as monomer is available.

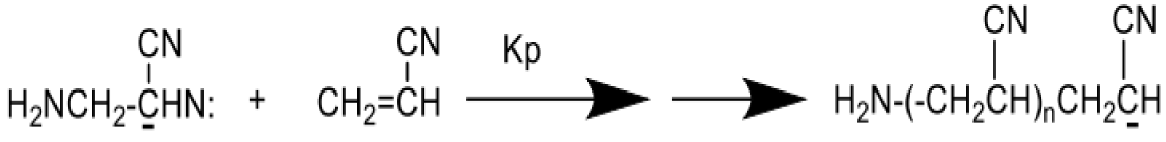
Reaction mechanism and kinetics: Take acrylonitrile as an example

Initiation step

$$\overset{-}{:NH_2} + CH_2{=}\overset{CN}{\overset{|}{CH}} \xrightarrow{Ki} H_2NCH_2\text{-}\overset{CN}{\underset{-}{C}}HN:$$

$$Ri = Ki[C][M]$$

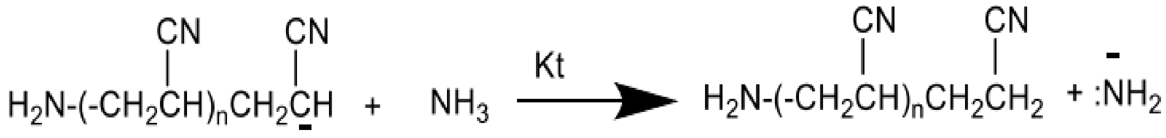
Propagation step:



$$H_2NCH_2\text{-}\underset{-}{\overset{CN}{C}}HN: + CH_2{=}\overset{CN}{C}H \xrightarrow{Kp} \longrightarrow H_2N\text{-}(\text{-}CH_2\overset{CN}{C}H)_nCH_2\underset{-}{\overset{CN}{C}}H$$

$$Rp = Kp[M][M-]$$

Termination step: occurred through solvent transfer



$$H_2N\text{-}(\text{-}CH_2\overset{CN}{C}H)_nCH_2\underset{-}{\overset{CN}{C}}H + NH_3 \xrightarrow{Kt} H_2N\text{-}(\text{-}CH_2\overset{CN}{C}H)_nCH_2\overset{CN}{C}H_2 + :\overset{-}{N}H_2$$

$$Rt = Kt[NH_3][M-]$$

At steady state Ri =Rt

$$[M^-] = \frac{Ki[C][M]}{Kt[NH3]}$$

Substitution in rate polymerization equation

$$Rp = \frac{Kp[M]Ki[C][M]}{Kt[NH_3]} = \frac{K^{/}[M]^2[C]}{[NH_3]}$$

Degree of polymerization

$$\overline{Dp} = \frac{Rp}{Rt} = \frac{Kp[M][M^-]}{Kt[NH_3][M^-]} = \frac{k^{\backslash}[M]}{[NH_3]}$$

Termination and Living Character: In a classical chain-growth polymerization, termination occurs through combination or disproportionation. However, in living anionic polymerization, no termination or chain transfer reactions occur, meaning the active carbanion remains at the chain end indefinitely, unless deliberately terminated.

This feature allows precise control over molecular weight, easy synthesis of block copolymers by sequential monomer addition, and narrow molecular weight distributions (typically $Đ < 1.1$).

The control of anionic polymerization depends on maintaining strict reaction purity and solvent conditions, since any trace of water, oxygen, or protic impurities can neutralize the carbanion and terminate the reaction.

Solvent effect: Polar solvents like tetrahydrofuran (THF) can stabilize the carbanion and influence the polymerization rate and stereochemistry. Nonpolar solvents like cyclohexane are used to obtain polymers with specific microstructures.

Temperature: Low temperatures are often used to slow down propagation and minimize side reactions.

Initiator type: Organolithium compounds (such as n-butyllithium or sec-butyllithium) are the most common initiators, providing high control over molecular weight and initiation efficiency.

Monomer purity: Monomers must be rigorously purified to remove inhibitors or moisture. Even trace amounts of water or oxygen can completely destroy the living character of the polymerization.

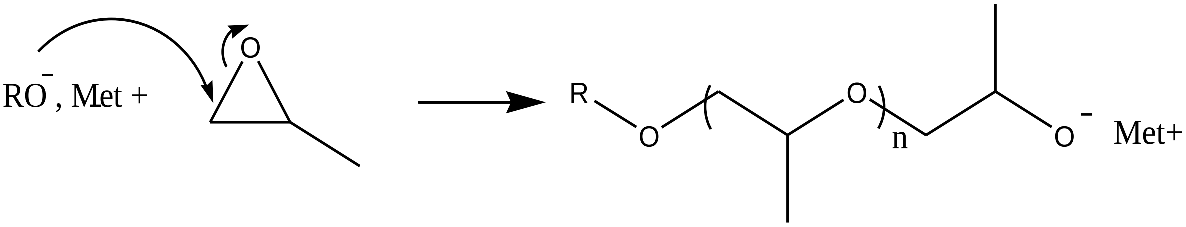
Control of Anionic Polymerization

Anionic polymerization is a living polymerization that involves a limited number of transfer reactions. To render it controlled, it is necessary to modify the initiator.

Initiation by alkali metal alkoxides:

- Alkyl, aryl, or polyolates of alkali metals are considered as initiators for anionic polymerization.
- The most commonly used alkali metals are sodium, potassium, and cesium.
- The solvents employed are polar aprotic solvents, such as DMSO or THF.

- The polymerization rate is proportional to the basicity of the alkoxide.



R = H, alkyl, polymer

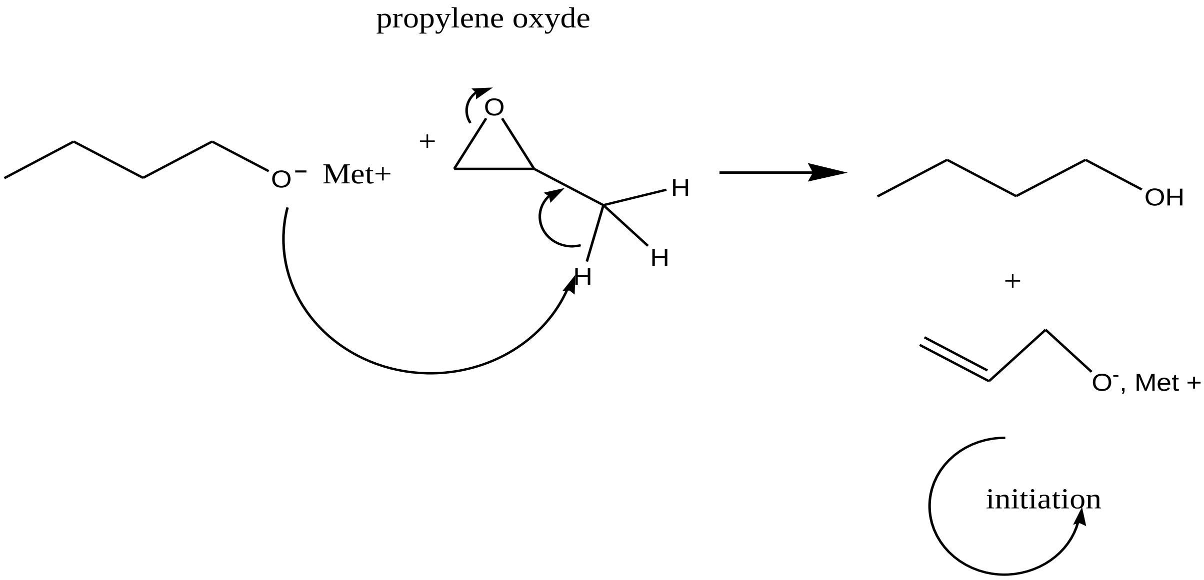
Met = Na, K, Cs

Transfer reactions are influenced by several parameters:

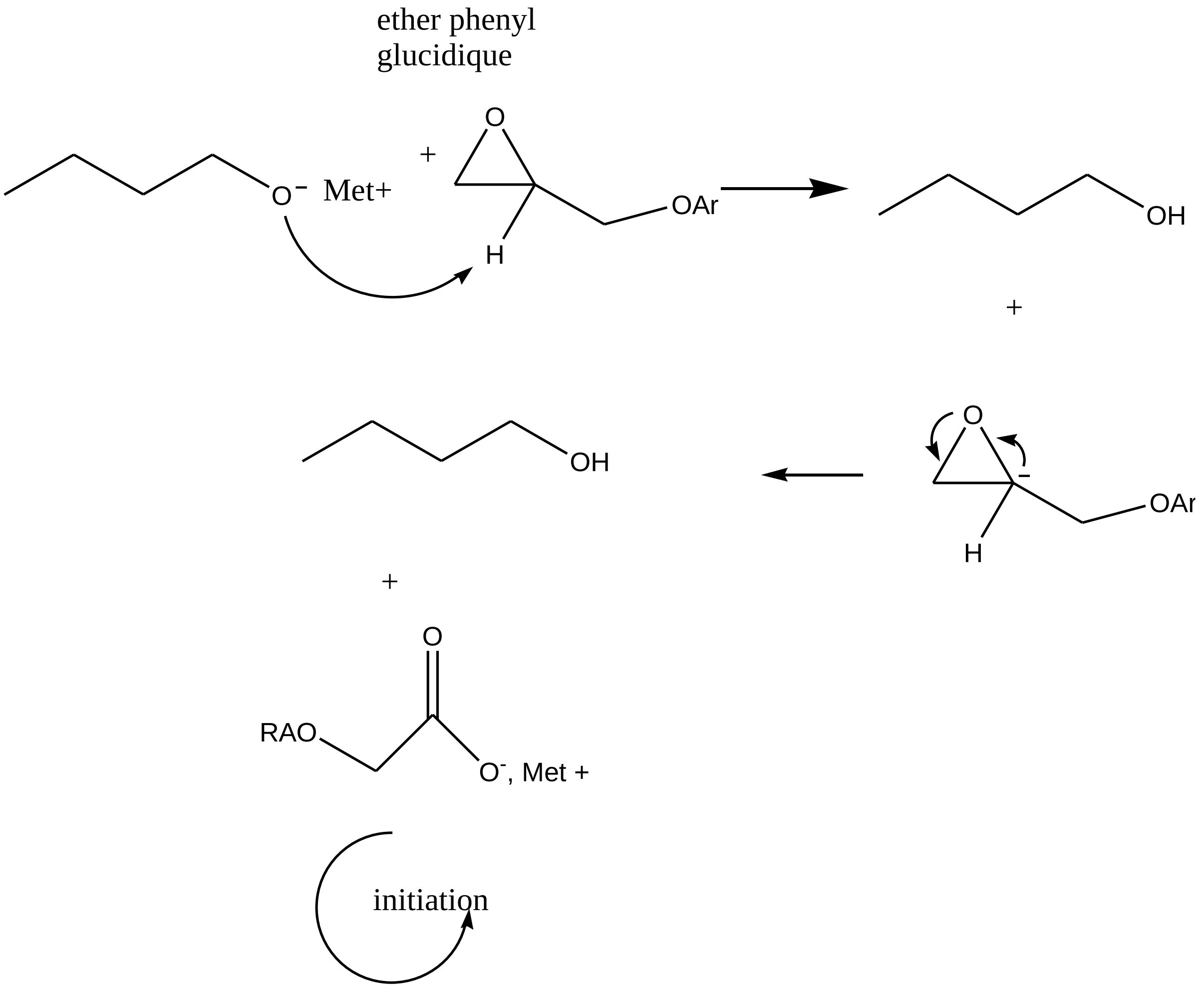
- Polymerization temperature
- The counterion: transfer decreases in the following order: $Na^+ < K^+ < Cs^+$

Possible transfer reactions

Example 1



Example 2



In many cases, alcohol is added to enhance the solubility of alkali metal alkoxides and to prevent their aggregation. This addition improves the efficiency of the initiating system by ensuring better dispersion of the active species within the reaction medium, which in turn contributes to a more controlled polymerization process.

An exchange between the alkali metal cation of an alkoxide and the proton of the alcohol leads to the formation of new chains.

$$R_1\,O^-, Met+ \quad + R_2\,OH \rightleftharpoons R_1OH + \; R_2\,O^-, Met+$$

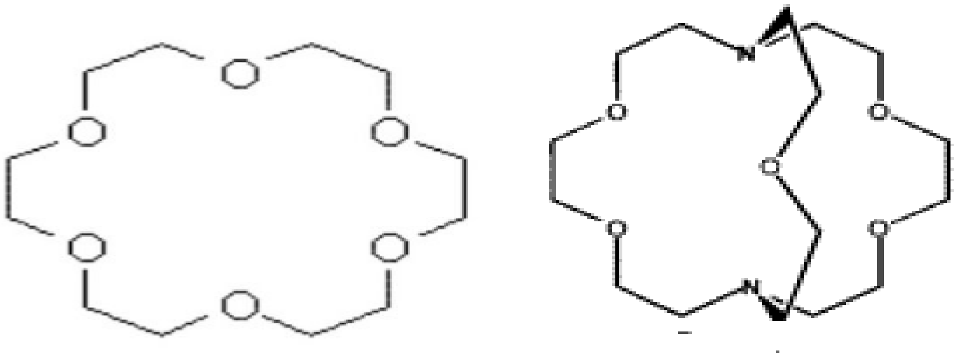
Active chain Dormant chain

To increase the polymerization rate, the addition of a complexing agent has been employed. These complexing agents fall into two categories:

- Crown ethers
- Cryptand ethers

Role of complexing agents

- To complex the alkali metal counterion
- To dissociate the propagating anion
- To increase the polymerization rate
- To increase the molecular weight of the polymer and reduce transfer reactions



A **(18C6)** B

Scheme: chemical structure of ACrown ether and B Cryptand ether.

18-crown-6 (18C6)

18 = number of atoms in the ring

6 = number of oxygen atoms

Somme polymerization are given in this table:

Monomer	**initiator**	**Complexing agent**	**[initiator]/[complexing agent]**	**T(°C)**	**Mn exp**	**Ip**
propylene Oxyde	$CH_3OCH_2CH(CH_3)$ OK	/	/	80	4200	1.32
propylene Oxyde	$CH_3OCH_2CH(CH_3)$ OK	18C6	1.5	80	9300	1.22
ethyleneoxyde	Ph COOK/ H_2O	18C6	1.34	40	3700	1.1

The data show that the addition of a complexing agent significantly enhances the control and efficiency of anionic ring-opening polymerization.

For propylene oxide, using the potassium alkoxide initiator alone at 80 °C gives a moderate molar mass (Mn = 4200 g/mol) and a relatively broad molecular weight distribution (PDI = 1.32). However, when 18-crown-6 is added under the same temperature and initiator conditions, the experimental molar mass more than doubles (Mn = 9300 g/mol), and the molecular weight distribution becomes narrower (PDI decreases to 1.22).This improvement results from the ability of 18-crown-6 to complex the K^+ counterion, thereby dissociating the propagating anion, which increases reactivity and reduces transfer reactions.

In the case of ethylene oxide, the combination of PhCOOK / H_2O with 18-crown-6 at 40 °C still leads to very good control (PDI = 1.10). Although the molar mass remains moderate (Mn = 3700 g/mol), the narrow distribution indicates that chain growth is highly controlled, showing that complexation also improves polymerization control at lower temperatures and with different monomers.

Overall conclusion: Adding 18C6:

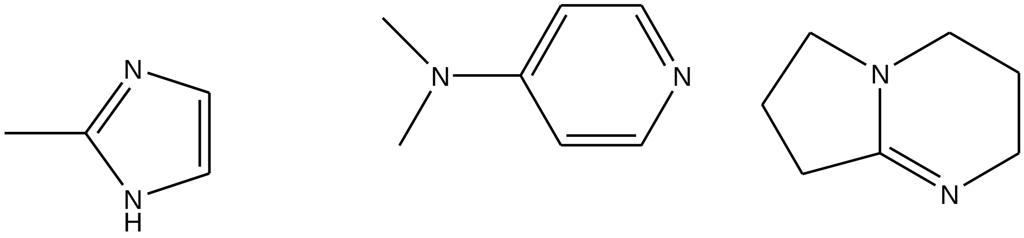
- increases the polymerization rate
- raises the achievable molar mass

- narrows the molecular weight distribution
- enhances control by reducing side reactions

This confirms the key role of complexing agents in improving anionic polymerization performance.

Initiation by tertiary Amines

Tertiary amines represent an important class of initiators in anionic ring-opening polymerization (AROP), particularly for the polymerization of alkylene oxides such as propylene oxide or ethylene oxide. Examples of widely used tertiary amines include triethylamine (TEA), 1,4-diazabicyclo[2.2.2]octane (DABCO), N,N-dimethylbenzylamine, and various substituted pyridines.



methyl imidazole 4 dimethyl aminopyridine1,5 diazo bicyclo 4,5 none 5diene

Scheme: Tertiary amine that are used as initiator

Although tertiary amines are capable of initiating the polymerization on their own, their intrinsic initiating efficiency is relatively low, mainly because they do not directly form a sufficiently reactive nucleophile. For this reason, the addition of an alcohol (ROH) is commonly employed. The presence of alcohol significantly enhances the initiation process andincreases the overall polymerization rate.

Mechanism and function of the alcohol:

When a tertiary amine is combined with an alcohol, an acid–base interaction takes place. The amine, acting as a base, abstracts a proton from the alcohol, leading to the formation of an alkoxide ion (RO^-). This alkoxide is the true active initiating species, as it readily performs nucleophilic attack on the monomer, opening the epoxide ring and starting the propagation step.

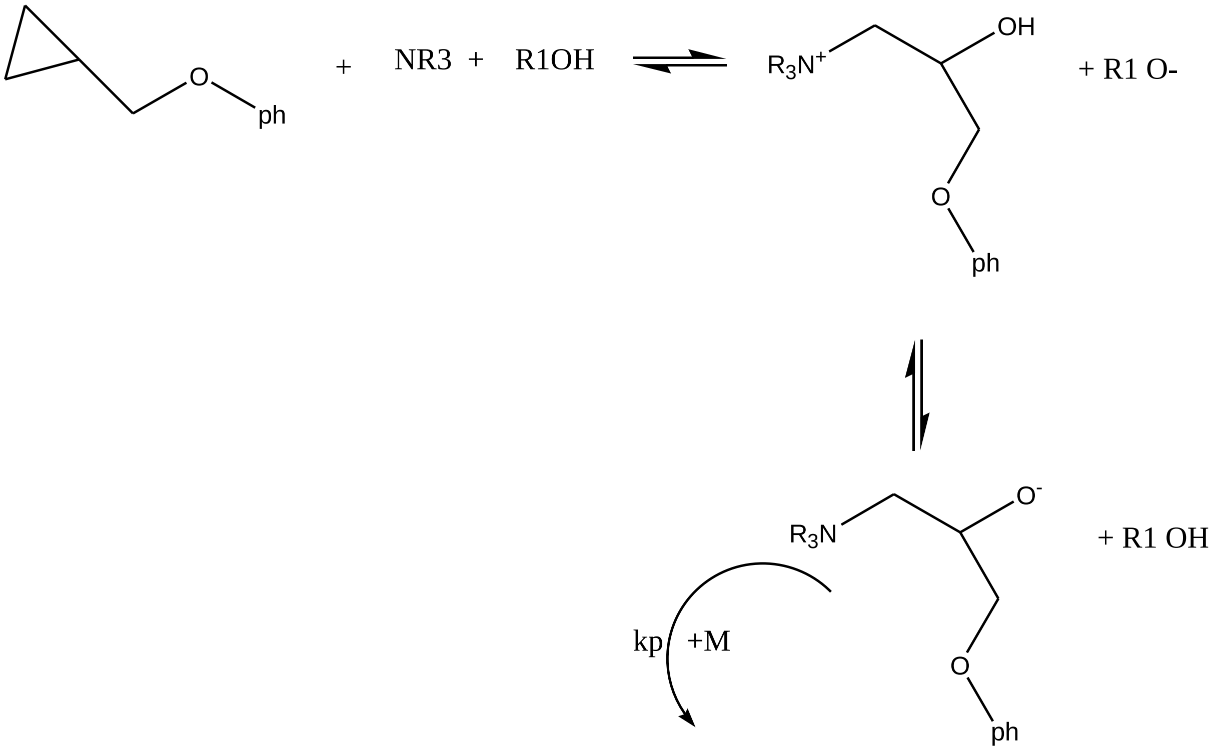
Tertiary amine + alcohol → alkoxide ion (active initiator) + protonated amine

Once formed, the alkoxide ion continues to react with successive monomer molecules, generating growing polymer chains via ring-opening propagation.

Advantages of using alcohol alongside tertiary amines

- Formation of stronger nucleophiles (RO^-)
- Increase in active ion concentration
- Faster initiation and propagation
- Higher polymerization rate
- Better control over polymer molar mass

Property	**Without alcohol (amine alone)**	**With alcohol (amine + ROH)**
Rate of initiation	low	significantly increased
Concentration of active species	limited	high formation of alkoxide ions
Control of propagation	moderate	improved due to stable ionic species
Molecular weight	often lower	can be increased due to faster propagation



Scheme: Control of the anionic polymerization by tertiary amine.

Tutorials List

First tutorial

Exercise 1: Write the elementary steps (initiation, propagation, termination) for a typical free-radical polymerization of a monomer M (styrene). For each step: give the chemical equation and briefly explain its role.

Exercise 2:N-vinyl-2-pyrrolidone (VP) is a liquid monomer that can undergo free radical polymerization at elevated temperatures. In this experiment, AIBN is used as a radical initiator. The initial concentrations are: [M]: 1mole/L, [AIBN]= 0.005mole/L.
kp = 120L·mol^{-1}. s^{-1}, kd = 1.10^{-5}s^{-1}, kt =10^{7}L·mol^{-1}. s^{-1}with AIBNefficiency (f = 0.6).
1. Draw the general structure of the polymer obtained from VP using AIBN as initiator.
2. Write the rate expression (Rp) for the propagation step.
3. Calculate the initial rate of polymerization assuming

Exercise 3: the polymerization of styrene (8.75 mol/L) at 60°C with l'AIBN as initiator was released. [A] = 0,5 mol.L^{-1}. The steady-state was proposed within transfer reactions.

- Draw the AIBN's dissolution equation and the Rate of this step.
- Draw all steps of this polymerization.

Kinetic chain length was given by the expression:

$$\bar{\nu} = \frac{k_p[M]}{2\sqrt{f k_a [I] k_t}}$$

Known experimentally that $\frac{k_p}{\sqrt{k_a}}$ = 0,02, calculate the kinetic chain length.

The obtained molecular weights are (Mn = 12,900g·mol^{-1}) and (Mw = 12700^{-1}). Calculate the polydispersity index (PDI) and draw a conclusion.

Calculate the monomer conversion after 5 hours of reaction, given that the polymerization rate constant is (K = 2.828 $10^{-5}s^{-1}$). Then, determine the instantaneous number-average molecular weight(Mn) at this time.

kp = 176 mol^{-1}.L.s.$^{-1}$; kt = 7,744.10^{7} mol^{-1}.L.s^{-1}, kd = 5.10-6 s^{-1}; f = 0,8

Exercise4:

Consider the polymerization of 0.2 mole/L of methyl methacrylate (MMA) in bulk at 60°C, initiated by 3,0 10^{-3} mole/L of benzoyl peroxide (BPO). The dissociation rate constant of BPO is (kd= 4,4×10^{-6} s^{-1}. The initiator efficiency factor is (f = 0.8). The propagation and termination rate constants are: k_p = 145 L. s^{-1}.mol^{-1} et k_t =7,0×10^{6} L. s^{-1}.mol^{-1}.

1. What does bulk polymerization mean?
2. Calculate the initiator conversion after 2 hours in the reaction medium.
3. Calculate thetime required to reach 10% monomer conversion, assuming a polymerization rate constant (K = 2.828 s^{-1}.

Exercise5 : Consider the polymerization of 0.3 mol/L styrene in bulk at 70 °C, initiated by benzoyl peroxide (BPO, 2 × 10^{-3} M). The kinetic parameters are: f = 0.65, kp = 150 L. s^{-1}.mol^{-1} , kt = 8. 10^{6}L. s^{-1}.mol^{-1} ,kd = 5.0 $10^{-5}$$s^{-1}$)

1. Write the equation for the formation of radicalsfrom benzoyl peroxide.
2. Calculate the steady-state radical concentration.
3. Determine the initial rate of polymerization (Rp).
4. Estimate the monomer conversion after 2 hours, assuming steady-state radicals.

Second tutorial

Exercise 1:

1. What happens if a solution of AIBN is added to a living radical polymerization at t∞?
2. What happens if a quantity of M_2 is added to a living polymerization at t∞?
3. What are the polydispersity index and molecular weight in a living polymerization?

Exercise 2:

Scanning Electron Microscopy (SEM) allowed the determination of the size of a macromolecular chain of PMMA synthesized by CRP, which is 0.632 μm.

Determine Mn and Mw of this polymer (molecular diameter of MMA = 1.93 nm).

Exercise 3:

We want to polymerize monomer B by mass. The medium mainly contains 0.2 mol/L of monomer B, using 10^{-6} mol/L of initiator A.

Initiation lasts 30 minutes, and T = 100°C.

Assuming there is no transfer or termination reaction, calculate the concentration of monomer consumed at t = 5 h and a conversion of 75%. What can you say about this polymerization? Given: $k_p = 10^5\ s^{-1}$

Exercise 4:

A reaction mixture for a polymerization contains AIBN, MMA, CH_3I, DMSO, at T = 110°C. Specify the type of polymerization possible, the role of CH_3I, and the polymerization mechanism.

Exercise 5:

A controlled radical polymerization (CRP) of 4-vinylbenzyl chloride was carried out in the presence of PMMA as a controlling agent.

Specify the type of control.

Give the polymerization mechanism, the type of polymer obtained, and the probable DPI of the polymer.

Exercise 6:

Give the mechanism of the controlled radical polymerization (CRP) of acrylamide and vinyl alcohol separately in the presence of $CH_2=N–CS_2CH_3$.

Exercise 7:

A CRP between styrene (1.5 g) and N-vinylpyrrolidone (1.5 g) was carried out in the presence of diphenylethylene (DPE).

Specify the amount of used DPE and the reaction mechanism, assuming that there is no reactivity between the two monomers.

Exercise 8:

Give the propagation mechanisms of controlled radical polymerizations (CRP) of styrene in the presence of the following control agents: PMMA, DPE, and $C_2H_5–CS_2–C_2H_5$.

Classify the resulting polymers according to their definitions.

Give the polymerization mechanism of MMA in the presence of the following reagents: AIBN, $CH_2OH–CS_2–CH_3$.

Give the mechanism of a CRP of maleic anhydride in the presence of AIBN and the hydroxylated TIPNO shown below.

Exercise 9:

Rank these nitroxides by their corresponding polymerization rates: SG1, TIPNO, and TEMPO.

Classify the polystyrenes obtained in the presence of these nitroxides according to their definitions, and by their monomer conversion: TEMPO, proxyl (DBN and Su-DBN), nitroxide proposed by Nakamura.

Rank these nitroxides by their corresponding polymerization rates: Su-DBN, SG1.

Classify these nitroxides according to the definitions of the corresponding polymers: DBN, proxyl ketone, morpholines, TEMPO, TIPNO.

Rank these nitroxides according to the molecular weights of the polymers obtained: the spiral nitroxides, TEMPO, DBN, proxyl and its derivatives.

Exercise 10:

A polymerization reaction medium contains AB, MR·, $CHCl_3$, and POB:AB: [AB] = 1.5 $mol \cdot L^{-1}$, MR·: [MR·] = 1.0×10^{-4} $mol \cdot L^{-1}$, POB: [POB] = 1.0×10^{-7} $mol \cdot L^{-1}$

Give the polymerization mechanism under these conditions.

Calculate the number-average degree of polymerization DPn and give the probable DPI.

Third tutorial

Exercise1:

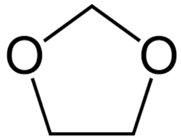
A system BF_3/H_2O was used to polymerize isobutene. NMR analysis showed 2 types of double bonds at the chain end.

1- Draw the initiation and the propagation reactions.
2- Draw the possible termination reactions.

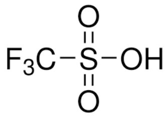
Exercise2 :

1- Draw the general mechanism of the cationic polymerization of THF.
2- 1,3 Dioxolane was polymerized using trifluorosulfonic acid as the initiator. Draw the initiation and propagation steps.

M:



I:

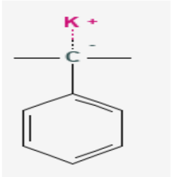


$F_3C-S(=O)_2-OH$

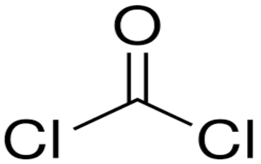
Exercise3 :

The polymerization of styrene was initiated by potassium cumyl (I). After complete consumption of the monomer, phosgene $COCl_2$(II) was added in excess to the reaction medium. At the end of the reaction, l'hexafluroantimonate argent salt was added, followed by the addition of THF. Write the different steps of this synthesis

I:



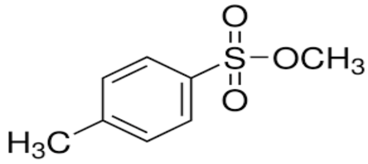
II:



, III: $CF_3\ SO_3^-$, H^+

Exercise4:

Give the initiation and propagation steps of the polymerization of methy2-oxazoline, where the initiator used is methyl tosylate.



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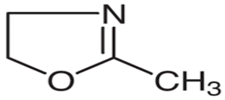
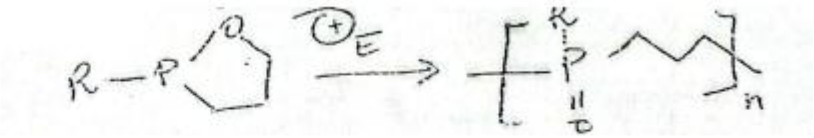


Exercise5:

The phosphorous heterocycle can be polymerized via cationic polymerization where the oxidation of the phosphorus atom. As shown in the reaction below.



Propose a polymerization mechanism for this compound, using methyl trifluoromethane sulfonate (methyl triflate) as the initiator (CF_3-SO_2-O CH_3).

Exercise 6:

Give the living cationic control of ethylene oxide, propylene oxide and epsilon caprolactone via activated monomer.

Fourth tutorial

Exercise 1:

A polymerization of styrene by the anionic route is carried out as follows: In a round-bottom flask under a nitrogen atmosphere, introduce 50 mL of benzene and 0.2 mL of THF, then add 1.4 mL of a 1 M n-butyllithium solution in heptane. Then slowly introduce 5 mL of styrene (d = 0.91). After 2 hours of reaction, add 1 mL of methanol to the reaction mixture to stop the polymerization.

1. What is the number-average degree of polymerization if the reaction is total?
2. If 4 g of polymer are recovered, what should be the actual degree of polymerization obtained?

Exercise 2:

Under an argon atmosphere, 1 g of sodium (Na = 23) was reacted with 5.6 g of naphthalene in 180 mL of THF. The resulting green solution is referred to as the initiator solution. It was used to carry out five styrene polymerization reactions, in which 3 mL of the initiator solution were added to 10, 100, 200, 280, and 350 g of a 10% styrene solution in THF. After the addition of the initiator, the solution turned red. Styrene (density= 0.91 g/mL).The resulting polymer is washed and dried.

1. Calculate the number-average molar masses of the polymers obtained at the end of the polymerization.
2. The polymer obtained from 280 g of the styrene solution is fractionated at 23°C into 9 fractions.

   The table below gives the weight of each fraction and its average molecular weight (M_v).

Fraction no.	**Weight of fraction (g)**	**M_v (g/mol)**
1	0.735	178500
2	1.865	140000
3	1.933	104 000
4	1.416	98000
5	1.015	94 000
6	0.51	87 000
7	0.455	64 000
8	0.445	58 000
9	1.065	27 000

Determine the number-average and weight-average molar masses of this sample.

Exercise 3:

A polymerization solution of tert-butyl methacrylate (0.26 mol/L) is carried out anionic route,using benzyl-α-methylstyryl sodium as the initiator at a concentration of 0.59×10^{-3} mol/L. The polymerization kinetics are given in the following table:

Time (s)	**0**	**4**	**6**	**10**	**16**	**25**	**102**
[M] (mol/L)	0.26	0.240	0.233	0.219	0.198	0.166	0.102
Xn	–	29	57	79	115	165	284

1. Show that the kinetics are first order with respect to the monomer and calculate the overall rate constant.
2. Calculate the propagation rate constant.
3. In what way are the Xn values necessary for this calculation?

Exercise 4:

A polybutadiene of number-average molar mass 40000 g/mol is to be synthesized by an anionic reaction in hexane.

1. In the first step, the initiator is prepared by the reaction of lithium with 1-chloro-2-butane in benzene. The product obtained is then titrated by acetanilide in DMSO in the presence of triphenylmethane as an indicator until a persistent red coloration appeared. 3.55mL of initiator solution is required to neutralize 309mg of acetanilide. Write the balanced chemical equations.
2. What is the origin of the red color?What is the concentration of the initiator?
3. 17.5 mL of distilled butadiene are polymerized in hexane.What quantity of initiator must be used to obtain the desired polymer mass?

*Given:*Acetanilide: C_6H_5–NH–$COCH_3$, M = 135 g/mol/ Butadiene: M = 54 g/mol, d = 0.65.

Exercise 5:

1. Write the resonance forms (mesomeric) of butadiene, resulting from a nucleophile attack.
2. Write the general structural formula of “polybutadiene” and “polyisoprene”, showing the different possible units.

Exercise 6:

Give the living anionic control of these systems:

1- CH_3COOK / H_2O, ethylene oxide
2- PhCOOK / MeOH, ethylene oxide
3- CH_3COOK / EtOH, propylene oxide
4- C_2H_5COOK / MeOH, epsilon caprolactone
5- Methyl imidazole, EtOH, Propylene oxide
6- 4-dimethyl aminopyridine, MeOH, caprolactone

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