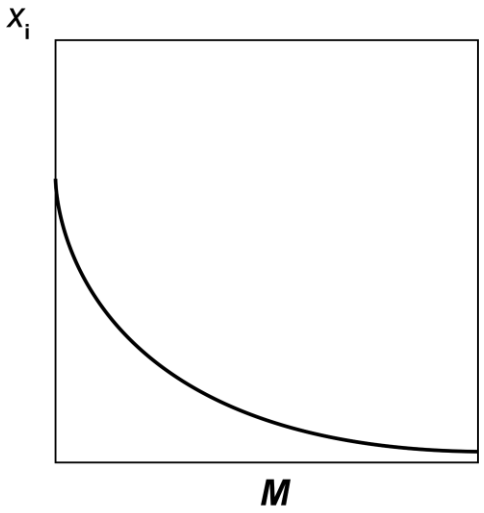
Controlled ("Living") Polymerization I

16:160:509 – Polymer Chemistry

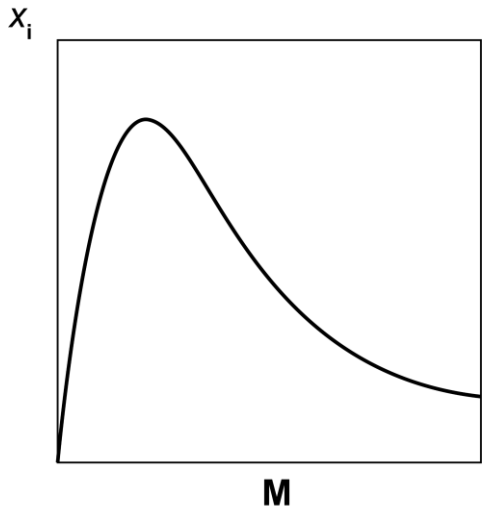
Lecture 9 to 10

RUTGERS
School of Arts and Sciences
DEPARTMENT OF CHEMISTRY
AND CHEMICAL BIOLOGY

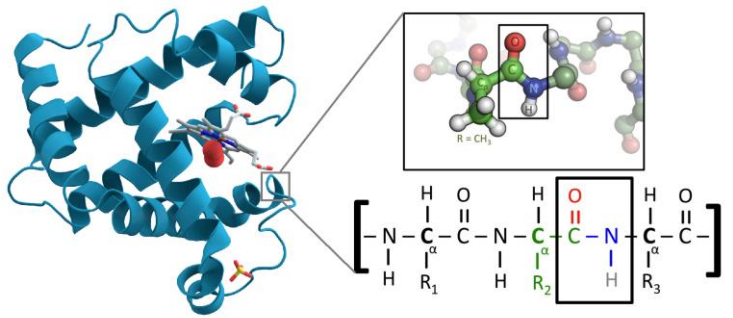
Synthetic vs Natural Polymers

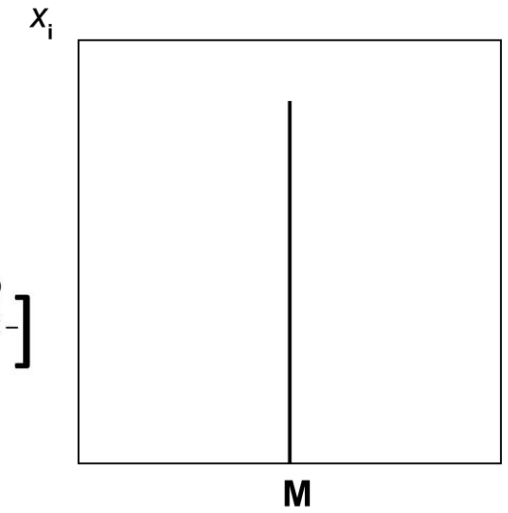


Step-growth polymerization



Free-radical chain-growth polymerization (combination)





Synthetic polymers are highly polydisperse

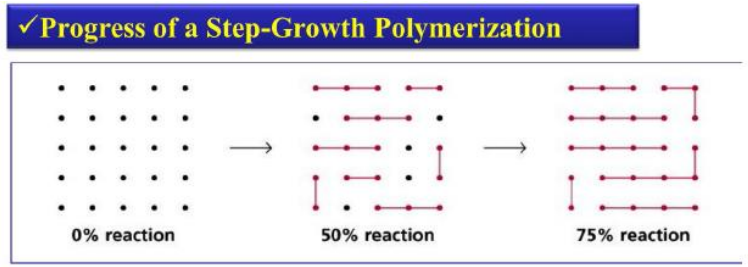
Biomacromolecules are perfectly monodisperse

Nature has a way better “control” over polymerization than us. How do we design polymerization processes that yield polymers with less heterogeneity?

Use What We Have Learned So Far to Design a Controlled Polymerization Process

Step-growth polymerization

Any molecule can react with any other at any time



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Free-radical chain-growth polymerization

Monomers only react with propagating species, but each propagating chain is short-lived:

- Chains may be initiated at any time.
- Chains may be easily terminated via termination or transfer events.

↓

What do we need to achieve a narrow distribution?

- Fix the total number of polymers—only chain-growth polymerization would meet this requirement
- All chains must be initiated at the same time—fast initiation ($k_i >> k_p$)
- Distribute monomers uniformly among the fixed number of growing chains—no termination or transfer events ("living" polymerization, $k_t = 0$, $k_{tr} = 0$)

Kinetics of an Ideal Living Polymerization with Fast Initiation

$$\text{Initiation: } I + M \xrightarrow{k_i} P_1^*$$

$$\text{Propagation: } P_1^* + M \xrightarrow{k_P} P_2^*$$

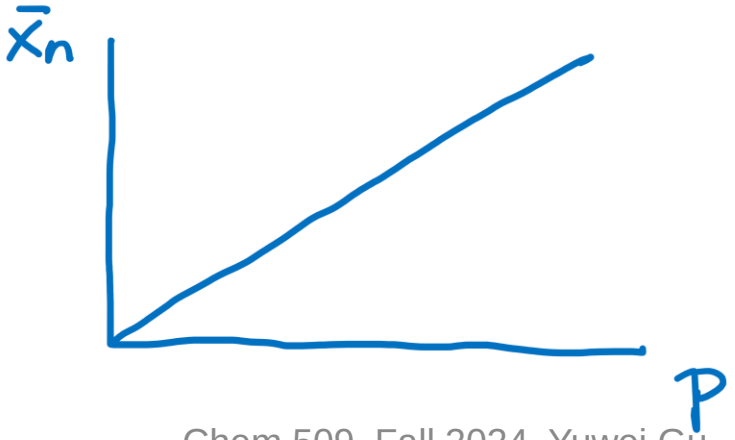
$$P_i^* + M \xrightarrow{k_P} P_{i+1}^*$$

- Fast initiation ($k_i >> k_p$)
- No termination or transfer events ($k_t = 0$, $k_{tr} = 0$)

- The total number of growing chains equals the total number of initiators.
- Monomers that have reacted are statistically evenly distributed among all growing chains.

$$\bar{X}_n = \frac{\text{Total \# of monomers that have reacted}}{\text{Total \# of growing chains}} = \frac{[M]_0 \cdot p}{[I]_0}$$

When all monomers are reacted ($p = 1$), $\bar{X}_n = \frac{[M]_0}{[I]_0}$



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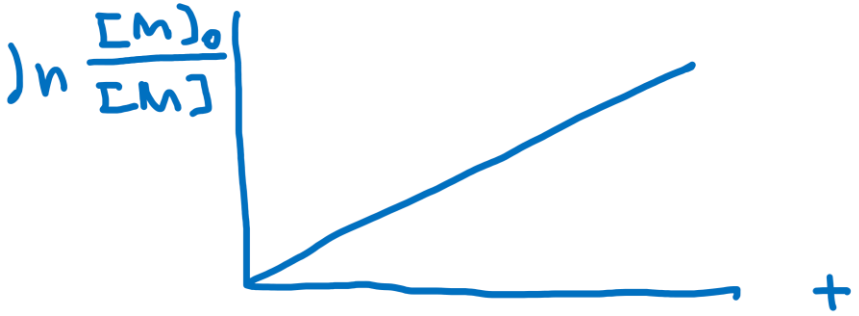
- Monomers that have reacted are statistically evenly distributed among all growing chains.

$$\frac{-d[M]}{dt} = k_p[P^*][M] = k_p \cdot [I]_0 [M]$$

$$\frac{-d[M]}{[M]} = k_p [I]_0 dt \Rightarrow \ln \frac{[M]_0}{[M]} = k_p [I]_0 t \Rightarrow \ln \frac{1}{1-p} = k_p [I]_0 t$$



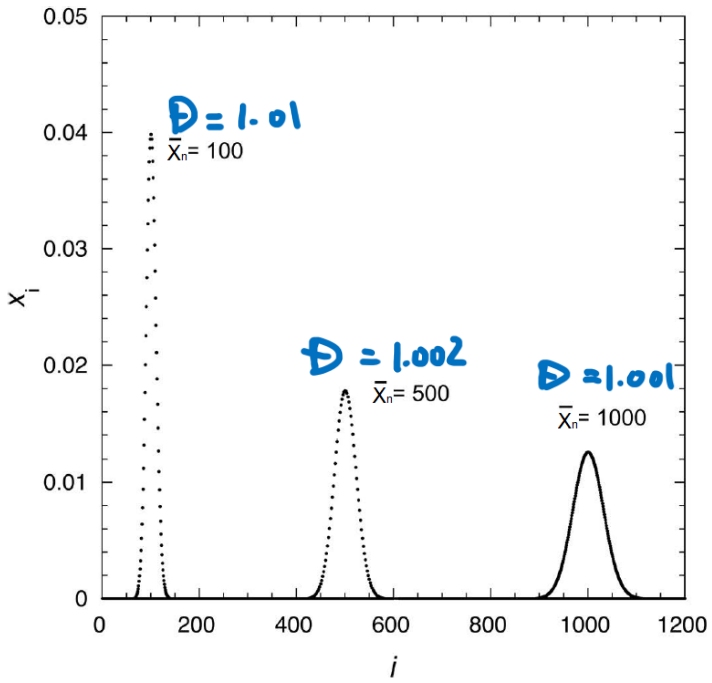
Distribution of an Ideal Living Polymerization with Fast Initiation

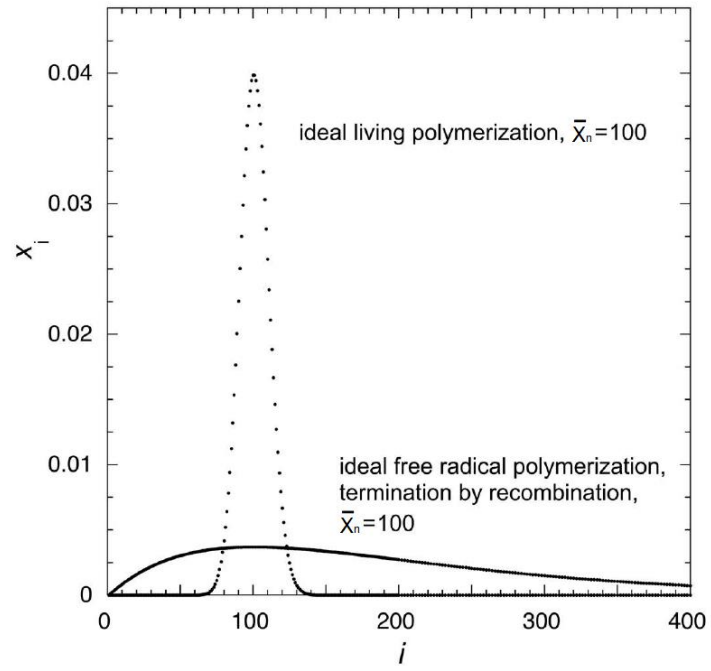
- Even with fast initiation and no termination or transfer, there will be a distribution of chain lengths. Hence, we say that “monomers that have reacted are **statistically evenly** distributed among all growing chains”.
- A good analogy: imagine placing an array of empty cups out in a steady rain. After many drops have fallen, the water level will be fairly equal among the cups, but some cups might collect 1000 drops, while others might have 998 or 1003 drops. This illustrates the distribution.
- The mole fraction of *i*-mer follows the *Poisson distribution* (see derivation on Page 127 in Lodge).

$$x_i = \frac{\bar{X}_n^{\,i-1} e^{-\bar{X}_n}}{(i-1)!}$$

$$Đ = \frac{\bar{X}_w}{\bar{X}_n} = 1 + \frac{\bar{X}_n}{(1+\bar{X}_n)^2} \approx 1 + \frac{1}{\bar{X}_n}$$

While the width of the distribution (i.e., standard deviation) increases with $\bar{X}_n$, the relative width (standard deviation divided by $\bar{X}_n$) decreases with $\bar{X}_n$. Dispersity *Đ* describes the relative width.



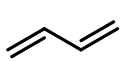
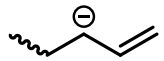
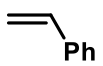
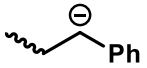
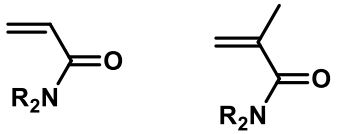
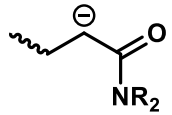
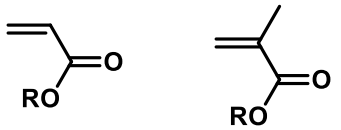
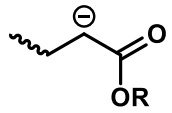
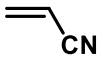
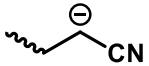
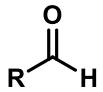
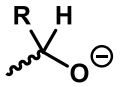
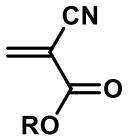
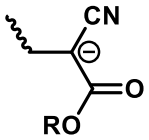


Anionic Polymerization

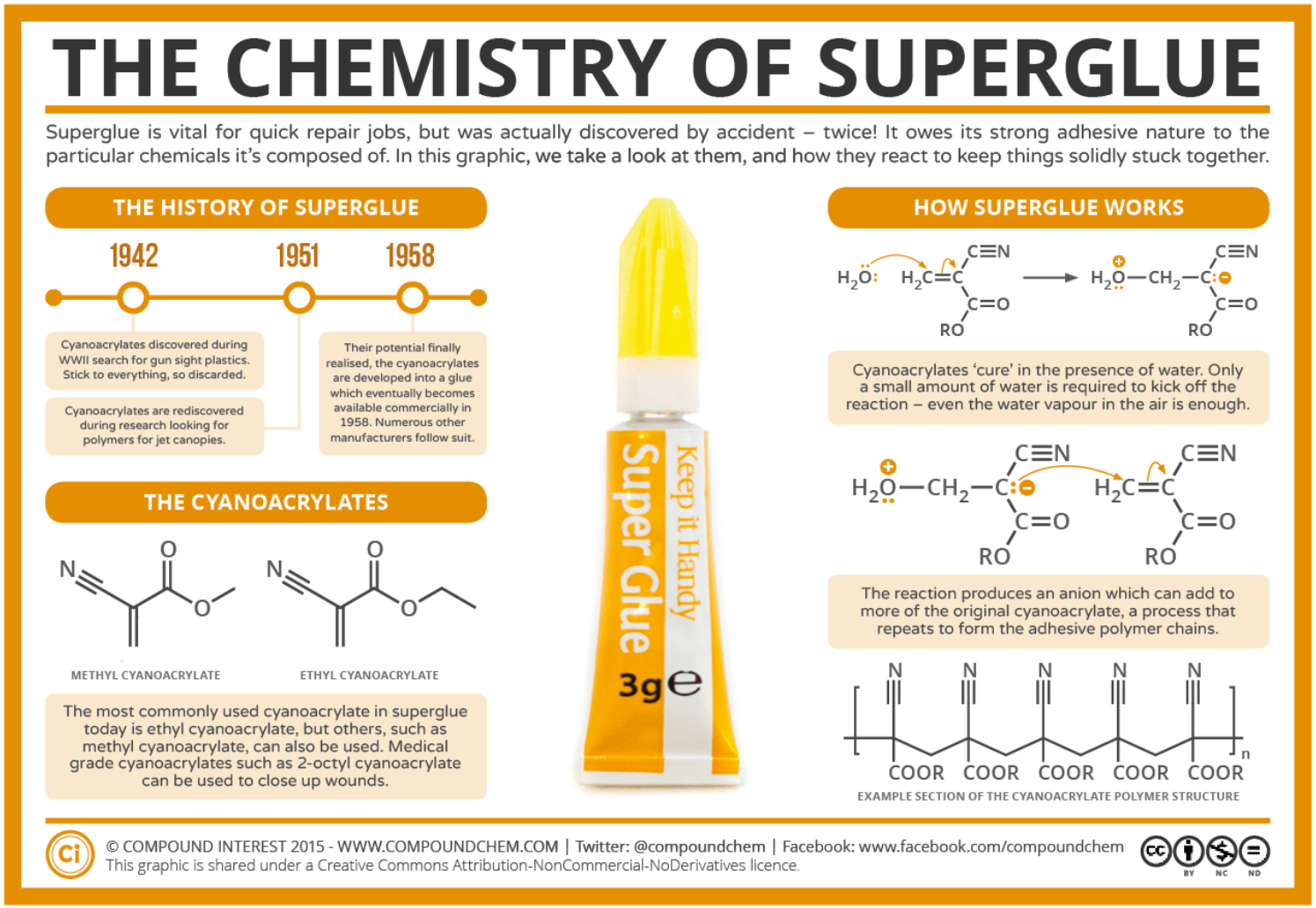
Initiating systems:

- BuLi
- Sodium metal with naphthalene
- RMgBr
- $NaNH_2$
- RO^-, OH^-
- R_3N, R_3P

- The more stable the carbanion (i.e., the smaller the pK_a value), the more reactive the monomer in anionic polymerization.
- Choose an initiator that has comparable or slightly higher reactivity than the intended carbanion (pK_a values are a useful guide).
- The initiator must be soluble in the same solvent as the monomer and the resulting polymer.

			pK_a
1,3-Butadiene			43
Styrene			41
(Meth)acrylamides			30
(Meth)acrylates			25
Acrylonitrile			25
Aldehydes			15
Cyanoacrylates			13

We All Have Encountered Anionic Polymerization in Daily Life



- Cyanoacrylates are so reactive that anionic polymerization can be initiated by water vapor in the air (not all chains initiate simultaneously).
- The carbanion propagating species can be quickly quenched by water vapor (presence of termination).

Hence, this is not a living polymerization process. How do we design a controlled anionic polymerization process?

Living Anionic Polymerization

The carbanion propagating species is sensitive to electrophilic impurities such as water, alcohol, oxygen, carbon dioxide, etc., in the system. Under conditions where such impurities are rigorously excluded from the system, the absence of inherent termination processes in anionic polymerization makes living polymerization possible. This was first demonstrated by Michael Szwarc in 1956 using polystyrene initiated with sodium naphthalenide in tetrahydrofuran (THF) at low temperatures.

'LIVING' POLYMERS

By Prof. M. SZWARC

Chemistry Department, State University of New York, College of Forestry, Syracuse 10, New York

POLYMERIC molecules are born in an initiation process, they grow by a propagation process, and finally they 'die' in a termination process. This death is regulated by the conditions prevailing in the polymerization process, and thus, the rate of death, the average molecular weight of the polymer formed, and its molecular weight distribution are all well-determined functions of experimental conditions.

An interesting situation arises when a polymerization process does not involve a termination step. The polymeric molecules then 'live' for an indefinite period of time, and such a system should be profitable in many investigations. A 'living' polymer does not grow indefinitely, nor does its molecular weight increase beyond certain limits. Any growth requires food, and the food for a growing polymer is the monomer. Consequently, if the supply of monomer is exhausted the growth is interrupted, although the living ends are potentially able to grow further if an additional amount of monomer is available.

The exclusion of natural death does not mean immortality either. Reagents may be visualized which convert a living end into an unreactive dead end. Treatment of living polymers with such reagents represents, therefore, a killing process. The difference between the normal termination process—described here as a natural death—and the killing process lies in the unavoidable character of the former reaction, whereas the latter takes place at the time chosen freely by the experimenter. The advantage of such a termination is obvious.

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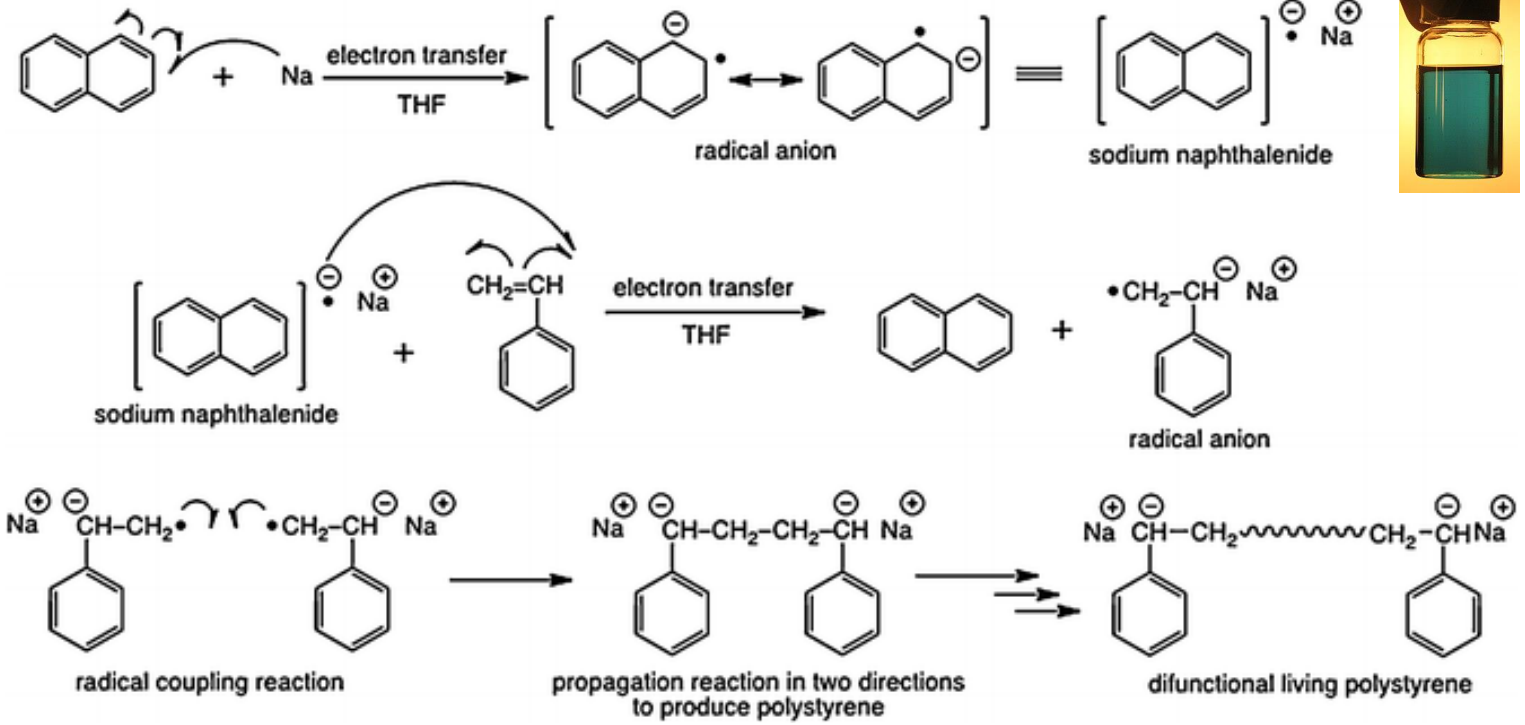
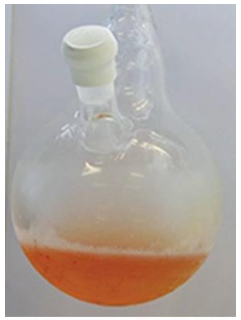
Michael Szwarc

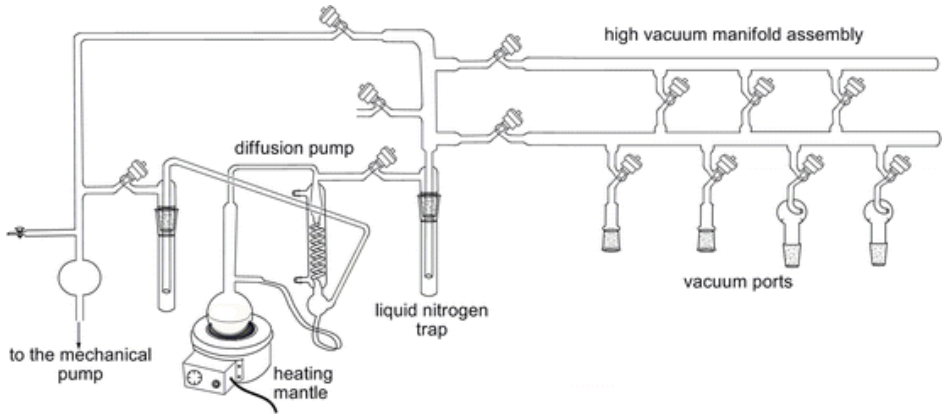
Szwarc, M., *Nature* **1956,** *178*, 1168-1169.

Living Anionic Polymerization



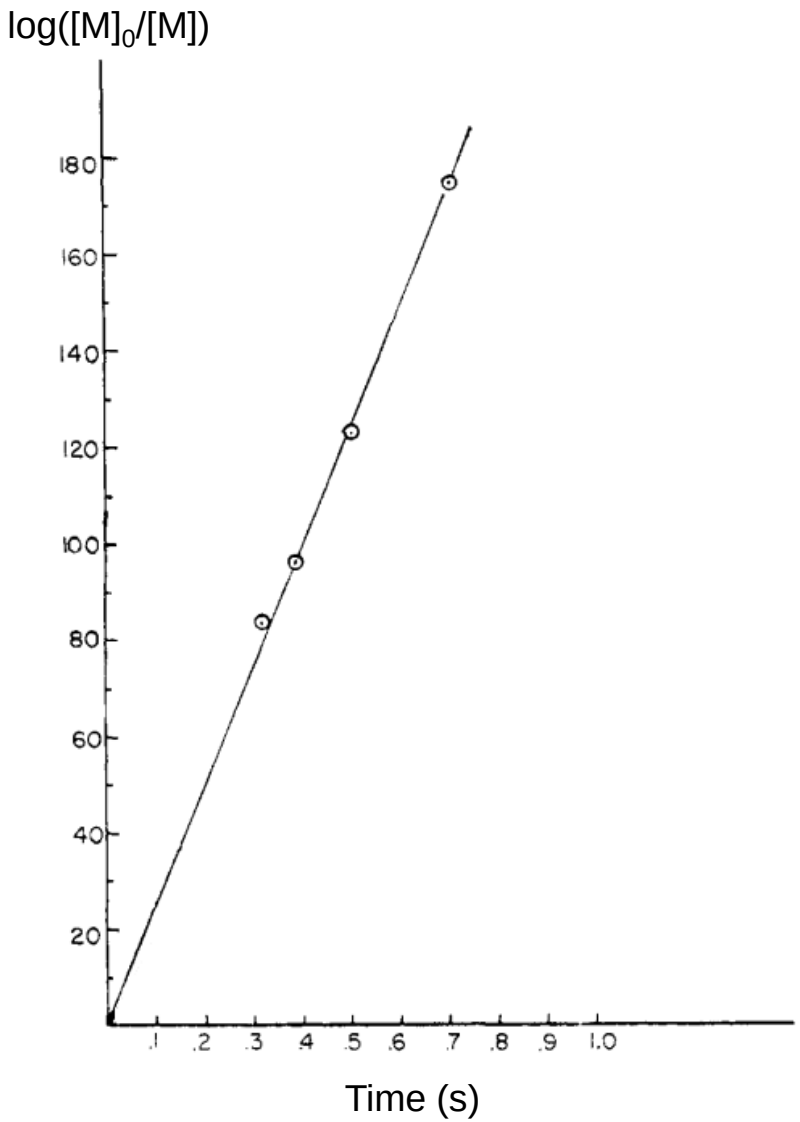


The “living” polystyryl carbanion is bright red; it is stable for weeks in hydrocarbon solvents.



Living anionic polymerization is extremely sensitive to impurities and thus is practically very difficult to do. It requires a high vacuum line that can bring the pressure to a value below 5 mTorr. As a comparison, common Schlenk lines used in organic labs operate at 50 mTorr at best.

Kinetics of Living Anionic Polymerization



$$R_p = k_p^{app}[M^-][M]$$

$$\frac{-d[M]}{dt} = k_p[P^*][M] = k_p \cdot [I]_0[M]$$

$$\frac{-d[M]}{[M]} = k_p[I]_0 dt \Rightarrow \ln\frac{[M]_0}{[M]} = k_p[I]_0 t$$

Anionic polymerization is very rapid (especially when solvent polarity is high). The concentration of growing species in anionic polymerization is 10^{-2} to 10^{-4} M, whereas the radical concentration in free-radical polymerization is 10^{-7} to 10^{-9} M.

Geacintov, C.; Smid, J.; Szwarc, M., *J. Am. Chem. Soc.* **1962,** *84*, 2508-2514.

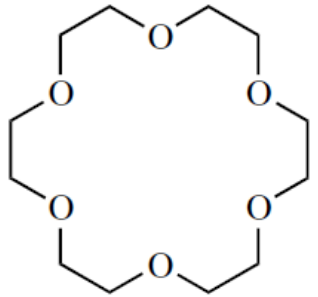
Ion Separation Dictates Reactivity of Anionic Propagating Centers

Effect of Solvent on Anionic Polymerization of Styrene

Solvent	k_p^{app} (L mol^{-1} s^{-1})
Benzene	2
Dioxane	5
Tetrahydrofuran	550
1,2-Dimethoxyethane	3,800

Polarity

Pentane
Hexane
Cyclohexane
Benzene
Dioxane
DME
THF
DMF



Crown ethers can result in very large rate increase

Why does increasing solvent polarity enhance the reaction rate?

$\sim AB$ Covalent species

$\sim A^-B^+$ Contact ion pair

$\sim A^- \| B^+$ Lose ion pair

$\sim A^- + B^+$ Free ion

The more “free” the anionic propagating center is, the more reactive it becomes. Increasing the solvating power of the reaction medium facilitates cation-anion separation.

Further Discussion on How the Identity of Chain Ends Affects Reaction Rates

$$P^-(C^+) \underset{}{\overset{K}{\rightleftharpoons}} P^- + C^+$$

$$R_p = k_p^{app}[M^-][M] \qquad R_p = k_p^-[P^-][M] + k_p^{\mp}[P^-(C^+)][M]$$

- The anionic propagating centers exist in an equilibrium between ion pairs (less reactive) and free ions (more reactive). While the equilibrium constant depends on solvents, temperature, and additives, in general, the equilibrium lies far to the left (i.e., ion pairs).
- The k_p we measured is an apparent rate constant that can be further decoupled to chain growth contributed by ion pairs and free ions, respectively. Refer to Page 424 in Odian for a more quantitative treatment.

For polystyrene initiated with sodium naphthalenide in THF, it was measured

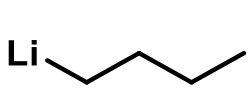
$[P^-(C^+)] = 10^{-3}$ M $\qquad [P^-] = 1.2 \times 10^{-5}$ M $\qquad (K = 1.5 \times 10^{-7})$

$k_p^{\mp} = 80$ L mol^{-1} s^{-1} $\qquad k_p^- = 6.5 \times 10^4$ L mol^{-1} s^{-1}

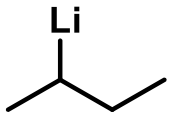
$k_p^{\mp} \cdot [P^-(C^+)] = 8 \times 10^{-2}$ s^{-1} $\qquad k_p^- \cdot [P^-] = 0.78$ s^{-1}

- Although free ions are only a minor species (1.2%), they contribute to the majority (90%) of chain growth.
- The free ions and ion pairs are in rapid equilibrium, causing each polymer chain to propagate as both free ions and ion pairs throughout its lifetime. This leads to narrow molecular weight distribution.

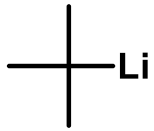
Alkyllithium Compounds as Initiators for Anionic Polymerization



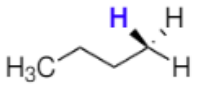
n-BuLi



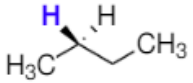
s-BuLi



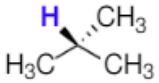
t-BuLi



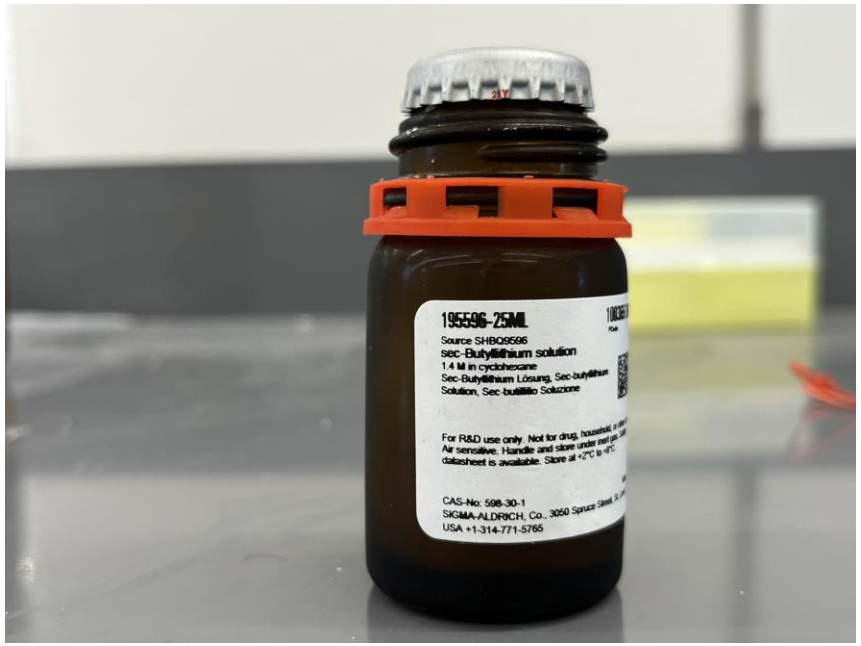
pK_a ~ 50

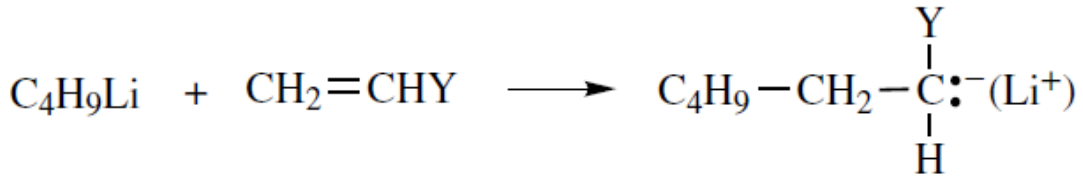


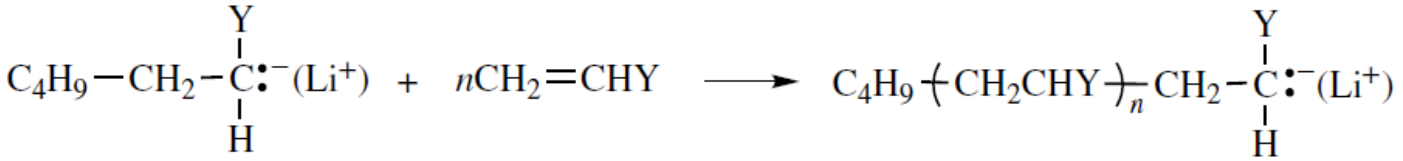
pK_a ~ 51



pK_a ~ 53





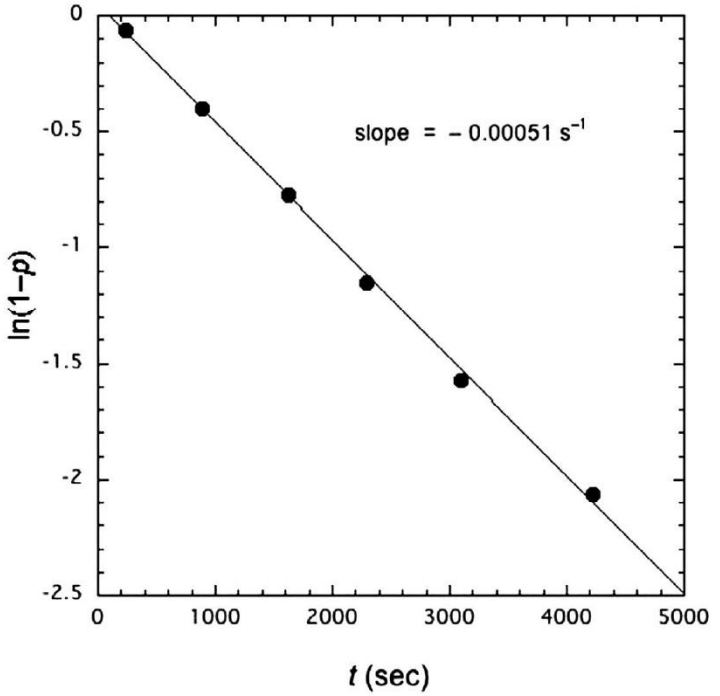


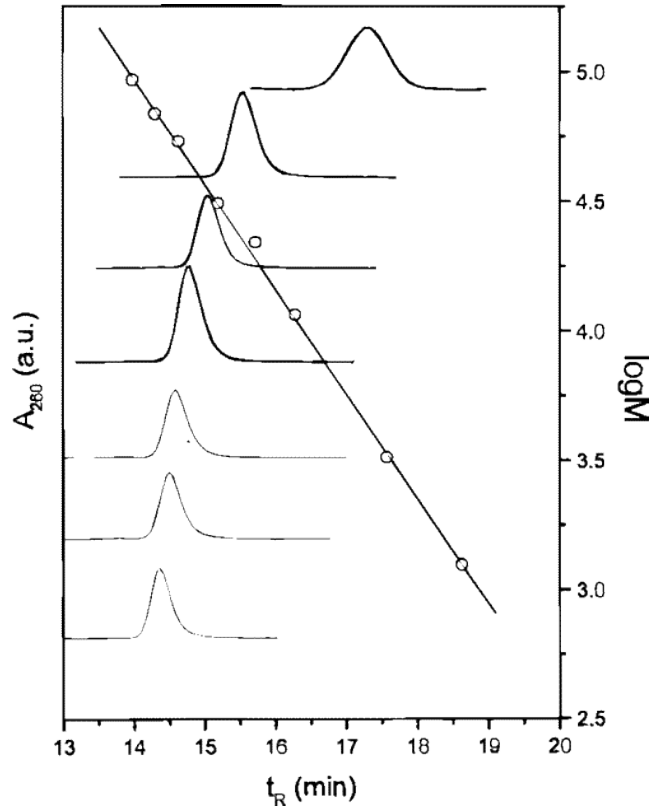
Alkyllithium compounds are very strong nucleophiles and are probably the most useful initiators for anionic polymerization due to their solubility in non-polar solvents (e.g., hexane, pentane, cyclohexane, benzene). Note that some monomers have better solubility in non-polar solvents and are best suited for polymerization by alkyllithium compounds.

Kinetics of Polymerization Initiated by Alkyllithium Compounds

Polymerization of styrene initiated by *s*-butyllithium in cyclohexane at 45 °C

t (s)	M_n (g/mol)	N_n	$Đ$	$1-p$
238	3,770	36.3	1.06	0.940
888	20,600	198	1.02	0.672
1,626	33,700	324	1.02	0.463
2,296	43,000	413	1.01	0.316
3,098	49,800	479	1.008	0.207
4,220	54,900	528	1.006	0.127
14,345	61,700	593	1.005	0.018

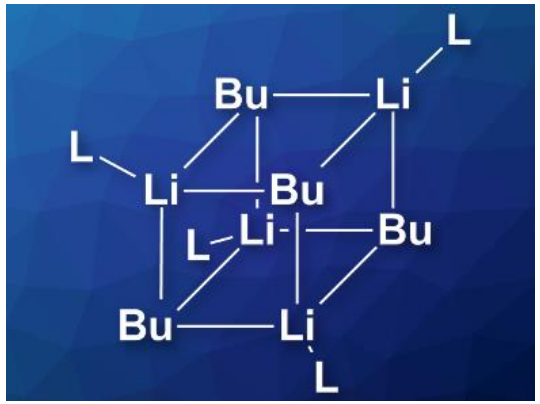


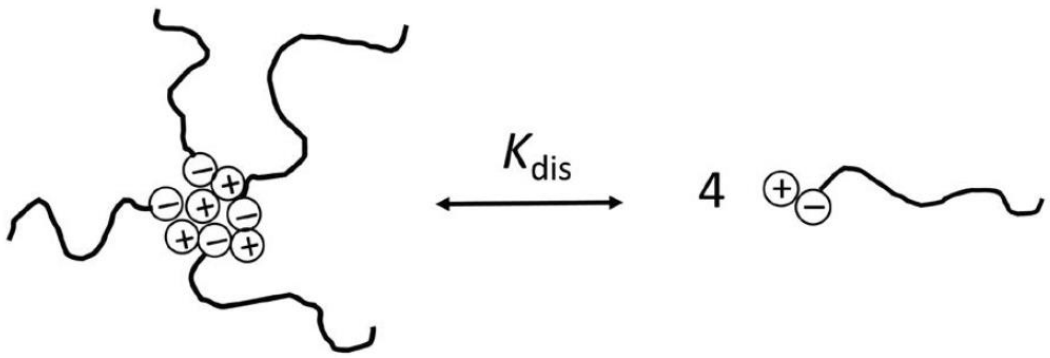


The polymerization exhibits characteristics of ideal living polymerization, although the reaction rate is much slower than that of analogous polymerization initiated by sodium naphthalenide in THF.

Lee, W.; Lee, H.; Cha, J.; Chang, T.; Hanley, K. J.; Lodge, T. P., *Macromolecules* **2000,** *33*, 5111-5115.

Association Phenomena in Alkyllithium





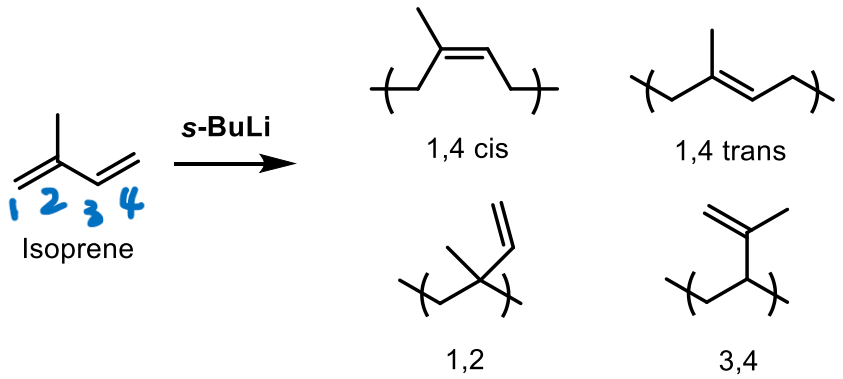
- Ionic species tend to be sparingly soluble in hydrocarbons, so organolithium compounds in nonpolar solvents have a strong tendency to associate into small clusters with perhaps n = 2, 4, or 6 chains.
- The equilibrium of clusters and free chains lies far on the left side (i.e., formation of clusters).
- Monomer addition occur primarily when the living chain end is not associated.

$$R_p = -\frac{d[M]}{dt} = k_p[M][P^*]_{free} \qquad K_{dis} = \frac{([P^*]_{free})^4}{[(P^*)_4]}$$

$$R_p = k_p(K_{dis})^{1/4}[M][(P^*)_4]^{1/4} = k_{app}[M][P^*]^{1/4}$$

The rate of polymerization has a (1/n) fractional dependence on initiator concentration, where n is the average aggregate size.

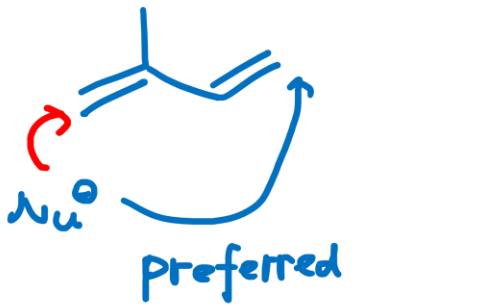
Anionic Polymerization of 1,3-Dienes



Solvent	Counterion	*T*, °C	1,4 *cis*	1,4 *trans*	1,2	3,4
THF	Li^+	30	12 combined		29	59
Dioxane	Li^+	15	3	11	18	68
Heptane[a]	Li^+	−10	74	18	—	8
Heptane[b]	Li^+	−10	97	—	—	—

[a] Initiator concentration 6×10^{-3} M
[b] Initiator concentration 8×10^{-6} M

① 1,2 vs 3,4



preferred
(less hindered)

② 1,4 vs 3,4

free ions prefer this

contact ion pairs prefer this

Anything that promotes ion separation favors 3,4

③ cis vs trans

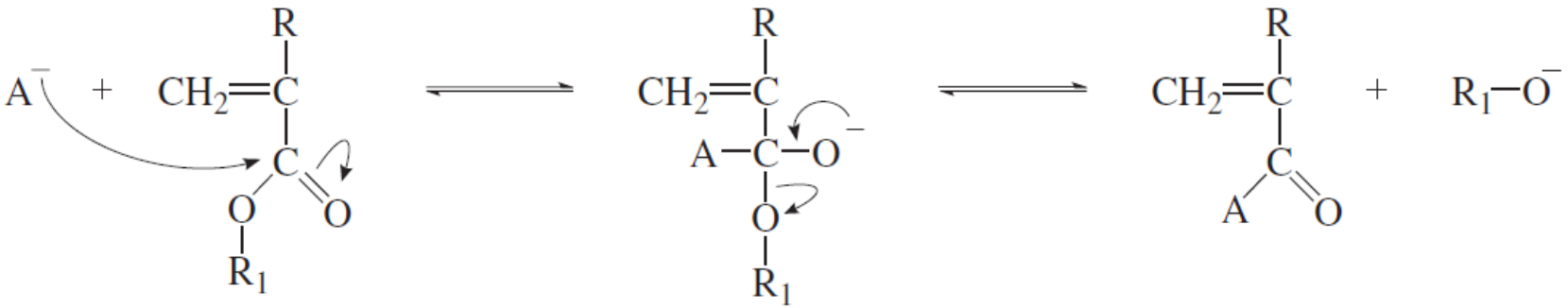
cis is the kinetic product and trans is the thermodynamic product.

This isomerization is proposed to occur only within clusters.

Alkyllithium-initiated anionic polymerization of butadiene and isoprene was once used in industry by companies such as Phillips, Firestone, and Shell to produce *cis*-rich polyisoprene and polybutadiene. However, these plants are no longer in operation and have largely been replaced by coordination polymerization.

Side Reactions

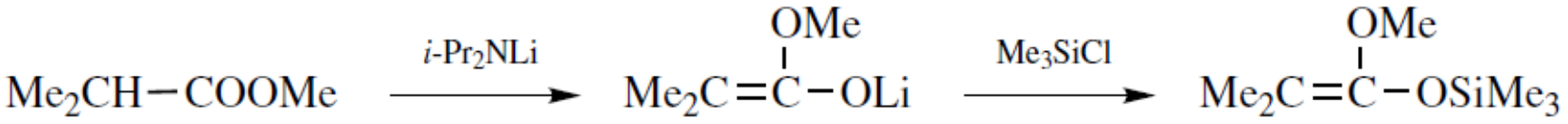
Polar monomers, such as methyl (meth)acrylate, are more reactive than styrene and 1,3-dienes in anionic polymerization, but their polymerization is complicated by side reactions.



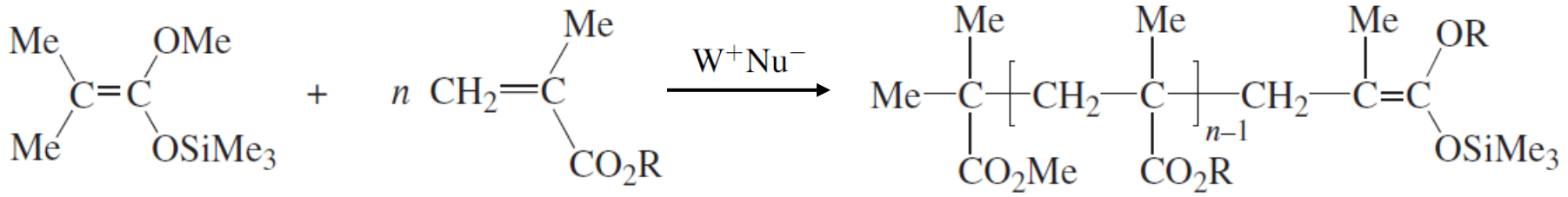
While such side reactions can be reduced by carefully screening reaction conditions (e.g., low temperatures, bulky initiators, polar solvents, large counter cations), they still present significant challenges in the anionic polymerization of polar monomers.

Group Transfer Polymerization

Group transfer polymerization was developed by Owen Webster at Dupont in 1983 and demonstrates excellent control over the polymerization of methacrylates at 50–80 °C.

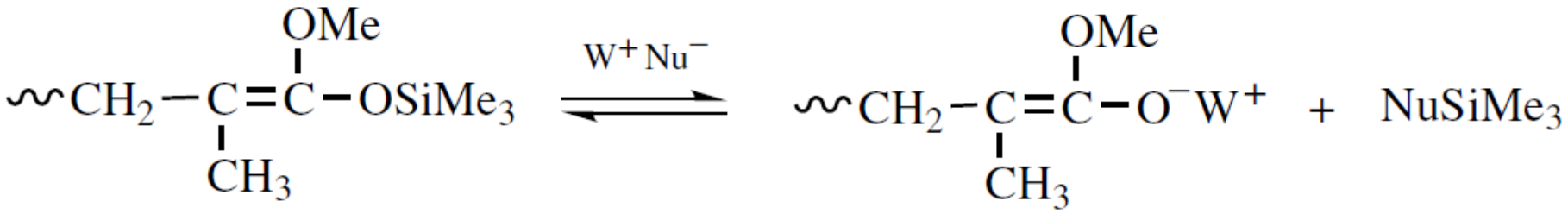


Silyl ketene acetal (initiator)



Nucleophilic catalysts (W^+Nu^-): $(Me_2N)_3S^+HF_2^-$ is the common choice

Group Transfer Polymerization



Dormant species

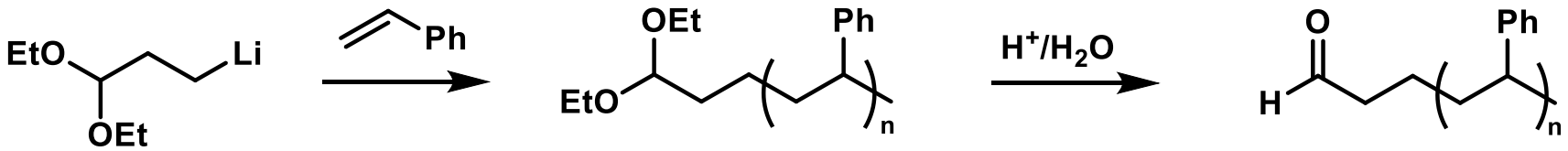
Anionic species

- Control of the side reactions is achieved through two factors:
  1. The equilibrium between dormant and anionic species maintains the concentration of the anionic propagating species at a low level.
  2. The bulky counterion W^+ decreases the reactivity of the anionic propagating centers toward terminating side reactions.
- Such a process is now termed *reversible deactivation*, which 1) maintains the concentration of active propagating species at a low level (i.e., better control) and 2) minimizes the occurrence of side reactions resulting from overly reactive end groups (i.e., minimize irreversible termination/transfer events).
- Polymerization based on this concept shows characteristics of *living polymerization*, although chain termination or transfer may still occur. Polymerization employing the concept of reversible deactivation was once termed "*quasi-living*" or "*pseudo-living*," but for various reasons, these names are not popular today. We will see more examples of such reactions later in this chapter.

Quirk, R. P.; Lee, B., *Polym. Int.* **1992,** *27*, 359-367.
Grubbs, R. B.; Grubbs, R. H., *Macromolecules* **2017,** *50*, 6979-6997.

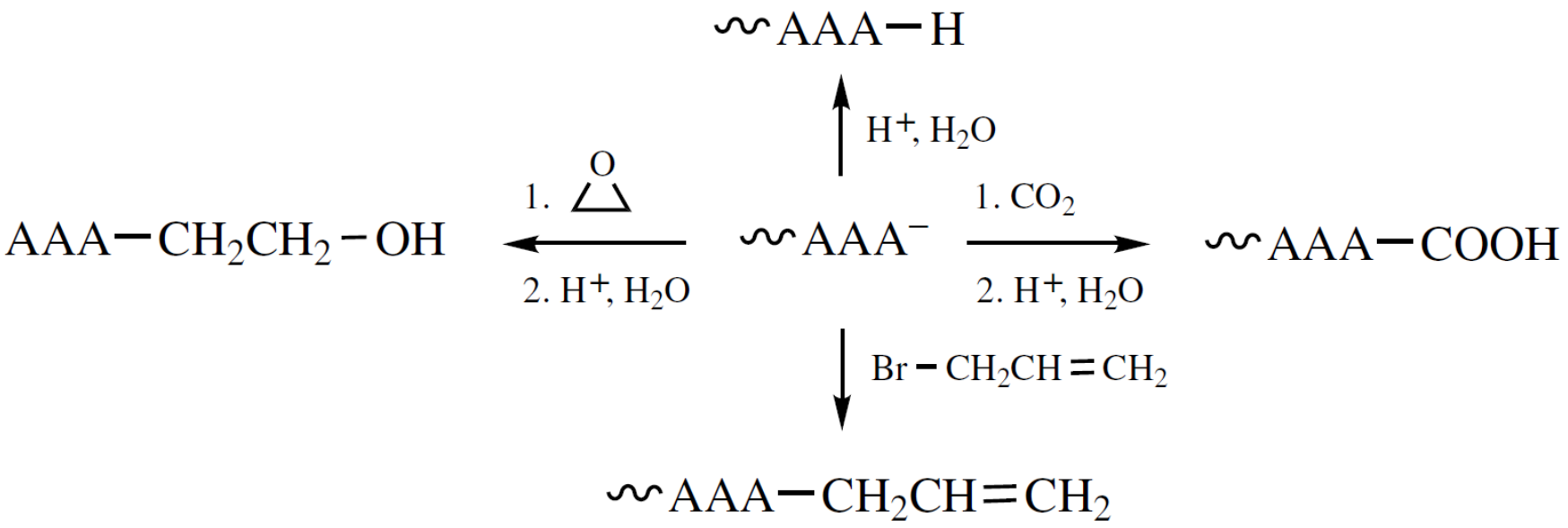
Telechelic (End-Functionalized) Polymers

1. Using functional initiator (protection is often needed)



Initiator

2. Using various electrophilic reagents to terminate the polymerization



Anionic Polymerization of Aldehydes

Formaldehydes can also be polymerized using anionic initiators:

Initiation

$$HO^-(G^+) + CH_2{=}O \longrightarrow HO{-}CH_2{-}O^-(G^+)$$

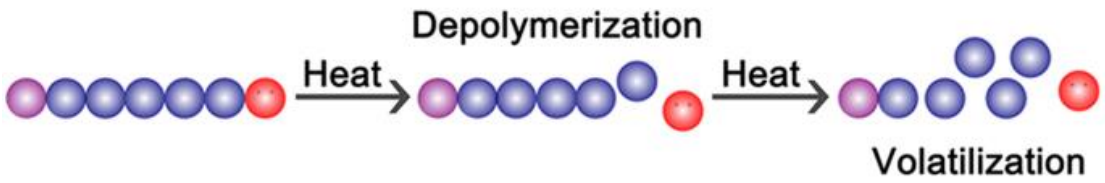
Propagation

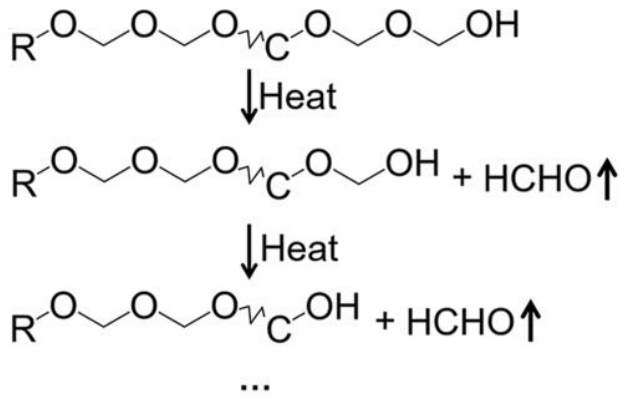
$$HO{-}(CH_2{-}O)_n{-}CH_2{-}O^-(G^+) + CH_2{=}O \longrightarrow HO{-}(CH_2{-}O)_{(n+1)}{-}CH_2{-}O^-(G^+)$$

Termination by chain transfer

$$HO{-}(CH_2{-}O)_n{-}CH_2{-}O^-(G^+) + ZH \longrightarrow HO{-}(CH_2{-}O)_n{-}CH_2{-}OH + Z^-(G^+)$$

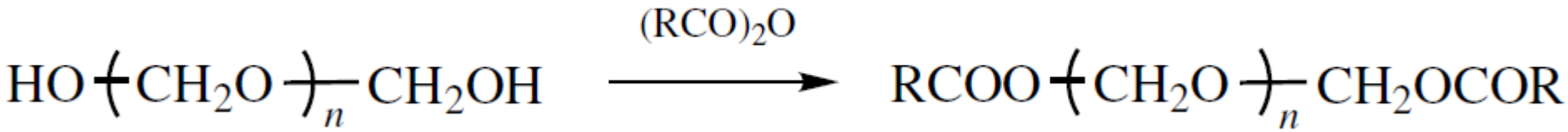
However, such polymers are not stable for use:





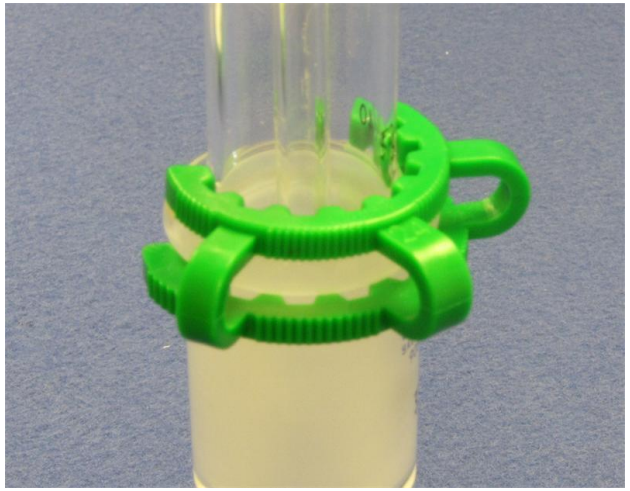
Anionic Polymerization of Aldehydes

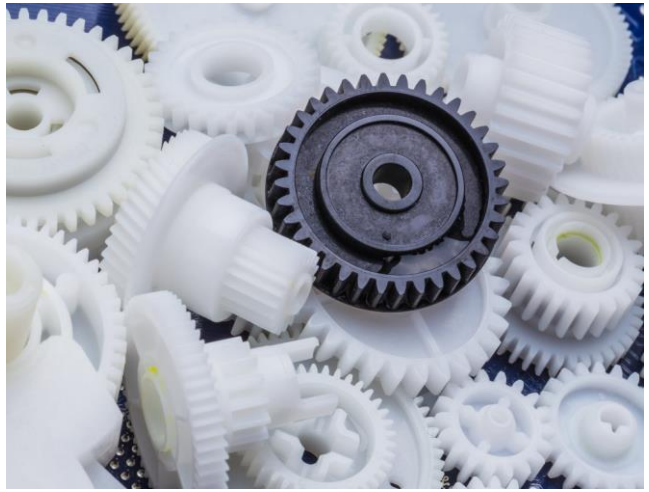
This can be solved by end-capping:

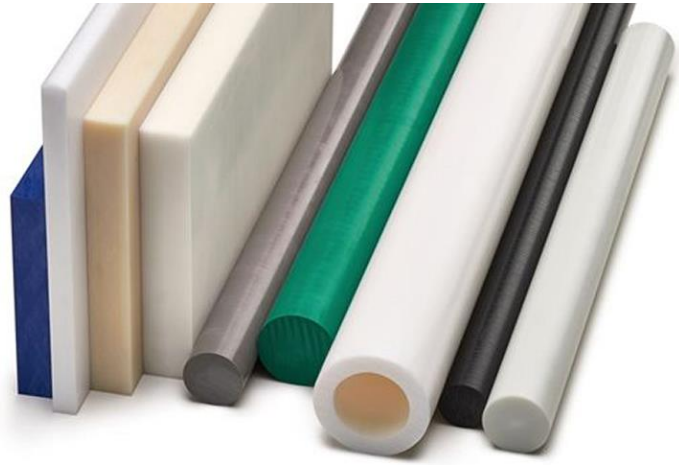


Unstable polymers

Stable polymers

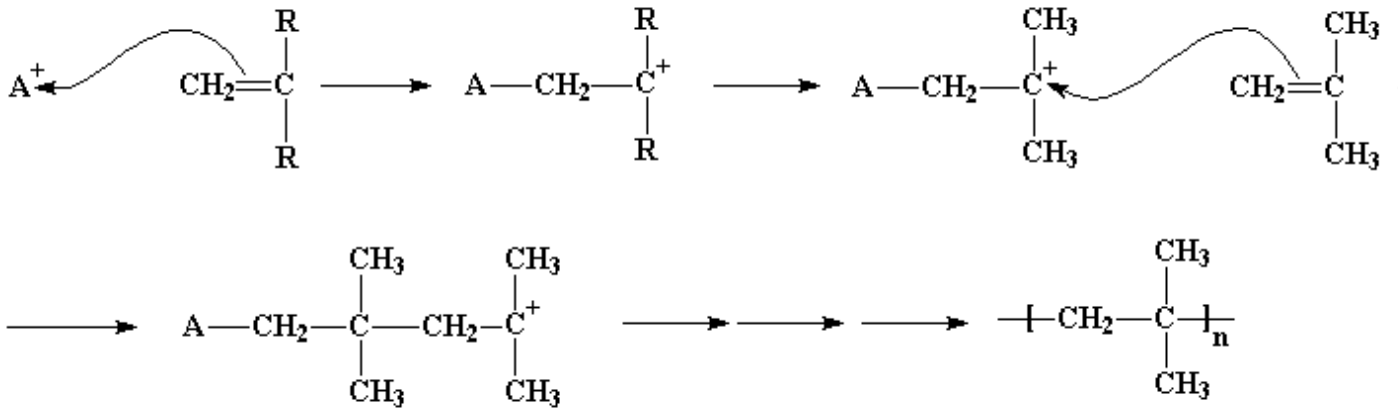






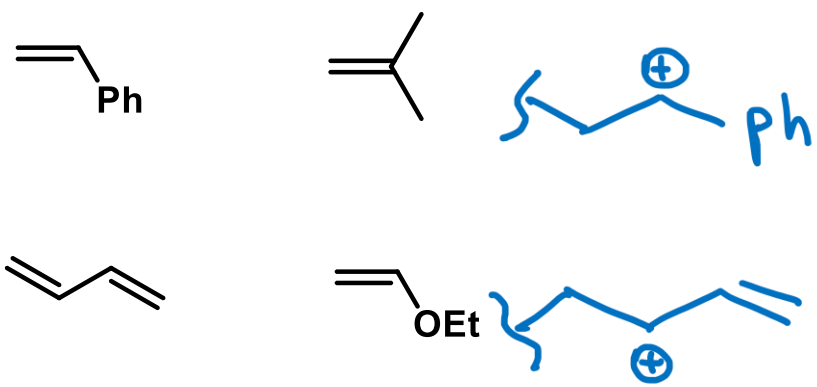
Polyoxymethylene (POM) is an engineering thermoplastic used in precision parts requiring high stiffness, low friction, and excellent dimensional stability.

Monomer Scope for Cationic Polymerization

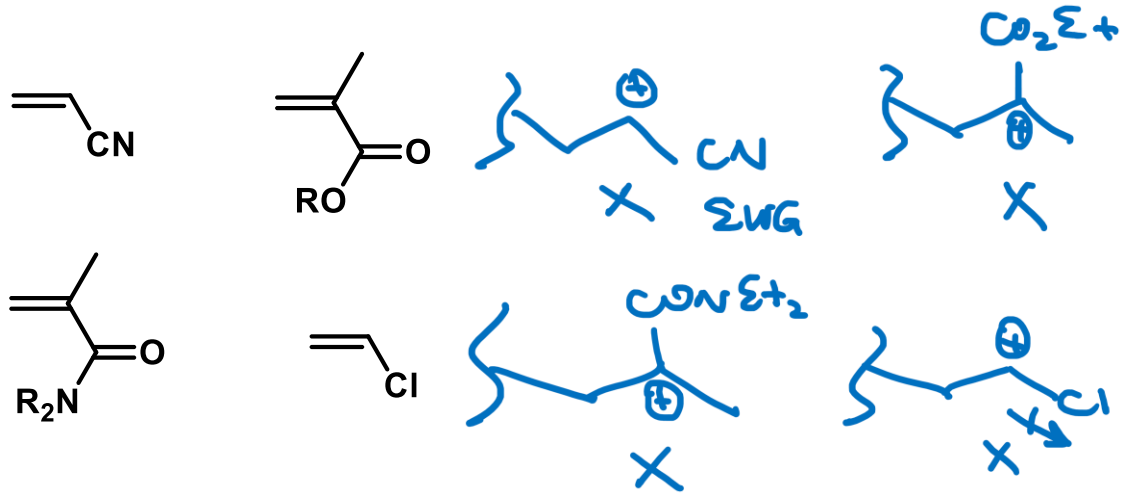


To promote cationic polymerization, the substituents on the monomers need to be able to stabilize carbocation.

Monomers that can undergo cationic polymerization



Monomers that cannot undergo cationic polymerization



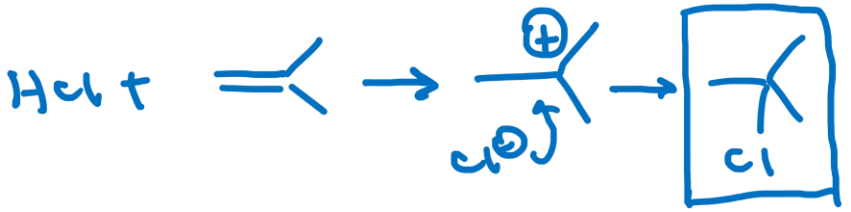
Initiation of Cationic Polymerization

1. Protonic (Brønsted) acids as initiators

$$H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$$

$$HClO_4 \rightleftharpoons H^+ + ClO_4^-$$

$$HA + RR'C{=}CH_2 \longrightarrow RR'\overset{+}{C}(A)^-\,CH_3$$



- The acid needs to be strong enough to protonate monomers
- The anion of the acid should not be highly nucleophilic (e.g., HCl)

unable to propagate further

2. Lewis acids (initiators) plus a proton donor or a carbocation donor (coinitiator)

$$BF_3 + H_2O \rightleftharpoons BF_3{\cdot}OH_2$$

$$BF_3{\cdot}OH_2 + (CH_3)_2C{=}CH_2 \longrightarrow (CH_3)_3C^+(BF_3OH)^-$$

$$AlCl_3 + (CH_3)_3CCl \rightleftharpoons (CH_3)_3C^+(AlCl_4)^-$$

$$(CH_3)_3C^+(AlCl_4)^- + CH(Ph){=}CH_2 \longrightarrow (CH_3)_3CCH_2\overset{+}{C}H(Ph)\,(AlCl_4)^-$$

- A more common and efficient way to initiator cationic polymerization
- The optimum initiator to coinitiator ratio varies considerably depending on the reaction conditions (e.g., initiator, coinitiator, monomer, solvent, and temperature)

How the Identity of Chain Ends Affects Reaction Rates

$\sim BA$	$\sim B^+A^-$	$\sim B^+ \| A^-$	$\sim B^+ + A^-$
Covalent species	Contact ion pair	Loose ion pair	Free ion

The counteranion is typically quite large for cationic polymerization, so the ion pair is a very loose ion pair.

$$YM^+(IZ)^- \underset{}{\overset{K}{\rightleftharpoons}} YM^+ + IZ^-$$

$$R_p = k_p^{app}[M^+][M] \qquad R_p = k_p^+[YM^+][M] + k_p^{\pm}[YM^+(IZ)^-][M]$$

For polymerization of styrene initiated by CF_3SO_3H in 1,2-dichloroethane, it was measured

$[YM^+(IZ)^-] = 5 \times 10^{-3}$ M $[YM^+] = 4.6 \times 10^{-5}$ M ($K = 4.2 \times 10^{-7}$)

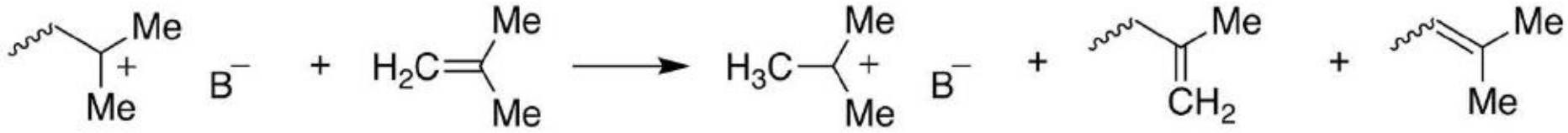
$k_p^{\pm} = 1 \times 10^5$ L mol^{-1} s^{-1} $k_p^{+} = 1.2 \times 10^6$ L mol^{-1} s^{-1}

$k_p^{\pm} \cdot [YM^+(IZ)^-] = 500$ s^{-1} $k_p^{+} \cdot [YM^+] = 55.2$ s^{-1}

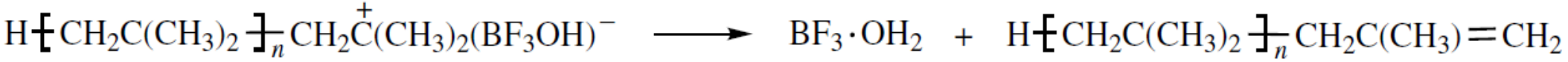
- Cationic polymerization is very fast, with many reactions essentially completing within seconds or minutes. It is often desirable to conduct cationic polymerization at low temperatures (e.g., -78°C).
- The free ions do not contribute as much to the chain growth as they do in anionic polymerization.

Built-in Chain Transfer/Termination Events in Cationic Polymerization

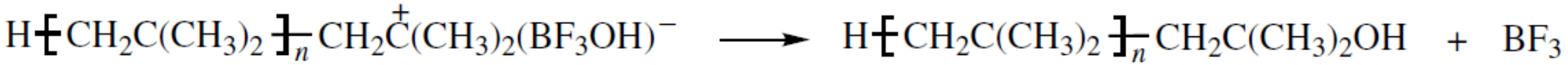
- ***β*-proton transfer**



- **Chain transfer to counterion (*spontaneous termination*)**



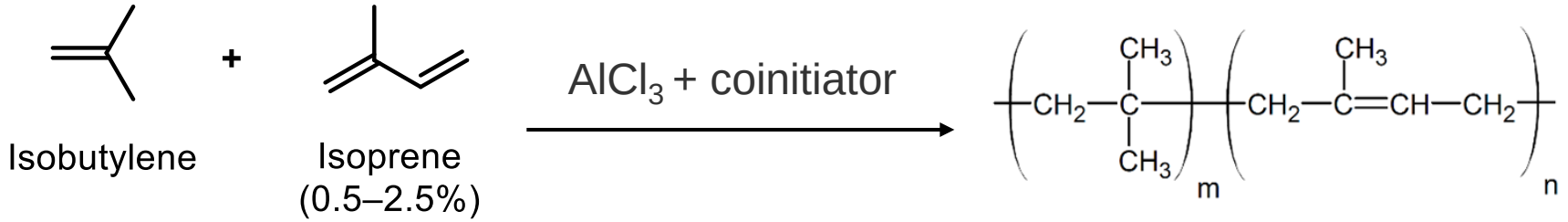
- **Combination with Counterion**



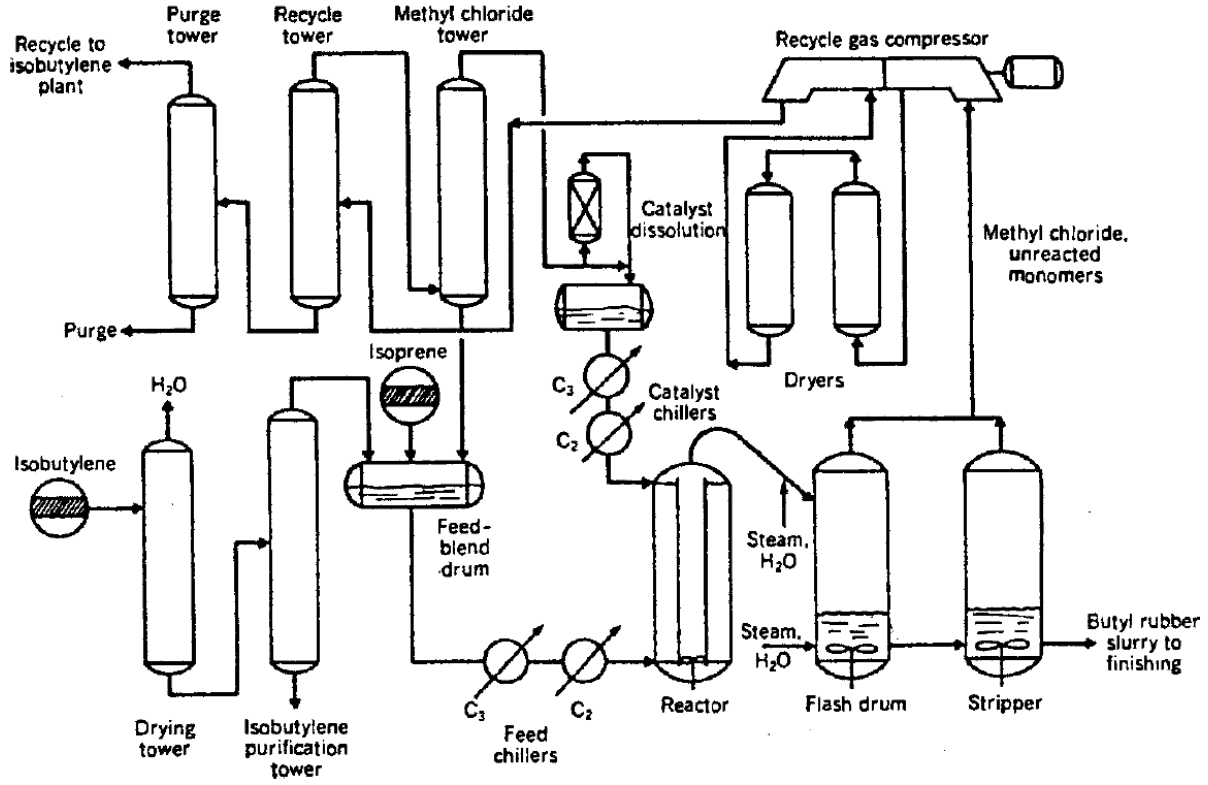
- Because of these built-in chain transfer and termination events, common cationic polymerization is hardly living, resulting in decreased molecular weight and a broadened molecular weight distribution.
- See pages 388 to 391 in Odian for a detailed quantitative discussion of the kinetics of cationic polymerization.

Cationic Polymerization of Isobutylene

The most important application of cationic polymerization is the polymerization or copolymerization of isobutylene (a monomer that cannot be polymerized using any other polymerization methods) to produce polyisobutylene.



Butyl rubber

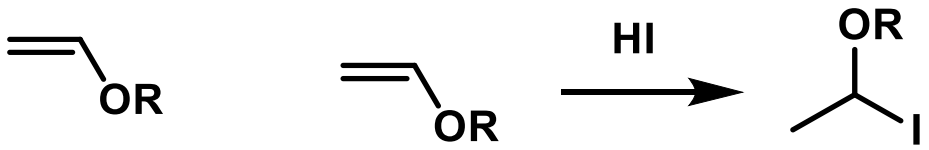


How Can We Achieve "Living" Cationic Polymerization?

- **Challenge 1**: cationic polymerization is very rapid and thus highly exothermic (i.e., lack of control)
- **Challenge 2**: cationic polymerization has inherent chain transfer/termination events to monomers and counterions.

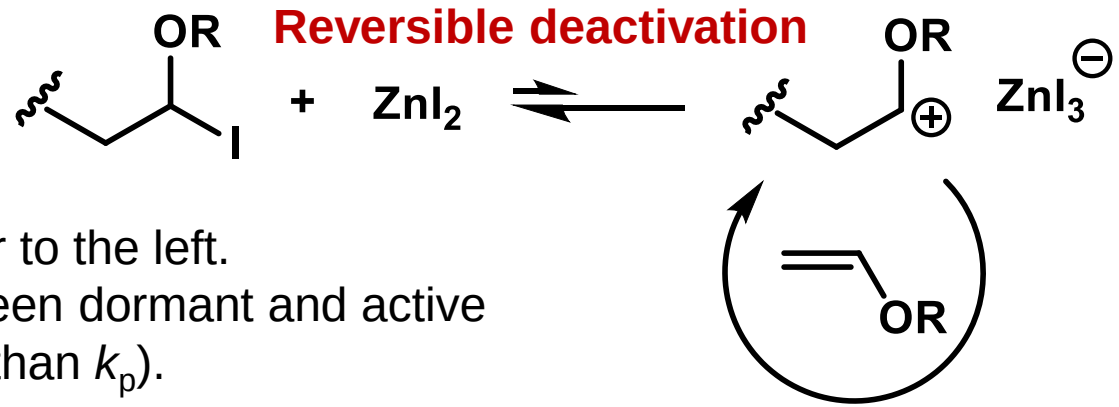
Running cationic polymerization at low temperatures (e.g., -78 °C) often helps to achieve better control. However, can we do even better?

Initiator: HI/ZnI_2 Monomer:



I^-: both a good nucleophile and good leaving group (especially with the help of ZnI_2)

Dormant species (covalent) Active species (Ion pairs)



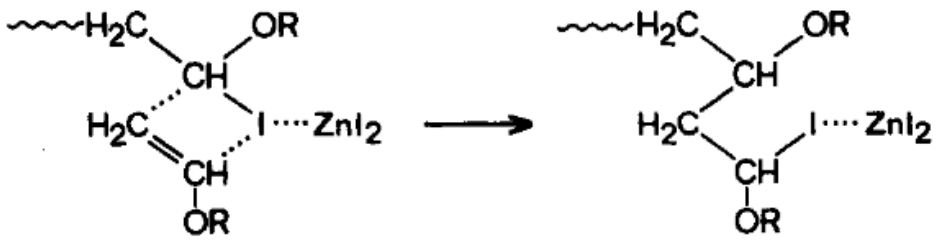
- The equilibrium lies far to the left.
- The interchange between dormant and active species is fast (faster than k_p).

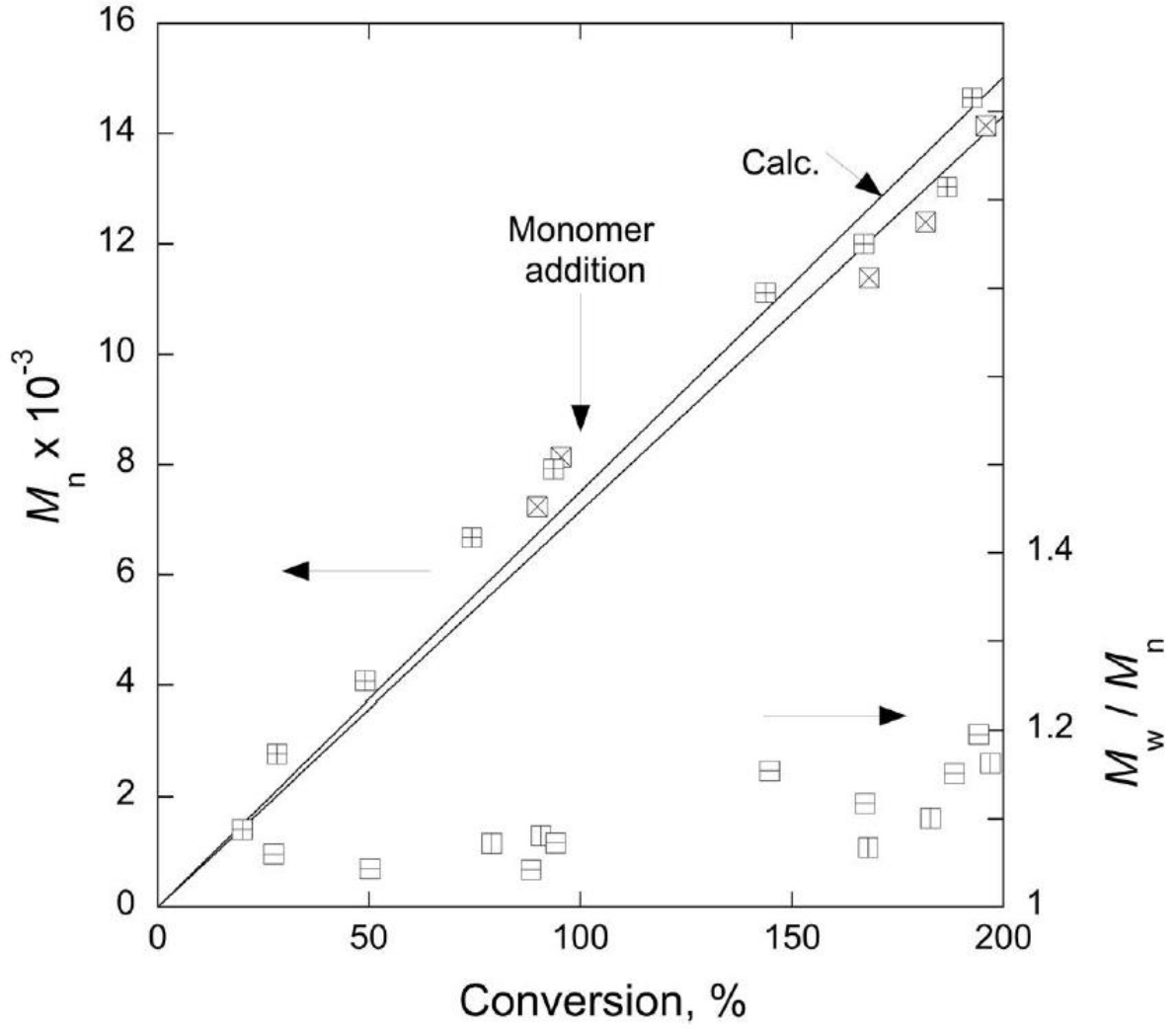
“Living” Cationic Polymerization

Reversible deactivation:

1. Significantly lowers the rate of polymerization (i.e., better control) by keeping most chains in the dormant state.
2. Greatly suppresses chain transfer by reducing the charge associated with the terminal carbon atom (i.e., no free ions).
3. Allows all chains to grow at the same rate on average due to fast equilibrium.

We may even represent the transition state of propagation as:





Note such polymerization is not truly “living”, as chain transfer/termination may still occur (i.e., “living-like”, “quasi-living”, “pseudo-living”)

Sawamoto, M.; Okamoto, C.; Higashimura, T., *Macromolecules* **1987,** *20*, 2693-2697.