

## VIII. CATIONIC POLYMERIZATION

### A. Introduction to Cationic Polymerization

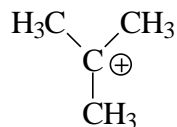
Cationic polymerization is defined as chain-growth, addition polymerization of an unsaturated monomer, in which the propagating species is a carbenium ion. Cationic polymerizations are initiated by acids.

#### 1. Carbocations (Carbenium Ions)

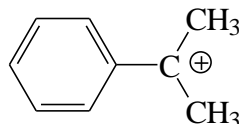
##### a. Nomenclature

A carbenium ion is a positively charged  $sp^2$  carbon atom bonded to three substituents and possessing only six valence electrons. The term “carbocation” may also be used. The examples below indicate the proper naming scheme to be used depending upon whether the term carbenium ion or carbocation is used.

Figure VIII-1



trimethyl carbenium ion  
or  
*tert*-butyl carbocation

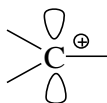


dimethylphenyl carbenium ion  
or  
cumyl carbocation

##### b. Properties of carbenium ions

- Carbenium ions are planar,  $sp^2$  hybridized, and possess an empty p orbital.

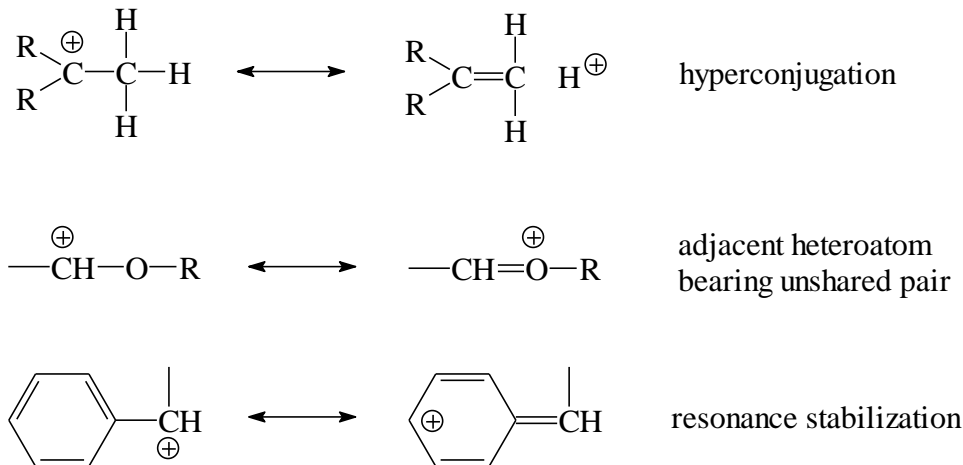
Figure VIII-2



- They are always associated with a negative counterion or gegenion. In solution they may exist as an ion pair or as a free ion. Coulombic forces are too weak to maintain a stable solvent-separated ion pair, due to the large diameter of negative gegenions. Polar solvents and low temperatures promote dissociation to free ions. The nature of the gegenion largely determines the stability of the ion pair.
- Among simple carbenium ions, the order of stability is tertiary > secondary > primary. Both hyperconjugation and the field effect (induction) may explain this order. An unshared pair on an adjacent heteroatom is highly stabilizing. Stabilization also occurs through resonance conjugation; the more contributing

structures the greater the stability. Larger carbenium ions are more stable than small ones.

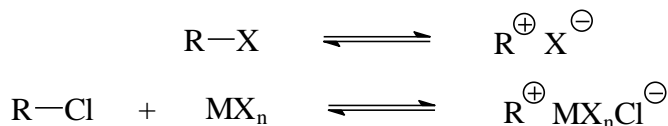
**Figure VIII-3**



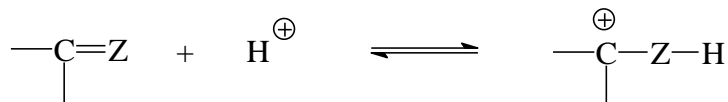
*c. Generation of carbenium ions*

**Figure VIII-4**

Direct ionization, unassisted (upper) or assisted by a Lewis acid (lower), in which a group attached to carbon leaves with its pair of electrons:



Addition of a positive species, usually a proton, to one atom of an unsaturated system, leaving the adjacent carbon with a positive charge:



For direct ionization, the concept of back strain is important. H.C. Brown showed that the larger and more bulky are the three groups attached to the positively charged carbon, the faster the carbenium ion is formed. The rationale is that conversion from  $sp^3$  to  $sp^2$  hybridization relieves steric strain, and therefore the more bulky the R group, the higher the ground state energy.

d. *Reaction of carbenium ions*

- Reaction with a species possessing an electron pair (essentially the reverse of direct ionization).
- Loss of a positive species, usually a proton, from a position  $\beta$  to the positive carbon (so-called  $\beta$ -proton elimination).
- Rearrangement to form a more stable carbenium ion:
- Addition to an unsaturated system, usually a carbon-carbon double bond (propagation mechanism in cationic polymerization).

## 2. Scope of Cationic Polymerization

a. *Cationic Initiating Systems*

Definition – Any chemical or physical method, which will generate a positive species such as  $H^{\oplus}$  or  $C^{\oplus}$ . The positive species adds to the double bond of an olefin to complete the initiation process.

**Table VIII-I: Cationic Polymerization Initiators**

Type	Examples	Initiating Species	Counter-Anion
Protic Acids	$HClO_4$	$H^{\oplus}$	$ClO_4^{\ominus}$
	$CF_3SO_3H$	$H^{\oplus}$	$CF_3SO_3^{\ominus}$
Lewis Acids	" $H_2O$ "/ $BF_3-OEt_2$	$H^{\oplus}$	$BF_3OH^{\ominus}$ or $BF_4^{\ominus}$
	$R-Cl/TiCl_4$	$R^{\oplus}$	$Ti_2Cl_9^{\ominus}$
	$HCl/AlCl_3$	$H^{\oplus}$	$AlCl_4^{\ominus}$
Other	$(I_2)_2/M$	$IM^{\oplus}$	$I_3^{\ominus}$
	$CH_3CO-ClO_4$	$CH_3CO^{\oplus}$	$ClO_4^{\ominus}$
	$(AlBr_3)_2$	$AlBr_2^{\oplus}$	$AlBr_4^{\ominus}$
	$(C_6H_5)_3C^{\oplus}SbCl_6^{\ominus}$	$(C_6H_5)_3C^{\oplus}$	$SbCl_6^{\ominus}$
	Ionizing radiation	$M^{\oplus}$ or $M^{\oplus}$	None

b. *Cationically Polymerizable Monomers*

Monomers for cationic polymerization must have an electron rich double bond, and the double bond must be the most nucleophilic site on the molecule. If this is not the case, the attacking carbocation will seek out the site of greatest nucleophilicity, which might then give a stable, non-propagating structure. This explains why acrylates, acrylonitrile, etc., will not polymerize cationically. Therefore, substituents to the vinyl group must be electron donating either by resonance or induction.

**Table VIII-II: Cationically Polymerizable Monomers**

Type	Example
1-Alkyl olefin	Propylene, 1-butene
1,1-Dialkyl olefin*	Isobutylene
1,3-Diene	Butadiene, isoprene, chloroprene
Styrene family	Styrene, <i>p</i> -methylstyrene
$\alpha$ -Alkylstyrene family	$\alpha$ -methylstyrene
Vinyl ethers*	Isobutyl vinyl ether
Cyclic conjugated dienes	Cyclopentadiene
Indene family	Indene
N-Vinylcarbazole	N-Vinylcarbazole

\*Only polymerizable cationically

*c. Solvents for Cationic Polymerization*

Solvents for cationic polymerization should be inert toward carbocations and should have a low freezing point. Low freezing points are useful because cationic polymerizations are often carried out at low temperatures. Polar solvents are preferred in traditional (non-living) polymerizations because they lead to higher rates and molecular weights. Highly nucleophilic solvents like CH<sub>3</sub>OH and H<sub>2</sub>O are unsuitable; they in fact are often used to terminate cationic polymerizations. Solvents that are easily alkylated such as toluene or solvents with tertiary hydrogens may lead to low molecular weight polymer because of transfer activity.

**Table VIII-III: Solvents for Cationic Polymerization**

	Type	Example
Low polarity	<i>n</i> -Alkane	<i>n</i> -Hexane, <i>n</i> -pentane, etc.
	Cycloparaffins	Cyclohexane, methycyclohexane
	CS <sub>2</sub> , CCl <sub>4</sub> , CO <sub>2</sub>	
Medium polarity	Halogenated alkanes	CH <sub>3</sub> Cl, CH <sub>2</sub> Cl <sub>2</sub> , CH <sub>3</sub> CH <sub>2</sub> Cl, (CH <sub>2</sub> Cl) <sub>2</sub> , CH <sub>3</sub> CH <sub>2</sub> Br, CH <sub>3</sub> Br, (CH <sub>2</sub> Cl) <sub>2</sub>
	Chlorobenzene	
	SO <sub>2</sub> , dioxane	
High polarity	Nitrobenzene	
	CH <sub>3</sub> NO <sub>2</sub> , CH <sub>3</sub> CH <sub>2</sub> NO <sub>2</sub>	

*d. Reaction conditions for cationic polymerizations*

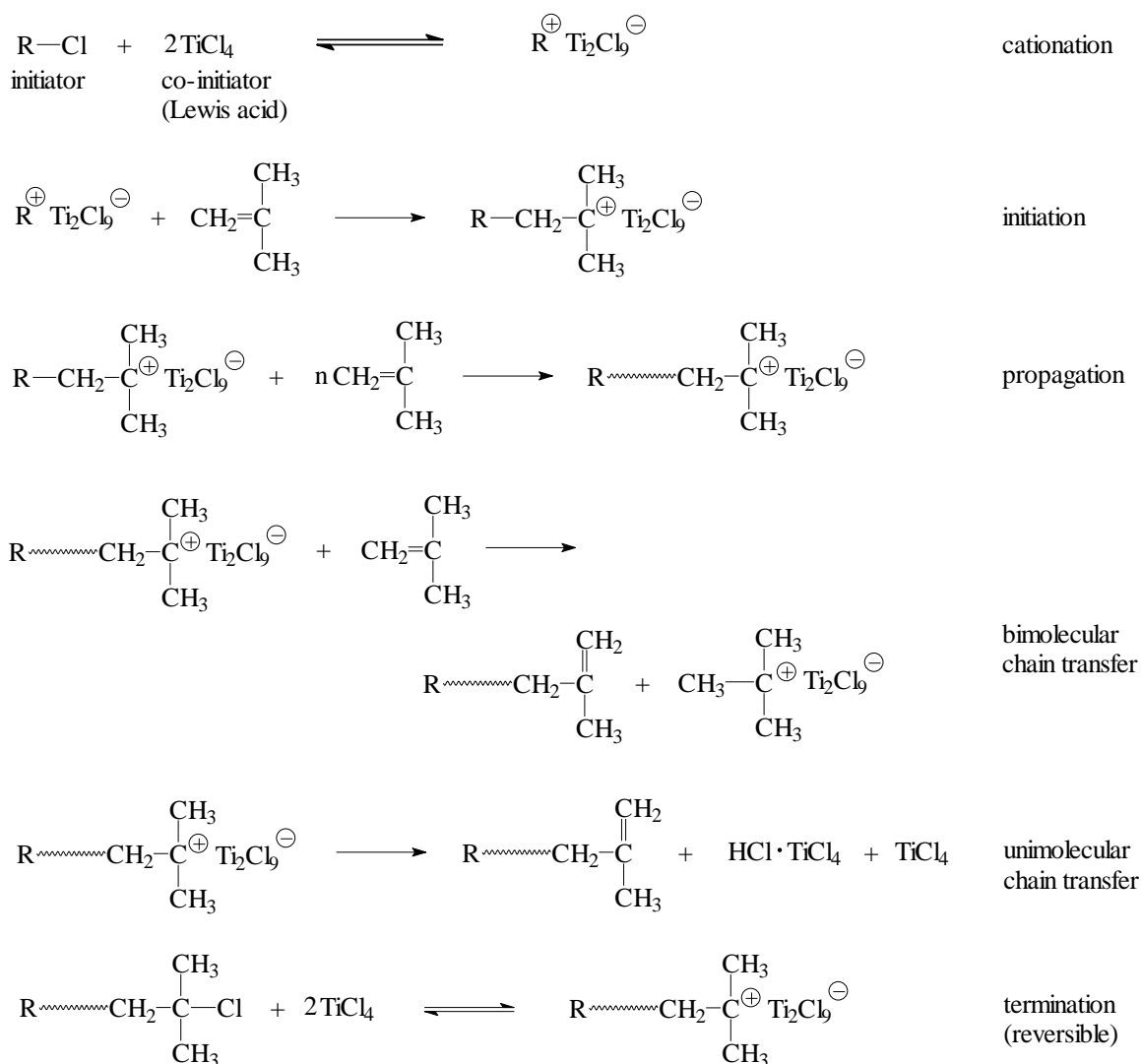
Cationic polymerizations are usually carried out in the liquid phase in solution under an inert atmosphere, e.g. N<sub>2</sub>, Ar. All reagents and glassware must be thoroughly dried. Depending on its concentration in the system, water may be a initiator, transfer agent, or inhibitor. Glassware should be baked at 150-200°C preferably overnight, and allowed to

cool under inert gas. Liquid monomers and solvents must be distilled under inert gas from an exhaustive drying agent, e.g.,  $\text{CaH}_2$ . Gaseous solvents and monomers may be dried by passing through a glass column packed with  $\text{BaO}$  and or powdered  $3\text{\AA}$  molecular sieves.

The initiator and monomer are generally diluted with suitable solvents to alter the polarity of the medium and to moderate the sometimes extremely rapid (explosive) reaction rates. Carbocationic polymerizations are usually carried out at low temperatures, e.g.,  $-100$  to  $-20^\circ\text{C}$ , to retard undesired reactions, especially chain transfer.

### 3. Mechanism of Carbocationic Polymerization

Figure VIII-5



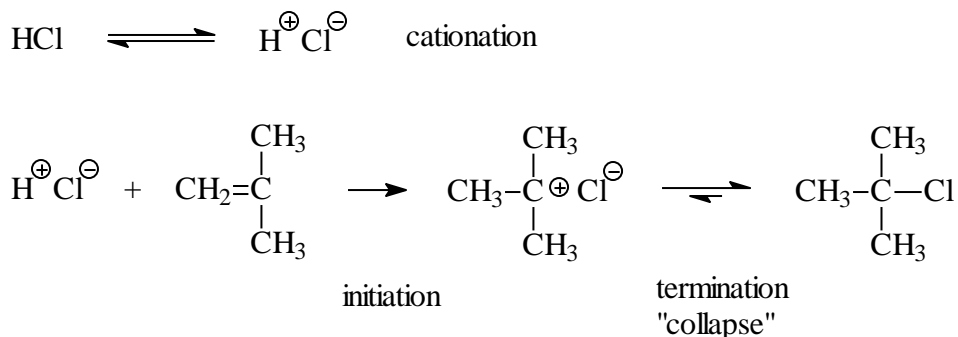
## B. Initiation of Cationic Polymerization

Cationic initiation consists of two steps. The first is generation of the positively charged species (cationation), be it a proton or a carbenium ion. For a protic or Bronsted acid, this step is simply an acid ionization reaction. For a Lewis acid it consists of complexation of the Lewis acid with a Bronsted acid (e.g., HCl, H<sub>2</sub>O) or a carbenium ion precursor such as an alkyl halide. The second step is the actual initiation by addition of the positive fragment to the first monomer. For many systems initiation is exceedingly slow in non-polar hydrocarbon solvents and must be carried out in chlorinated hydrocarbons or mixture of chlorinated hydrocarbons and hydrocarbons.

### 1. Protic acids

Protic acids can initiate cationic polymerization by protonation of the olefin; however, only very strong acids, which yield non-nucleophilic counterions are effective. The general problem can be illustrated by the action of a hydrogen halide: the halide counterion is too strongly nucleophilic to allow the cation to survive sufficiently long to propagate.

Figure VIII-6

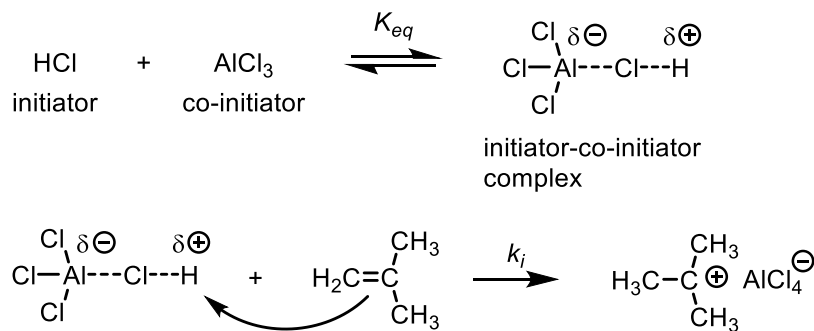


In general, the more reactive the monomer toward cationic polymerization, the weaker the protic acid that can successfully initiate that monomer. The following acids have been shown to initiate polymerization with certain monomers: perchloric, fluor- and chlorosulfonic, methanesulfonic, and trifluoromethanesulfonic (triflic) acids.

### 2. Lewis acids

Lewis acids, in conjunction with a protic acid or other cation source, comprise the most important class of cationic initiators. AlCl<sub>3</sub> and EtAlCl<sub>2</sub> (EADC) are the most important Lewis acids for industrial cationic polymerizations and are used for the production of butyl rubber (-100 C in MeCl). EADC is more expensive but easier to use because it is soluble. Reaction of a Lewis acid with a protic acid yields a much stronger protic acid with a non-nucleophilic gegenion.

**Figure VIII-7**

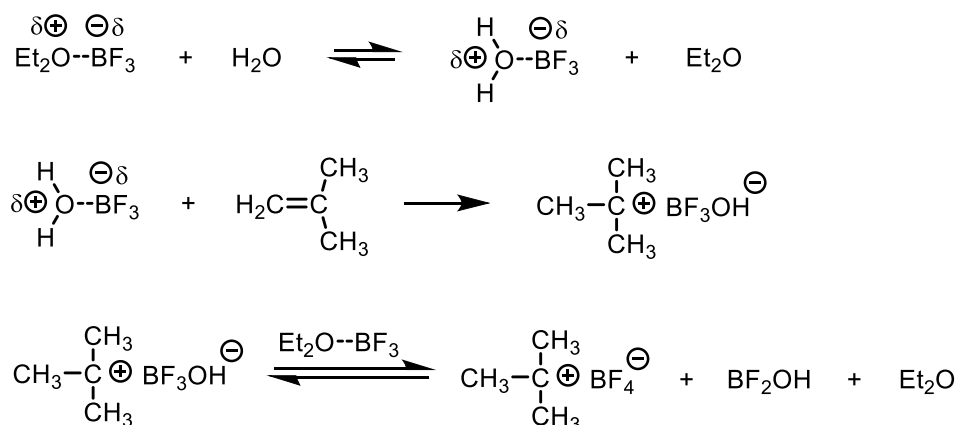


In contrast to the use of HCl alone, the chloride ion has been rendered non-nucleophilic by complexation with AlCl<sub>3</sub>, and the monomer can compete with the counterion for the carbocation. The result is propagation. As shown above, the compound that donates the positive species that becomes the head group of the polymer chain is termed the initiator. The Lewis acid is termed the coinitiator. Common initiators include: proton donors (protogens) such as water, hydrogen halide, and carboxylic acids; and carbocation donors (cationogens) such as 2-chloro-2,4,4-trimethylpentane, 2-chloro-2-phenylpropane (cumyl chloride), and 5-*tert*-butyl-1,3-di(1-chloro-1-methylethyl)benzene (*t*-Bu-*m*-dicumylchloride).

The extent of formation of the initiator-coinitiator complex (i.e., the value of  $K_{eq}$  in Figure VIII-7) and its rate of addition to monomer (i.e., the value of  $k_i$ ) generally increase with increasing acidity of the Lewis acid coinitiator.

In general, when a Lewis acid or a Lewis acid complex such as BF<sub>3</sub> etherate is used alone to initiate polymerization, the hidden protic acid is water, regardless of all rigorous efforts to dry the system.

**Figure VIII-8**

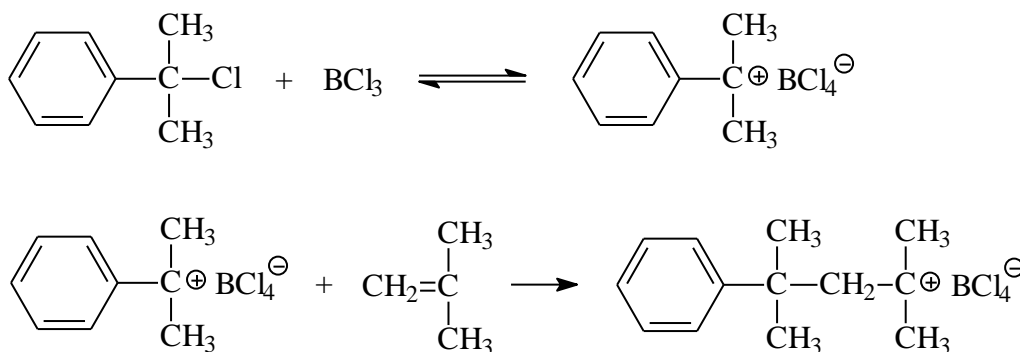


It should be noted that for a protic initiator, the initiator-coinitiator complex should be shown as above, rather than as H<sup>+</sup> BF<sub>3</sub>OH<sup>-</sup>. Also, as shown above (bottom reaction), if the Lewis acid is in excess to water, which is usually the case, then the counterions for the

growing chains become  $\text{BF}_4^\ominus$ . This reflects the preponderance of fluoride ligands relative to hydroxide ligands and the stronger Lewis acidity of  $\text{BF}_3$  relative to  $\text{BF}_2\text{OH}$ .

Initiation by a cationogen and a Lewis acid is exemplified by the cumyl chloride/ $\text{BCl}_3$  system:

**Figure VIII-9**

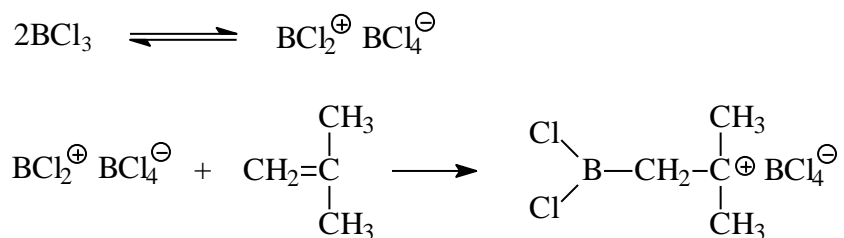


In addition to organic halides, organic alkoxides and carboxylates have also been used as cationogens. The reactivity of a given cationogen depends on carbocation stability in a complex manner. Increased stability yields formation of higher concentrations of cations, but they are of lower reactivity. Very important is the relative stability of the initiating cation compared to the propagating cation derived from the monomer. If the initiating cation is too unstable (e.g., a primary or secondary alkyl cation), it is formed too slowly and in very low concentration. If the initiating cation is very stable (e.g., trityl) it will react only with very reactive monomers which yield very stable propagating cations. The best initiator will generally yield cations of similar stability and reactivity to the propagating cation.

It is generally accepted that some, but not all, Lewis acids can initiate polymerization by a self-ionization process. Lewis acids for which self-ionization is believed to occur include  $\text{AlBr}_3$ ,  $\text{AlCl}_3$ , and  $\text{BCl}_3$ . This reaction is typically much slower than initiation involving an initiator-coinitiation complex, and thus can only be observed when all protic sources have been removed from the system. Most of the evidence for self-ionization is indirect, but in the case of  $\text{BCl}_3$  systems, actual spectroscopic identification of  $\text{BCl}_2^-$  end groups has been reported.

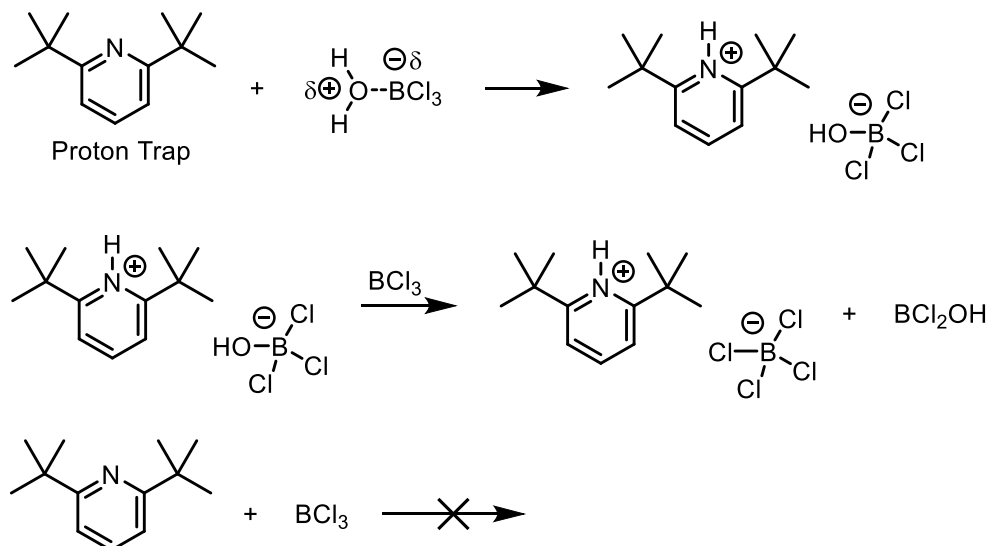


**Figure VIII-10**



One way in which protic sources are removed from cationic polymerization systems is through the use of proton traps, the most common of which are sterically hindered pyridines such as 2,6-di-*tert*-butylpyridine (the latter is actually trademarked as “Proton Trap”).

**Figure VIII-11**

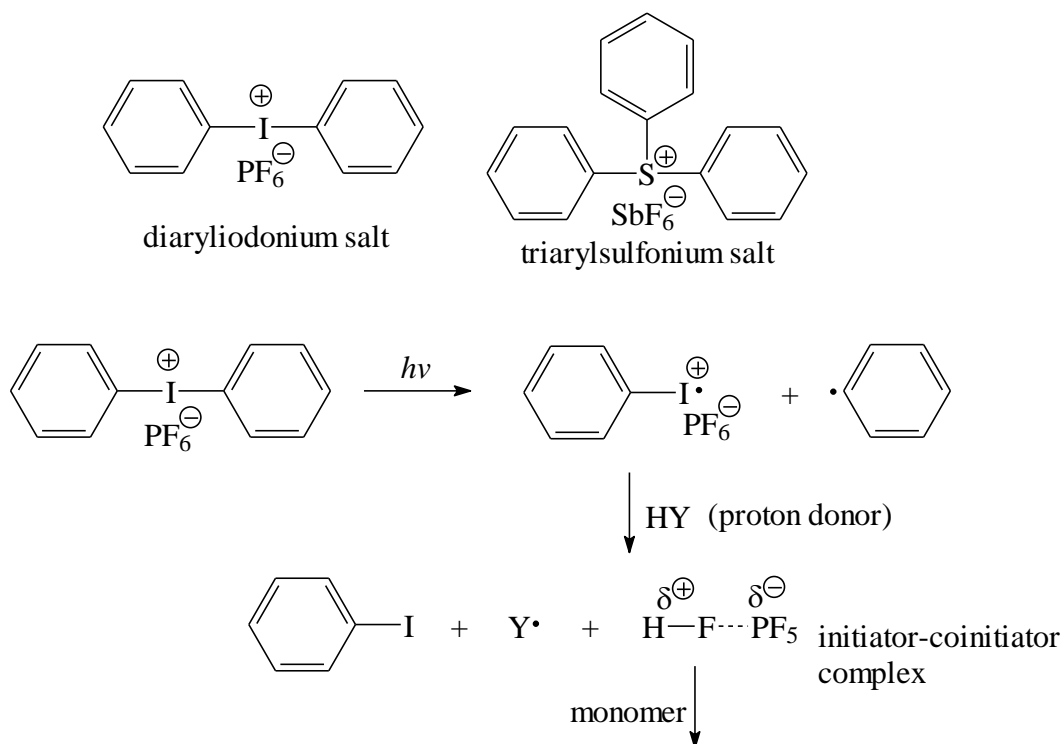


Iodine can be used alone to initiate polymerization of more reactive monomers such as *p*-methoxystyrene, vinyl ethers, and *N*-vinyl carbazole. Here the initiator and cointiator are the same compound. I<sup>⊕</sup> is the initiating species and the gegenion is I<sub>3</sub><sup>⊖</sup>. Use of HI/I<sub>2</sub> as the initiator/cointiator results in a significantly more efficient initiating system.

### 3. Photoinitiation

Diaryliodonium and triarylsulfonium salts with non-nucleophilic and photostable anions such as BF<sub>4</sub><sup>⊖</sup>, SbF<sub>6</sub><sup>⊖</sup>, and PF<sub>6</sub><sup>⊖</sup> are effective photoinitiators of cationic polymerization. Initiators of this type have found commercial applications in the photocrosslinking of epoxy resins (ring-opening polymerization with oxonium ion propagating species).

**Figure VIII-12**

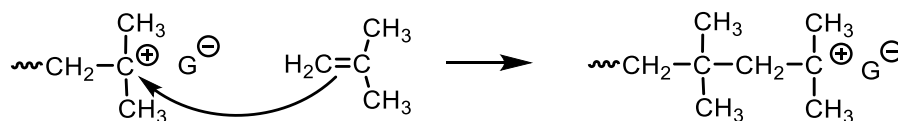


Application of UV light causes a redox reaction between an arylidonium cation-radical and a protogen. The same result can be achieved in the absence of light using a chemical reducing agent. Substituents can be placed on the aromatic rings to extend the spectral response to longer wavelengths, if desired.

### C. Propagation, Transfer, and Termination in Cationic Polymerization

Propagation in carbocationic polymerization involves nucleophilic attack by the  $\pi$ -electrons of monomer on the carbenium ion at the tip of the growing chain. At the low polymerization temperatures that are typical, propagation is essentially irreversible, as shown.

**Figure VIII-13**



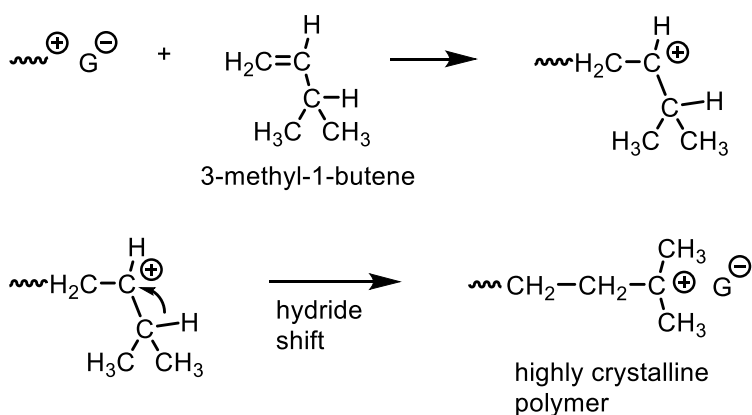
Carbenium ion polymerizations, like anionic polymerizations, most probably involve paired ions, with only a very low proportion of free ions. Compared to anionic polymerization, however, where the counterion is small (i.e., an alkali metal cation), cationic polymerizations generally involve large, bulky counterions (e.g.  $\text{AlCl}_4^-$ ,  $\text{Ti}_2\text{Cl}_9^-$ ,

etc.). Thus, the difference in reactivity between ion pairs and free ions is much less in cationic polymerization compared to anionic polymerizations. In the former, free ions may be 5-50 times more reactive; whereas in the latter they are 3-4 orders of magnitude higher. This also implies that an intermediate third category, namely "solvent-separated" ion pairs, could not be distinguished even if they did exist.

### 1. Isomerization Polymerizations

Carbenium ion rearrangements during polymerization have been observed in many cases; such polymerizations are referred to as isomerization polymerizations. The extent of rearrangement depends on the relative stabilities of the propagating and rearranged cations and the relative rates of propagation and rearrangement. Polymerizations of 1-alkenes are especially subject to rearrangement due to the inherent instability of the propagating secondary carbenium ions; extensive rearrangement is typically accompanied by chain transfer, leading to low molecular weight oligomers with complicated structures (e.g. branching, odd carbon numbers, etc.). A well known example in which a single rearranged structure dominates is the polymerization of 3-methyl-1-butene. Note that the propagating secondary carbocation rearranges to a thermodynamically more stable tertiary carbocation.

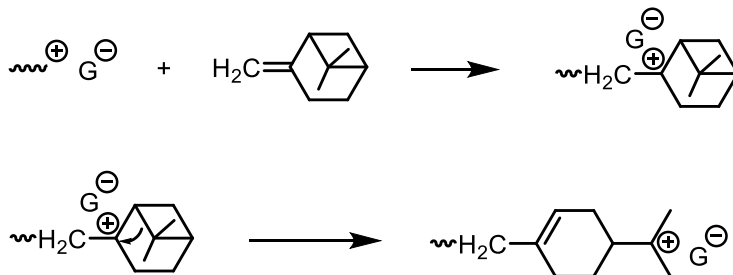
Figure VIII-14



The proportion of rearranged repeat units is high and increases with decreasing temperature. At  $-130^{\circ}\text{C}$  essentially 100% rearrangement occurs and the polymer is highly crystalline.

In some cases the tendency for rearrangement is due to relief of steric strain. In the isomerization polymerization of  $\beta$ -pinene, the propagating and rearranged carbocations are both tertiary.

**Figure VIII-15**



## 2. Copolymerization

The number of copolymerizable monomer pairs by cationic polymerization is much smaller than the corresponding number of pairs which undergo radical copolymerization. Also there is a general lack of tendency toward alternation, i.e., one often will obtain either block copolymers or simply two homopolymers. Relative reactivities of various cationically polymerizable monomers are often influenced by reaction conditions such as solvent, counterion, and temperature. In general, the order of monomer reactivity is:



The following table gives selected copolymerization data for several important cationically polymerizable monomers.

**Table VIII-IV**      **Reactivity Ratios in the Cationic Copolymerization of Styrene (M<sub>1</sub>)**

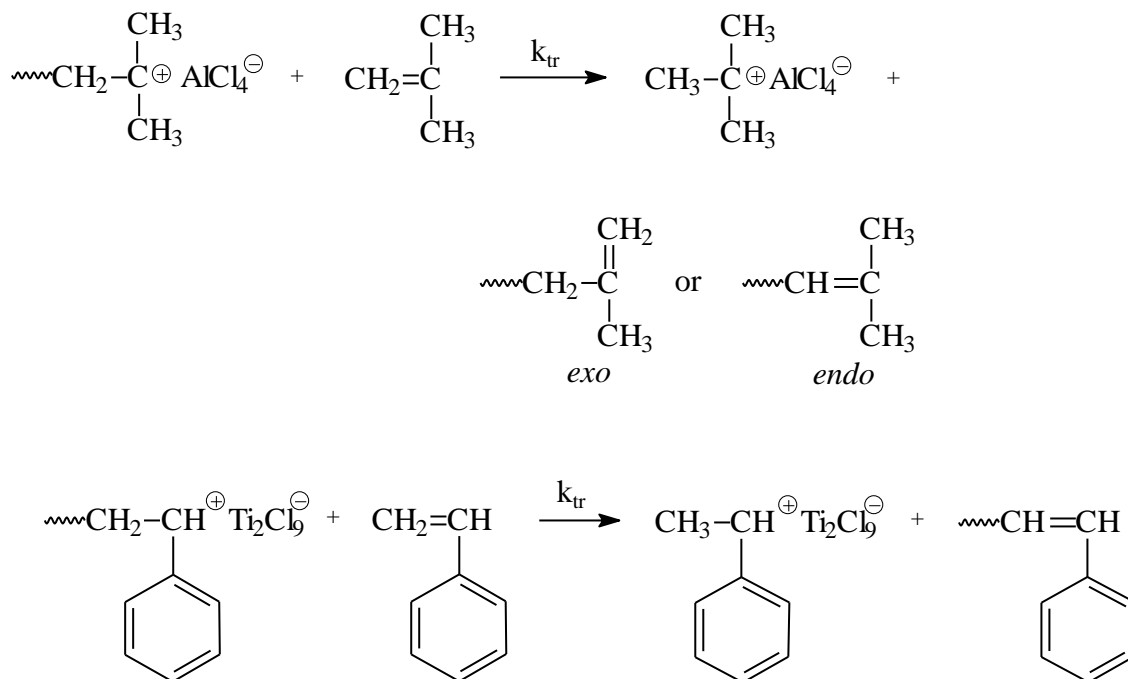
M <sub>2</sub>	Initiator	Solvent	Temp. (°C)	r <sub>1</sub>	r <sub>2</sub>
α-methylstyrene	Et <sub>2</sub> O·BF <sub>3</sub>	SO <sub>2</sub>	-40	<0.1	>20
	Et <sub>2</sub> O·BF <sub>3</sub>	CH <sub>2</sub> Cl <sub>2</sub>	-20	0.2-0.5	12±2
	CCl <sub>3</sub> COOH/ TiCl <sub>4</sub>	CH <sub>2</sub> Cl <sub>2</sub>	-78	0.24±0.05	1.12±0.09
Isobutylene	TiCl <sub>4</sub>	Toluene	-78	1.20±0.10	1.78±0.10
	TiCl <sub>4</sub>	<i>n</i> -hexane	-20	1.20±0.11	0.54±0.24
	SnCl <sub>4</sub>	SO <sub>2</sub>	-78	1.1	3.1
Isoprene	SnCl <sub>4</sub>	EtCl	-30 to 0	0.8	0.1

## 3. Bimolecular Chain Transfer to Monomer

Chain transfer to monomer is the single most important molecular weight determining step for many carbenium ion polymerizations, and especially for isobutylene polymerization at higher temperatures and isobutylene/isoprene copolymerizations (butyl rubber synthesis).

The reaction is first order both in monomer and growing chains, and it involves abstraction by monomer of a  $\beta$ -proton from the carbocation. Certain monomers such as isobutylene and  $\alpha$ -methylstyrene can form two different olefinic structures at the chain end; others such as styrene can only form one.

**Figure VIII-16**

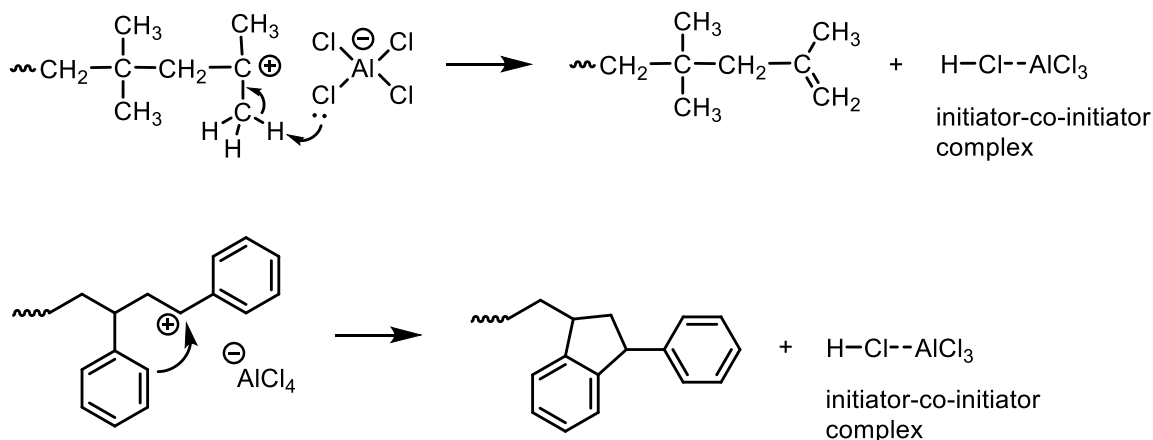


Chain transfer is kinetically indistinguishable from propagation, and it does not terminate the kinetic chain. However, the ratio  $k_{\text{tr},M}/k_p = C_M$  = chain transfer constant to monomer, can be obtained from molecular weight data. Since the activation energy for chain transfer is higher than that for propagation, it can be "frozen out" at low temperatures, and this is responsible for the well known phenomenon of increasing molecular weight with decreasing temperature.

#### 4. Unimolecular chain transfer ( $\beta$ -proton elimination)

Unimolecular chain transfer ( $\beta$ -proton elimination) is one of two unimolecular termination events that occur in carbocationic polymerization (the other is combination or collapse with the counterion). For the usual case of contact pairs (species II in the Winstein spectrum)  $\beta$ -proton elimination is essentially a transfer of the proton from the carbocation to the counterion, with regeneration of the initiator/coinitiator complex (Figure VIII-17, top). In the absence of proton traps, the latter generally adds quickly to monomer, and the kinetic chain is preserved. Although this process yields products identical to those obtained from bimolecular chain transfer, unlike the latter reaction, it is kinetically distinguishable from propagation since it is zero-order in monomer.

**Figure VIII-17**

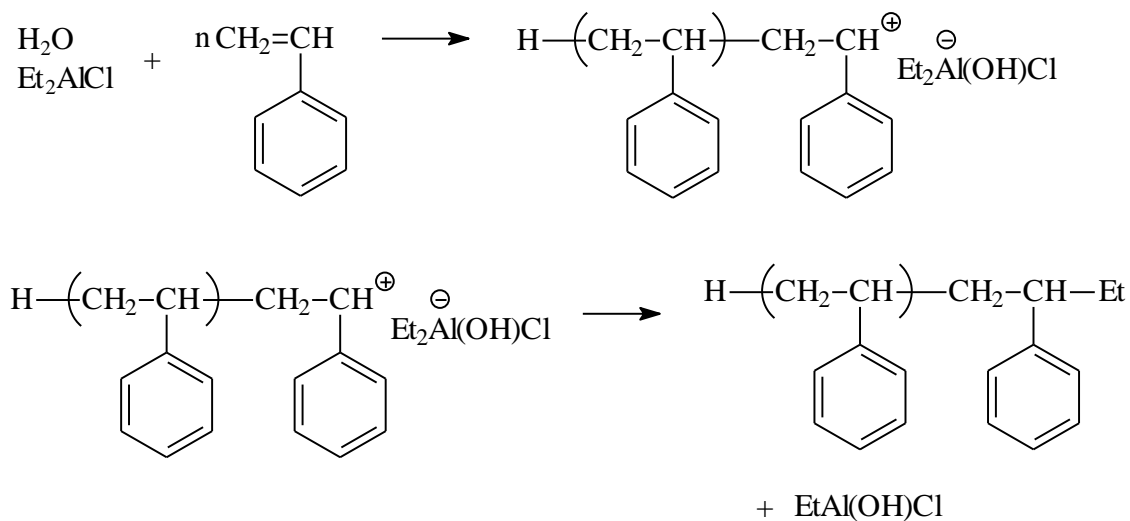


Styrenic monomers can undergo unimolecular chain transfer by an alternative mechanism involving electrophilic aromatic substitution (EAS) at the penultimate phenyl ring (back-biting) (Figure VIII-17, bottom).

### 5. Termination

Combination (collapse) with the counterion, or a negative fragment from the counterion, is a true termination reaction since the kinetic chain is terminated and the initiator-coinitiator complex is consumed. In Figure VIII-18, the proton initiator from water is consumed and the Et<sub>2</sub>AlCl cointiator is replaced by the inactive EtAl(OH)Cl.

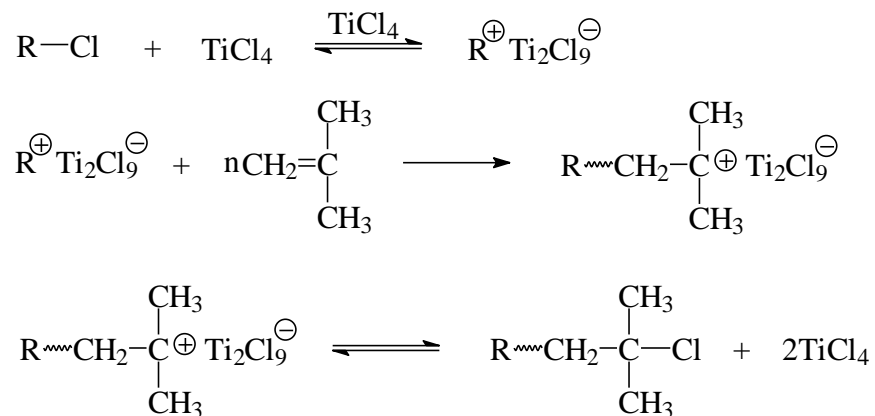
**Figure IV-18**



In many cases, particularly when a halide is transferred to the chain end and the solvent medium is of sufficient polarity, the termination reaction is reversible; in such cases it

represents only a temporary deactivation of the growing chain. This is the fundamental principle involved in living carbocationic polymerization.

**Figure VIII-19**



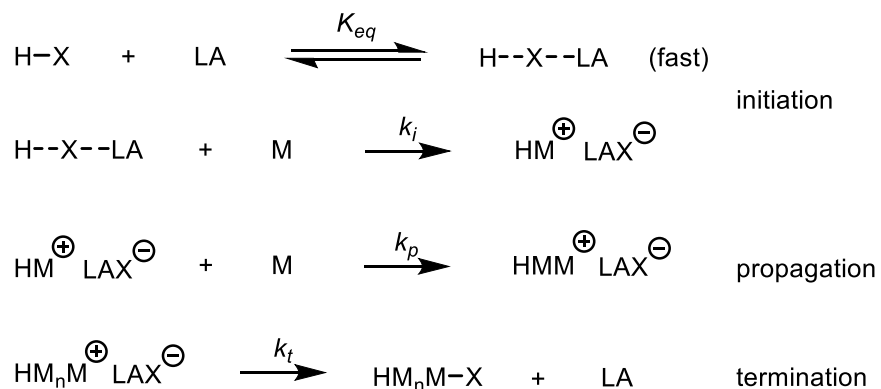
#### D. Kinetics and Energetics of Cationic Polymerization

The kinetics of cationic polymerization do not follow a general rate law due primarily to the complexity and variety of the kinetic expressions for the rate of initiation, and due to variations in the mode of termination. Rarely is the concentration of the propagating carbenium ions known, and almost never is that concentration simply equal to the initiator concentration. Situations such as this are often handled by making use of the steady-state approximation; however, the assumption of a rapidly established steady-state concentration of propagating carbenium ions is generally much less valid than the corresponding assumption for radical polymerization. Often a substantial fraction of the reaction occurs within the period in which the concentration of carbocations is still rising.

The general scheme below demonstrates the application of a steady-state approximation for a hypothetical system, with the following assumptions:

- ion pairs only
- 2<sup>nd</sup> step of initiation is rate limiting
- termination (absolute) by combination with counterion

**Figure VIII-20**



where, LA = co-initiator (Lewis acid)  
H-X = initiator (protogen or cationogen)  
M = monomer

The rates ( $R$ ) of initiation, propagation, and termination are written as follows, where brackets refer to molar concentrations and the various symbols are defined in Figure VIII-20.

$$R_i = k_i K_{eq} [\text{H-X}][\text{LA}][\text{M}] \quad \text{VIII-1}$$

$$R_p = k_p [\text{HM}^{\oplus} \text{LAX}^{\ominus}][\text{M}] \quad \text{VIII-2}$$

$$R_t = k_t [\text{HM}^{\oplus} \text{LAX}^{\ominus}] \quad \text{VIII-3}$$

Assuming a steady state concentration of active species:

$$R_p = \frac{k_i k_p K_{eq}}{k_t} [\text{H-X}][\text{LA}][\text{M}]^2 \quad \text{VIII-4}$$

The number average degree of polymerization,  $\bar{X}_n$ , is given by:

$$\bar{X}_n = \frac{R_p}{R_t} = \frac{k_p}{k_t} [\text{M}] \quad \text{VIII-5}$$

Traditional cationic polymerizations yield relatively broad molecular weight distributions due to the simultaneous occurrence of several chain-breaking reactions, and the fact that initiation is often not fast relative to propagation.

When chain transfer to monomer occurs, either bimolecular or unimolecular, the number of propagating cations does not change, provided unimolecular transfer is characterized by



fast re-initiation . However, the degree of polymerization,  $\bar{X}_n$ , is decreased by all chain breaking events. Thus, when bimolecular chain transfer is important but unimolecular chain transfer is not,  $\bar{X}_n$  is given by,

$$\bar{X}_n = \frac{R_p}{R_t + R_{tr}} = \frac{k_p[M]}{k_t + k_{tr}[M]} \quad \text{VIII-6}$$

where,  $R_t$  = rate of absolute termination

$k_{tr}$  = rate constant for bimolecular chain transfer to monomer

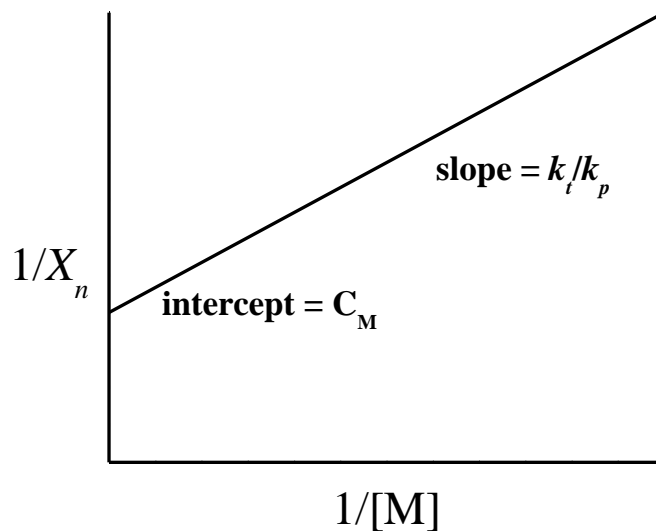
$R_{tr}$  = rate of bimolecular chain transfer to monomer

Equation VIII-6 can be rearranged to the familiar Mayo form with introduction of the unitless chain transfer constant for monomer,  $C_M$ .

$$\frac{1}{\bar{X}_n} = \frac{k_t}{k_p[M]} + \frac{k_{tr}}{k_p} = \frac{k_t}{k_p[M]} + C_M \quad \text{VIII-7}$$

A plot of  $\frac{1}{\bar{X}_n}$  vs.  $\frac{1}{[M]}$  is often used to characterize a particular cationic polymerization system in terms of the relative importance of bimolecular transfer to monomer vs. unimolecular termination events, as a determinant of product molecular weight.

**Figure VIII-21**



Transfer constants for isobutylene and styrene are shown in the table below.

**Table VIII-V: Monomer Transfer Constants for Isobutylene and Styrene in CH<sub>2</sub>Cl<sub>2</sub>**

Monomer	Coinitiator-Initiator	Temperature (°C)	C <sub>M</sub> x 10 <sup>4</sup>
Styrene	TiCl <sub>4</sub> - "H <sub>2</sub> O"	-60	4
		-90	<0.5
	BF <sub>3</sub> - "H <sub>2</sub> O"	-50	5.7
	CF <sub>3</sub> SO <sub>3</sub> H	20	150
Isobutylene	TiCl <sub>4</sub> - "H <sub>2</sub> O"	-20	21.2
		-50	6.60
		-78	1.52
	TiCl <sub>4</sub> -Cl <sub>3</sub> CCO <sub>2</sub> H	-20	26.9
		-50	5.68
		-78	2.44
	SnCl <sub>4</sub> - Cl <sub>3</sub> CCO <sub>2</sub> H	-20	60.0
		-50	36.0
		-78	5.7
	BF <sub>3</sub> - "H <sub>2</sub> O"	-25	15
-50		3.9	

The most significant feature of the overall energetics of traditional (non-living) cationic polymerizations is the generally low activation energies for polymerization (and propagation), which in some cases will actually be negative. This causes the unusual phenomenon of increasing rate of polymerization with decreasing temperature. The activation energy for the degree of polymerization is almost always negative in traditional cationic polymerizations; thus the molecular weight invariably increases as the temperature decreases. To understand this phenomenon it is necessary to examine the temperature dependency of the various elementary steps, initiation, propagation, transfer, and termination.

The rate of initiation of a cationic polymerization, in direct contrast to a radical polymerization, is relatively temperature insensitive, meaning it has a low energy of activation. Thus the rate of polymerization and the degree of polymerization will be determined by the temperature dependencies of the other steps. This can be expressed quantitatively in terms of the Arrhenius equation,

$$R_p \propto \frac{k_i k_p}{k_t} = \frac{A_i A_p}{A_t} e^{-(E_i + E_p - E_t)/RT} \quad \text{VIII-8}$$

The quantity  $(E_i + E_p - E_t)$  is often negative because the activation energy for termination is often greater than that of propagation and initiation combined. This yields an overall negative activation energy for polymerization.

The degree of polymerization is given by equation VIII-6. Expressed as an Arrhenius equation, the following is obtained for transfer-dominated systems:

$$\bar{X}_n = \frac{k_p}{k_{tr}} = \frac{A_p}{A_{tr}} e^{-(E_p - E_{tr})/RT} \quad \text{VIII-9}$$

For termination-dominated systems, we obtain:

$$\bar{X}_n = \frac{k_p[M]}{k_t} \propto \frac{A_p}{A_t} e^{-(E_p - E_t)/RT} \quad \text{VIII-10}$$

## E. Controlled/Living Cationic Polymerizations

To properly discuss and understand living carbocationic polymerization, it is important to review the concept of a living polymerization. A living polymerization is a theoretical model or idealized system (akin to an ideal gas in thermodynamics) that is approached more or less closely by real systems.

Definition of Ideal Living Polymerization – Homogeneous chain polymerization in which propagation occurs in the complete absence of termination and chain transfer.

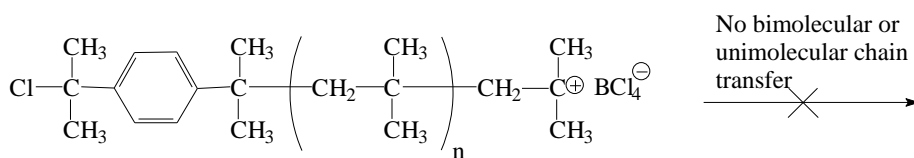
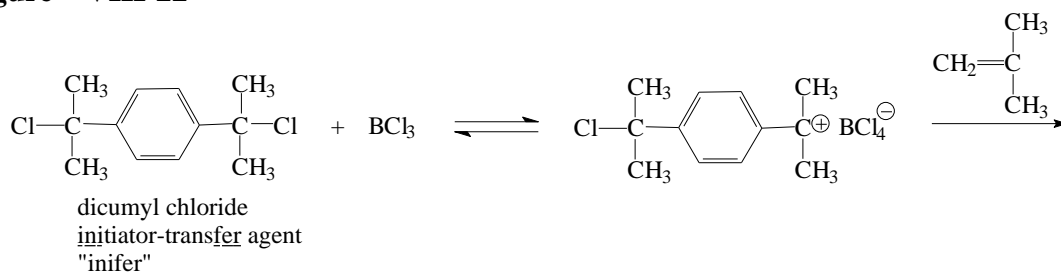
Fast initiation relative to propagation is a characteristic feature of living polymerizations, but it is not a strict requirement for a polymerization to be living. Slow initiation can be overcome by withholding monomer until initiation is complete. In an ideal living polymerization, all chains, once initiated, are active all of the time.

Important developments, which led to the development of living carbocationic polymerization will be covered in the next several sections.

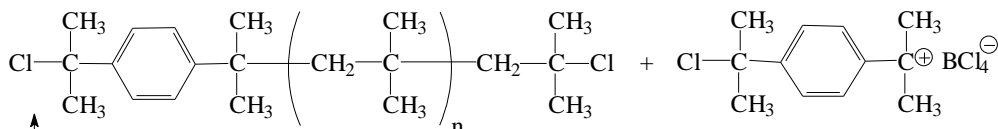
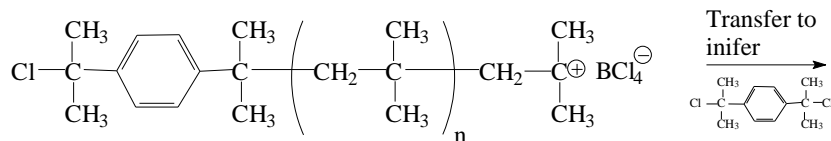
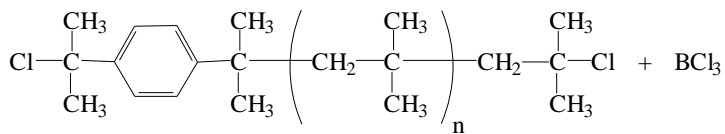
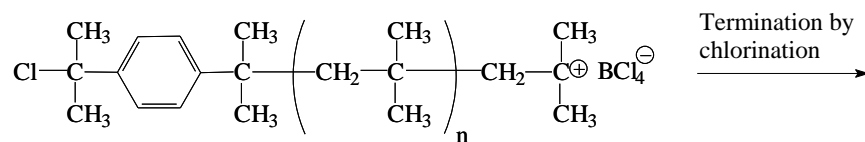
### 1. Inifer System

In the late 1970's Kennedy and his students at the University of Akron discovered the utility of inifers (initiator-transfer agents), which, when used with  $\text{BCl}_3$  coinitiator, could provide polymerizations of isobutylene that were largely free of bimolecular and unimolecular chain transfer to monomer and did not involve undesired initiation by protic impurities such as moisture. All chains possessed an inifer moiety as the head group and a *tert*-chloride functional group as the tail group.

Figure – VIII-22



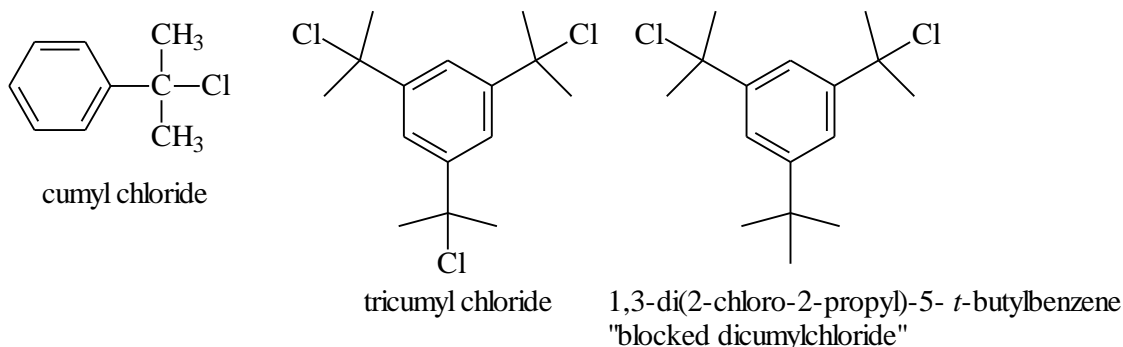
Chain-breaking reactions:



↑  
This chloride function  
may also initiate

Various inifers were developed, which provided linear and star-branched architectures.

**Figure VIII-23**



For the inifer system, the degree of polymerization is given by,

$$\bar{X}_n = \frac{2k_p[M]}{k_t + k_{tr,I}[I]} \quad \text{VIII-11}$$

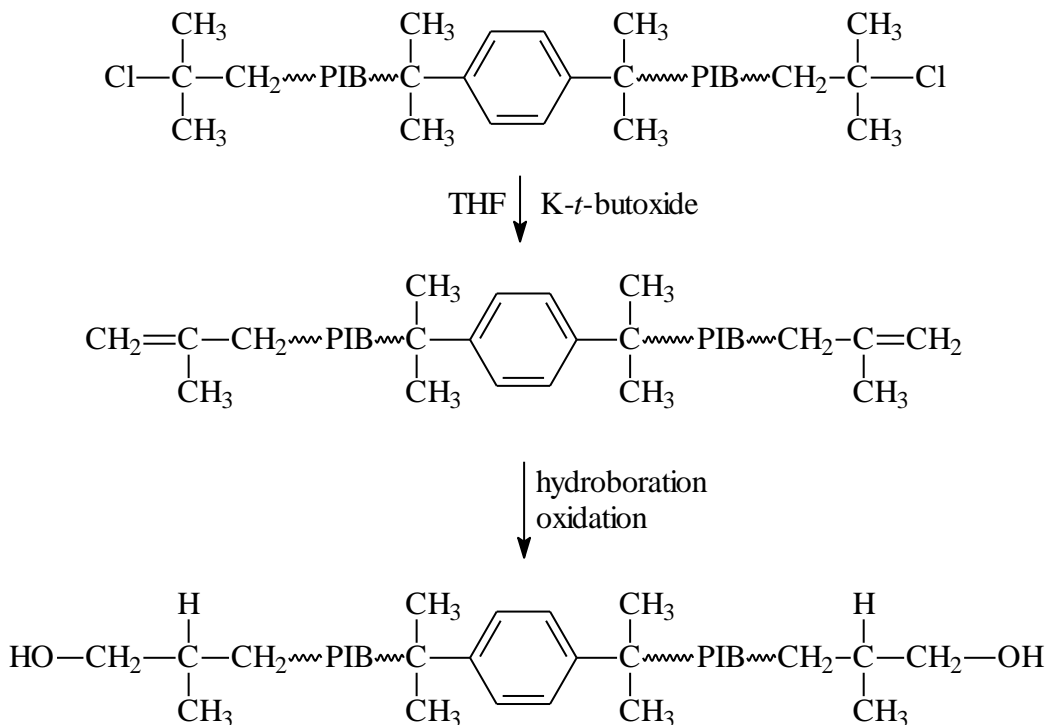
where, I = *p*-dicumylchloride inifer. Rearrangement yields a linear equation to which experimental data can be fitted:

$$\frac{2[M]}{\bar{X}_n} = \frac{k_{tr,I}}{k_p}[I] + \frac{k_t}{k_p} \quad \text{VIII-12}$$

A plot of  $2[M]/\bar{X}_n$  vs. [I] may be used to determine which is the predominant mode of formation of *tert*-chloride end groups. For *p*-dicumylchloride in CH<sub>3</sub>Cl at  $-70^\circ\text{C}$ ,  $k_{tr,I}/k_t \approx 30 \text{ L/mol}$ ; therefore, for typical inifer concentrations ( $10^{-4} - 10^{-2} \text{ M}$ ), termination is the predominant reaction.

The inifer system approximates a living system in the sense that chain transfer to monomer is absent; however, it is not controlled since initiation is not fast relative to propagation and molecular weight distributions are broad. The system is also heterogeneous since MeCl is a nonsolvent for PIB molecules of  $> 4,000 \text{ g/mol}$ . The inifer system does yield telechelic polyisobutylenes carrying *tert*-chloride end groups; the latter may be derivatized to yield various useful functionality such as hydroxyl.

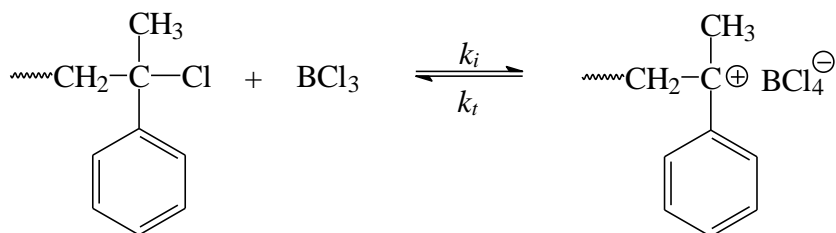
Figure VIII-24



## 2. Reversible-Deactivation Polymerizations

The inifer systems (discussed in the last section) were free of bimolecular chain transfer to monomer, but they were not free from termination. Collapse with the counterion produced *tert*-chloride chain ends that were considered to be essentially irreversibly terminated due to the particular monomer/Lewis acid combination employed. That is, it was believed that  $\text{BCl}_3$  was too weakly acidic to re-ionize the polyisobutylene *tert*-chloride chain ends. Therefore, early researchers seeking to develop living cationic polymerization systems began to investigate monomer/Lewis acid combinations that might yield reversible termination. The thought was that such systems, although not perfectly living according to the Szwarc definition, would display characteristics similar to living polymers. Representative of this idea is the  $\alpha$ -methylstyrene/ $\text{BCl}_3$  system shown in Figure VIII-25. Note that this monomer yields a terminated chain end that is a nearly perfect mimic of the initiators used in the inifer systems, and thus, it was demonstrably capable of being ionized by  $\text{BCl}_3$ . This phenomenon, embodied in the equilibrium shown in Figure VIII-25 (and also shown in the last reaction of Figure VIII-5) is termed reversible deactivation in the modern literature. It is the same phenomenon utilized in living radical polymerization systems such as ATRP.

Figure VIII-25

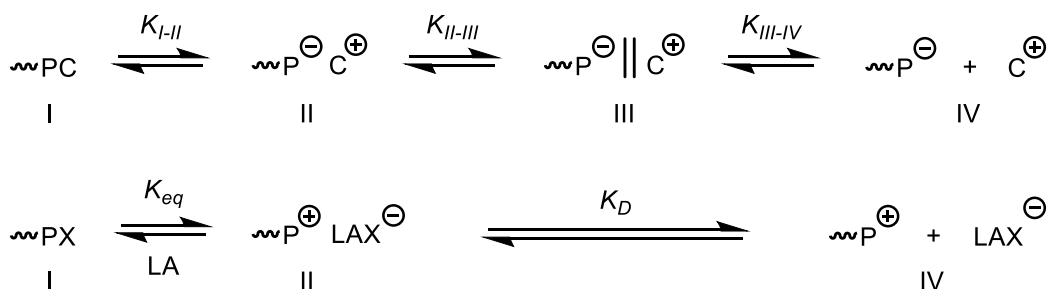


### 3. Mechanism of Living Carbocation Polymerizations

#### a. Dormant-active chain end equilibrium

With respect to termination and its relationship to livingness of a chain polymerization, it is now recognized that the operation of a reversible deactivation equilibrium is the more general behavior and that the anionic polymerization systems proposed originally by Szwarc are simply a special case. Figure VIII-26 shows the Winstein spectrum for anionic polymerization that we studied previously (top) compared with the Winstein spectrum re-drawn for the case of cationic polymerization (bottom). Note that for cationic polymerization, ionization (equilibrium between species I and II) is shown for the typical case of assistance by a Lewis acid (LA), and, that no solvent-separated ion pair (species III) is recognized, for reasons we have previously discussed ( $\text{LAX}^-$  is typically a very large ion).

Figure VIII-26

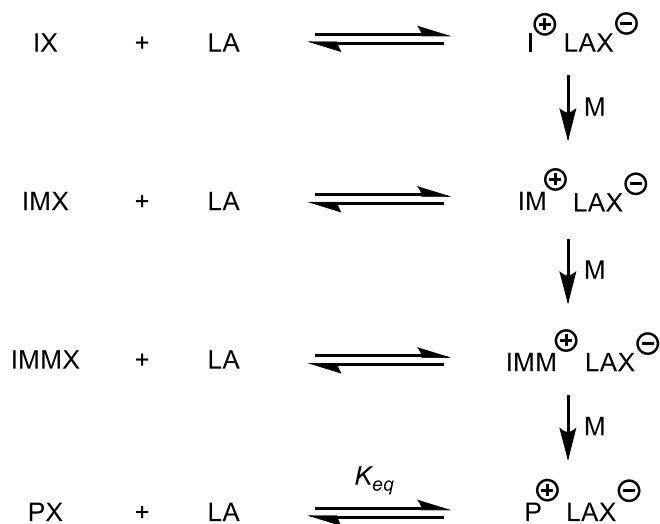


The equilibrium between species I and II is the reversible deactivation equilibrium. In Szwarc's classical living anionic polymerization of styrene, the equilibrium constant,  $K_{I-II}$ , was simply very large such that the concentration of terminated chains remained essentially zero. In contrast, living cationic polymerizations are typically designed (by choice of monomer, catalyst, and solvent polarity) to operate under conditions where  $K_{eq}$  is quite small ( $\ll 1$ ); under these conditions, active carbocations (typically species II only) are in equilibrium with a large reservoir of reversibly terminated, dormant chains (species I). This same principle is the basis for "living" free radical polymerizations such as ATRP. The current terminology for these types of living polymerizations is "reversible-deactivation polymerization."

*b. Ideal reversible-deactivation polymerizations*

Ideal reversible-deactivation polymerizations are characterized by an absence of irreversible chain breaking reactions, and will be considered first. Figure VIII-27 shows the ionization (reversible deactivation) equilibria for initiator and growing chains of degree of polymerization 1, 2, and n. The active species are assumed to be exclusively contact paired ions (species II in the bottom of Figure VIII-26).

**Figure VIII-27**



The kinetics of a reversible-deactivation polymerization are typically treated as follows:

$$\frac{-d[\text{M}]}{dt} = k_{app}[\text{CE}][\text{M}] \quad \text{VIII-13}$$

where,  $[\text{CE}] = [\text{PX}] + [\text{P}^{\oplus}\text{LAX}^{\ominus}]$  = concentration of growing chains (dormant plus active species), which is equal to the beginning initiator concentration,  $[\text{IX}]_0$ , in the absence of irreversible termination.

$k_{app}$  = apparent second-order rate constant for propagation ( $\text{M}^{-1}\text{s}^{-1}$ )

Integration yields,

$$\ln \frac{[\text{M}]_0}{[\text{M}]} = k_{app}[\text{CE}]t \quad \text{VIII-14}$$

$[\text{CE}]$  is related to the instantaneous concentration of active species through the ionization equilibrium in Figure VIII-27.



$$[\text{CE}] = \frac{K+1}{K} [\text{P}^{\oplus}\text{LAX}^{\ominus}] \quad \text{VIII-15}$$

where,  $K = K_{eq}[\text{LA}]$ .

It is noteworthy that the same proportionality seen in Equation VIII-15 must exist between  $k_p$ , the true bimolecular rate constant for propagation, and  $k_{app}$ :

$$k_p = \frac{K+1}{K} k_{app} \quad \text{VIII-16}$$

Substituting Equation VIII-15 into the integrated rate expression (Equation VIII-14) yields:

$$\ln \frac{[\text{M}]_0}{[\text{M}]} = k_{app} \frac{K+1}{K} [\text{P}^{\oplus}\text{LAX}^{\ominus}] t = k_p [\text{P}^{\oplus}\text{LAX}^{\ominus}] t \quad \text{VIII-17}$$

Note that for a living polymerization as classically defined by Szwarc, in which all the chains are active all the time (as distinct from a reversible deactivation polymerization),  $K = \infty$  and thus  $[\text{CE}] = [\text{P}^{\oplus}\text{LAX}^{\ominus}]$ , and  $k_{app} = k_p =$  true bimolecular rate constant for propagation.

*c. Non-ideal reversible deactivation polymerizations*

Non-ideal reversible-deactivation polymerizations are characterized by the presence of irreversible chain breaking reactions. The three most common chain breaking reactions are:

- bimolecular (direct) chain transfer to monomer (see Figure VIII-16)
- unimolecular chain transfer ( $\beta$ -proton elimination) (see Figure VIII-17)
- termination (combination or “collapse” with the counterion)

The rate expression for bimolecular (direct) chain transfer to monomer is given by:

$$\frac{d[\text{P}_=]}{dt} = k_{tr,M} [\text{P}^{\oplus}\text{LAX}^{\ominus}] [\text{M}] \quad \text{VIII-18}$$

where,  $[\text{P}_=]$  is the concentration of terminated chains possessing an olefinic end group (see Figure VIII-16).

Since Equation VIII-18 is identical in form to the rate expression for propagation,

$$\frac{-d[\text{M}]}{dt} = k_p [\text{P}^{\oplus}\text{LAX}^{\ominus}] [\text{M}] \quad \text{VIII-19}$$

the ratio between rate of chain transfer and rate of propagation will be independent of the concentration of active species and monomer. Dividing Equation VIII-18 by Equation VIII-19 and integrating yields the following equation, which indicates that the concentration of terminated chains,  $[P_-]$ , will be a linear function of monomer conversion,  $p = ([M]_o - [M])/[M]_o$ :

$$[P_-] = \frac{k_{tr,M}}{k_p} p[M]_o \quad \text{VIII-20}$$

The "livingness" of the polymerization with regard to direct chain transfer may be characterized by the ratio  $k_{tr,M}/k_p = C_M$  (unitless monomer transfer constant). The smaller this number, the greater is the degree of livingness. Note that the total number of chains in the system,  $[P]_{tot}$ , is given by:

$$[P]_{tot} = [CE] + [P_-] = [IX]_o + [P_-] \quad \text{VIII-21}$$

The higher the initiator concentration,  $[IX]_o$  (i.e., the lower the target molecular weight), the less significant becomes the fraction of terminated chains relative to the total number of chains. Therefore, for a given value of  $k_{tr,M}/k_p$ , a system appears more living-like as the target molecular weight is lowered.

Unimolecular chain transfer ( $\beta$ -proton elimination) consists of transfer of a proton to the counterion. Often the proton is immediately transferred to monomer, and hence this process is also called "indirect" chain transfer to monomer. The rate expression for unimolecular chain transfer is given by:

$$\frac{d[P_-]}{dt} = k_{-H}[P^{\oplus}LAX^{\ominus}] \quad \text{VIII-22}$$

Following the same procedure (dividing by Equation VIII-19 and integrating) yields Equation VIII-23, which indicates that the concentration of terminated chains will increase exponentially with monomer conversion:

$$[P_-] = -\frac{k_{-H}}{k_p} \ln(1-p) \quad \text{VIII-23}$$

The "livingness" of the polymerization with regard to unimolecular chain transfer may be characterized by the ratio  $k_{-H}/k_p$ . The smaller this number, the greater is the degree of livingness. If the transferred protons re-initiate monomer, then Equation VIII-21 holds, and the higher the initiator concentration,  $[IX]_o$  (i.e. the lower the target molecular weight) the less noticeable is the effect of unimolecular chain transfer. Equation VIII-23 clearly shows that the incidence of  $\beta$ -proton elimination increases dramatically at high monomer conversion. Thus, carrying a reversible deactivation polymerization to excessively long reaction times (i.e., excessively high monomer conversions, say, beyond 10-15 half-lives) may cause significant unimolecular chain transfer.

Often  $\beta$ -proton elimination does not lead to re-initiation, e.g., when proton traps are present; in this case, formation of new chains is prevented, but significant loss of living chain ends still occurs.  $\beta$ -Proton elimination without re-initiation is sometimes referred to as terminative chain transfer. When chain breaking is by terminative chain transfer or other irreversible unimolecular termination process that does not lead to re-initiation, the kinetics must be treated differently since  $[P]_{\text{tot}}$  remains constant and equal to  $[IX]_0$ . The following mass balance holds throughout polymerization,

$$[P]_{\text{tot}} = [IX]_0 = [CE]_0 = [CE] + [P_t] = [PX] + [P^{\oplus}LAX^{\ominus}] + [P_t] \quad \text{VIII-24}$$

where,  $[P_t]$  = concentration of irreversibly terminated chains. The rate of termination is written as,

$$\frac{d[P_t]}{dt} = k_t [P^{\oplus}LAX^{\ominus}] \quad \text{VIII-25}$$

where,  $k_t$  is the rate constant for termination. If termination is by terminative chain transfer and  $\beta$ -proton elimination is rate limiting, then  $k_t = k_H$ . Combination with Equation VIII-15 and substitution of the mass balance (Equation VIII-24) yields:

$$\frac{d[P_t]}{dt} = k_t \frac{K}{K+1} ([IX]_0 - [P_t]) \quad \text{VIII-26}$$

Solution of differential Equation VIII-26 yields the following,

$$[P_t] = [IX]_0 \left( 1 - e^{-k_t \frac{K}{K+1} t} \right) \quad \text{VIII-27}$$

Eq VIII-27 may be expressed in several alternate ways, all equally valid:

$$[CE] = [IX]_0 e^{-k_t \frac{K}{K+1} t} \quad \text{VIII-27A}$$

and,

$$[P^{\oplus}LAX^{\ominus}] = [P^{\oplus}LAX^{\ominus}]_0 e^{-k_t \frac{K}{K+1} t} \quad \text{VIII-27B}$$

Eqs VIII-27A and VIII-27B show that irreversible termination causes the same first-order decay in both growing chains (dormant plus active chains) and instantaneously active chains (active only). The latter assumes that the ionization equilibrium is established instantaneously).

Substituting Equation VIII-27B into the expression for the rate of propagation (Equation VIII-19), and noting that  $[P^{\oplus}LAX^{\ominus}]_0 = \frac{K}{K+1} [I]_0$  (see Equation VIII-15), yields,

$$\frac{-d[M]}{dt} = k_p \frac{K}{K+1} [IX]_0 e^{-k_t \frac{K}{K+1} t} [M] \quad \text{VIII-28}$$

Integration yields the following expression:

$$\ln \frac{[M]_0}{[M]} = \frac{k_p}{k_t} [IX]_0 \left( 1 - e^{-k_t \frac{K}{K+1} t} \right) \quad \text{VIII-29}$$

The form of Equation VIII-29 predicts a maximum conversion beyond which the system cannot progress (as  $t \rightarrow \infty$ , the exponential approaches zero). Thus:

$$p_{\text{MAX}} = 1 - e^{-\frac{k_p [IX]_0}{k_t}} \quad \text{VIII-30}$$

*d. Effect of the dormant-active chain end equilibrium on shelf-life*

The equations dealing with chain breaking may be used to demonstrate the concept of “shelf-life.” Shelf-life refers to the length of time that a living polymerization retains sufficient livingness to allow one to complete a desired synthetic objective, for example, block copolymer synthesis. Consider a traditional non-living carbocation polymerization. A typical system might be characterized by the following parameters:

$$\begin{aligned} k_p &= 10^5 \text{ M}^{-1}\text{s}^{-1} \\ k_H &= 0.1 \text{ s}^{-1} \\ k_{tr,M} &= 0 \\ K &= \infty \\ [IX]_0 &= [CE]_0 = [P^{\oplus}LAX^{\ominus}] = 5 \text{ mM} \end{aligned}$$

Thus, in the particular system chosen, chain breaking is by unimolecular chain transfer, and there is no dormant-active equilibrium (all centers are active all of the time). The rate constant of propagation represents the composite for paired and free ions. Equation VIII-17 (with  $K = \infty$  and  $k_{app} = k_p$ ) shows that for this system, 99% conversion is reached within about 9 ms. Moreover, Equation III-27B shows that 99% of the original chains have decomposed (lost a  $\beta$ -proton) within about 46 s. Clearly, such a system would not be considered living from a practical viewpoint (i.e., the shelf-life is too short).

Consider the same system, only now assume that the active chains are in equilibrium with a reservoir of dormant chains with  $K = 10^{-6}$ . Equation III-27A shows that now only 1% of the original chains have decomposed in 28 h. However, 95% of the monomer is consumed by these reversibly deactivated chains in about 100 min. The dormant-active chain end equilibrium has transformed a poorly controlled, non-living system into a controlled/living system with practical synthetic possibilities. This analysis also assumes that the ratio  $k_H/k_p$  was unaffected by whatever system change (solvent, counterion, etc.) that was carried out to create the large reservoir of dormant chain ends. Very likely, the decrease in ionicity (e.g., elimination of free ions in the system) also caused

this number to become smaller such that the intrinsic livingness of the system was also improved.

#### 4. Living Carbocationic Polymerization Systems

Living carbocationic polymerization systems have been developed using one of three basic strategies:

- Monomer starvation conditions (originally termed “quasiliving” polymerizations)
- Selection of a suitably nucleophilic counterion (common with reactive monomers)
- Addition of an external additive (typically a proton trap, a common ion salt, or an electron donor)

All of these techniques bring about reversible-deactivations polymerizations such that most of the chain ends exist at any given instant in a dormant state. The second two methods cause a general shift of the active chain ends toward lower ionicity along the Winstein spectrum. This increases shelf life, increases the rate of initiation compared to propagation (favorably affecting the molecular weight distribution), and may also favorably change  $k_{tr,M}/k_p$  and/or  $k_i/k_p$  by the elimination of free ions. Proton traps eliminate initiation by moisture.

##### *a. Monomer starvation conditions*

This was an early technique in which the monomer concentration was kept purposefully low in order to force reversibility of unimolecular transfer. The resulting polymerizations were described as “quasiliving.” This technique is inferior to the other two and will not be discussed further.

##### *b. Selection of a suitably nucleophilic counterion*

Since the late 1970's, researchers at Kyoto University (Higashimura, Sawamoto et al.) have systematically investigated potentially living cationic polymerization systems involving reactive monomers, principally vinyl ethers, *p*-methoxystyrene, and N-vinylcarbazole. Their technique has been to select polymerization conditions, i.e., solvent and especially counterion, such that the growing chain ends are mostly dormant, covalent species with a low concentration of ion pairs. Specific systems that they have described are as follows:

*p*-methoxystyrene/I<sub>2</sub>/CCl<sub>4</sub>  
Isobutylvinylether/HI-I<sub>2</sub>/Non-polar solvent  
*p*-methoxystyrene/HI-I<sub>2</sub>/Non-polar solvent  
N-vinylcarbazole/HI/  
*p*-methylstyrene/CH<sub>3</sub>COClO<sub>4</sub>

The earliest reported system was the polymerization of *p*-methoxystyrene (*p*MOS) initiated by iodine, in a non-polar medium such as CCl<sub>4</sub> (Figure VIII-28). In this system, I<sub>2</sub> serves

as both initiator and co-initiator. The  $I_3^\ominus$  counterion was chosen specifically for its appropriate degree of nucleophilicity (relative to the monomer reactivity), and the presence of a dormant-active chain-end equilibrium imparted livingness to the system. This early system is instructive in that it shows many characteristics of living, or at least long-lived, chain ends, i.e., molecular weight distributions are narrowed considerably compared to conventional non-living polymerizations, and there is a linear relationship between molecular weight and monomer conversion. However, initiation was slow, leading to broader than desired molecular weight distributions and poor molecular weight control at low  $[M]_0/[I]_0$ .

Higashimura et al. discovered that the problem of slow initiation was solved by the use of HI as initiator, in conjunction with  $I_2$  as coinitiator (Figure VIII-29). The HI/ $I_2$  system was shown by these researchers to be a versatile system capable of creating living polymers from vinyl ethers and reactive styrenic monomers such as *p*MOS. The authors showed that the number of growing chains is equal to the number of HI initiator molecules added, and that the number of growing chains is invariant over time.

**Figure VIII-28**

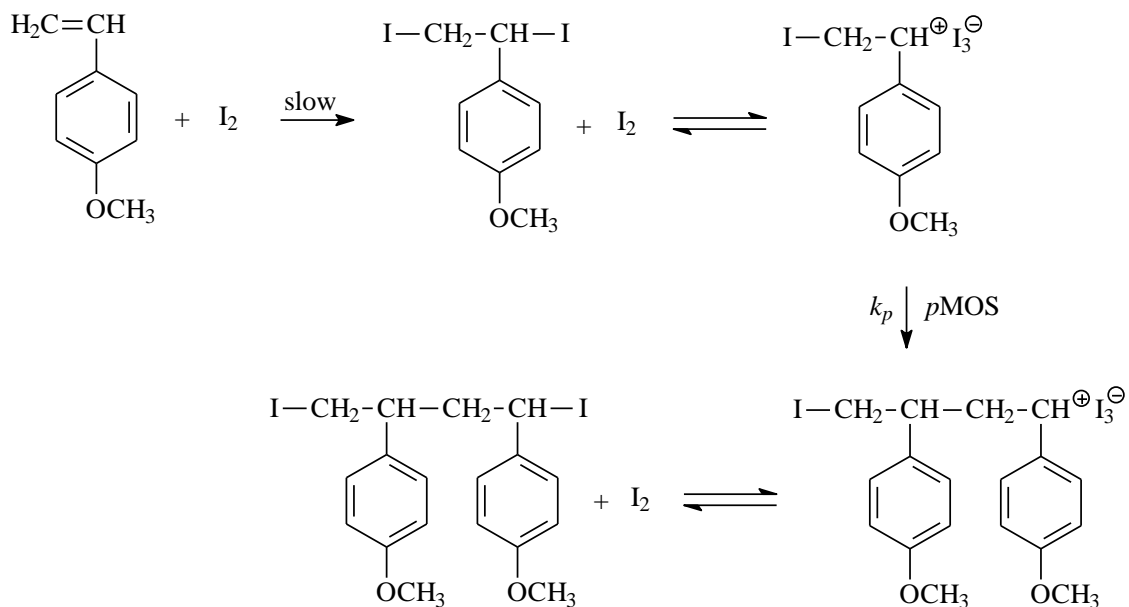
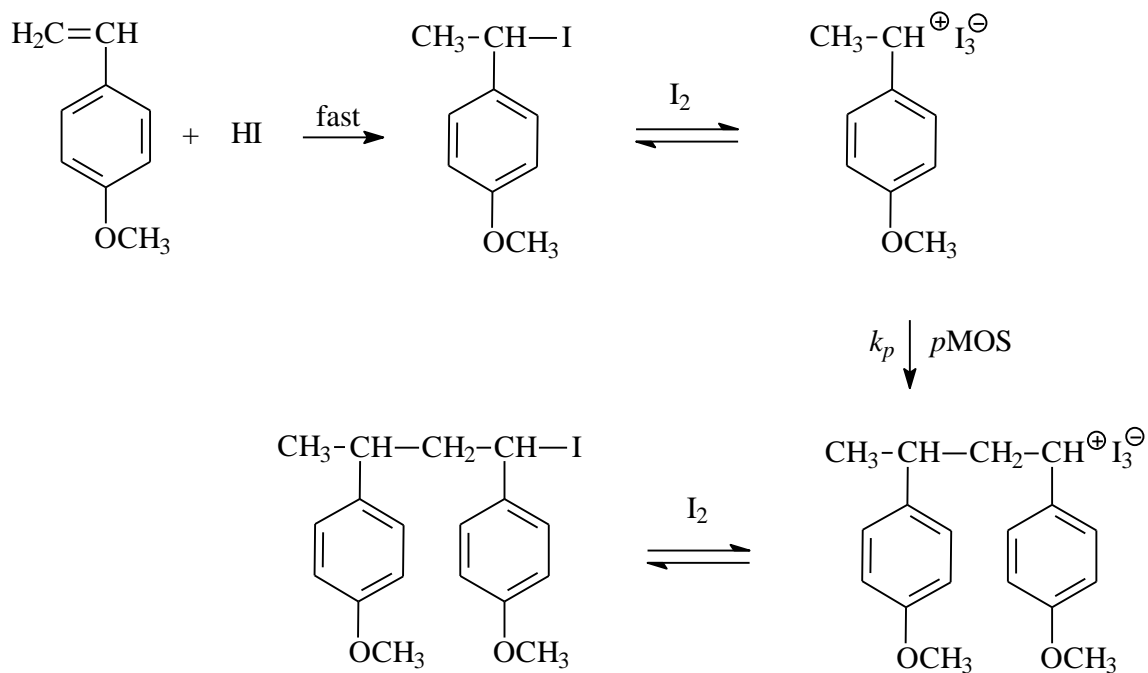
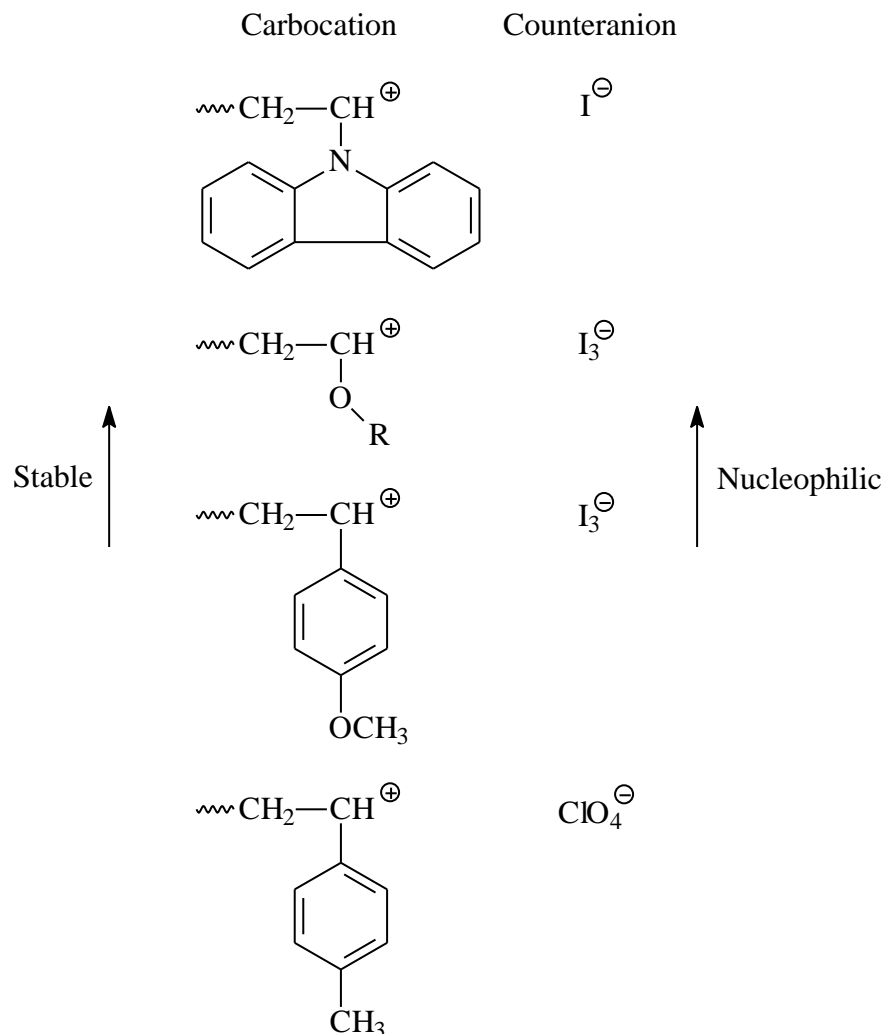


Figure VIII-29



Higashimura et al. later discovered that HI alone could bring about the living polymerization of N-vinylcarbazole, a monomer that is extremely reactive toward cationic polymerization. Further work by Higashimura et al. in this area with different monomers lead to the formulation of a general proposition: to achieve living polymerization the nucleophilicity of the counterion must be chosen to match the stability of the cation; the more stable the cation, the more nucleophilic must be the counterion. This idea is demonstrated in Figure VIII-30.

Figure VIII-30



The HI-I<sub>2</sub> initiation system for vinyl ethers does suffer some drawbacks. It is necessary to run the polymerizations at low temperatures to achieve living behavior, and the polymerization rates are relatively low. Higashimura et al. later made further improvements in this basic system through the substitution of iodine by ZnI<sub>2</sub>.

- c. *Addition of an external additive (typically a proton trap, a common ion salt, or an electron donor)*

The addition of an external additive is the most effective and popular way to achieve living cationic polymerization behavior for less reactive monomers such as isobutylene and styrene. In this method, a species is added externally to the polymerization mixture to bring about living conditions in cationic polymerization. Typically appropriate adjustments are also made to solvent and counterion (Lewis acid) to obtain the desired ionization (reversible deactivation) equilibrium constant, *K*. Most of these additives are Lewis bases, i.e., electron pair donors that contain no active hydrogens in their structure. Examples include tertiary amines such as pyridine, 2,4-dimethylpyridine, triethylamine, and 2,6-di-*tert*-butylpyridine



(proton trap), and weaker bases such as esters and ethers. In general, the more reactive monomers such as vinyl ethers respond well to the addition of weaker bases, but the less reactive monomers such as isobutylene and styrene require the stronger *tert*-amine bases to bring about living conditions. The added bases form onium salts through the scavenging of active hydrogen-containing compounds (typically water), which action serves two purposes: 1) to suppress protic initiation, and 2) to create common counterions, which suppresses ion pair dissociation.

Another broad category of additives is common ion salts. An example would be the addition of tetra-*n*-butylammonium chloride to a polymerization co-initiated with a metal chloride such as BCl<sub>3</sub>. Addition of chloride ion to such a polymerization causes the *in situ* formation of BCl<sub>4</sub><sup>⊖</sup> ions, which are identical to the counterions found at the growing chain ends. This creates a huge excess of counterions, which through the mass action law, suppresses ion pair dissociation.

**Figure VIII-31**

