Synthetic Rubber. II.

Disadvantages of natural or synthetic rubber:

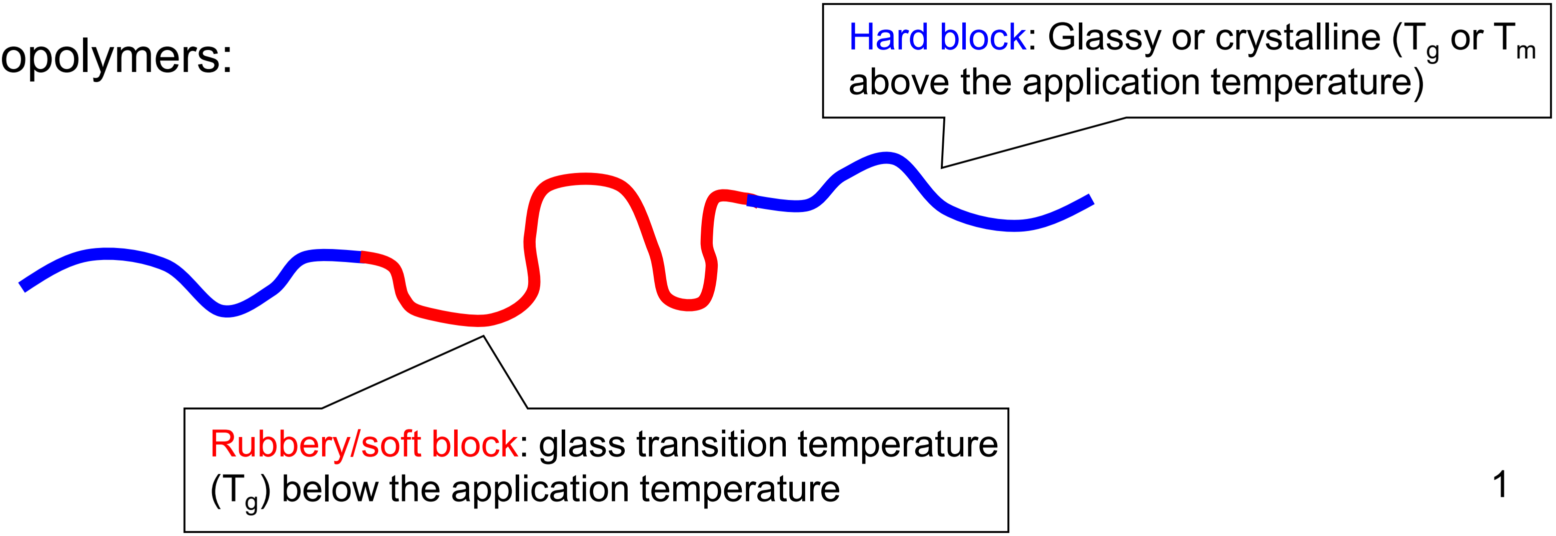
- Vulcanization (crosslinking) required prior to use
- Difficult to recycle scrap material

The ideal rubber:

Should behave as a crosslinked rubber at ambient temperature, but like a normal, linear polymer at elevated temperature to allow melt processing

How can this be realized? Thermoplastic elastomers

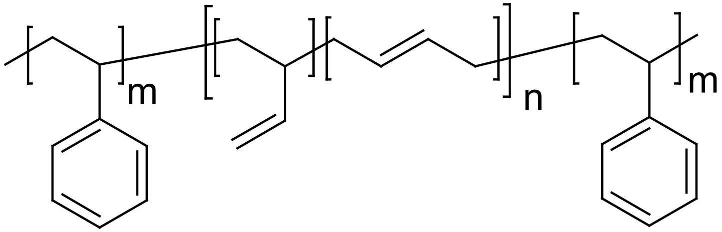
Triblock copolymers:



Hard block: Glassy or crystalline (T_g or T_m above the application temperature)

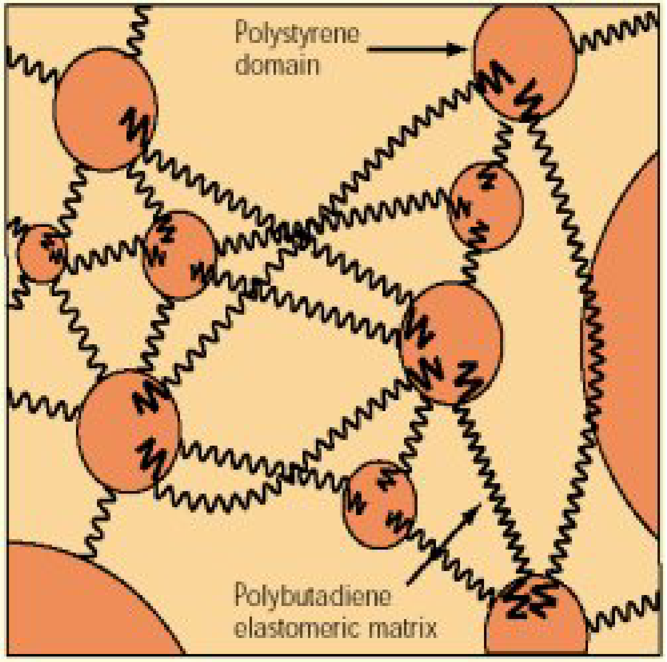
Rubbery/soft block: glass transition temperature (T_g) below the application temperature

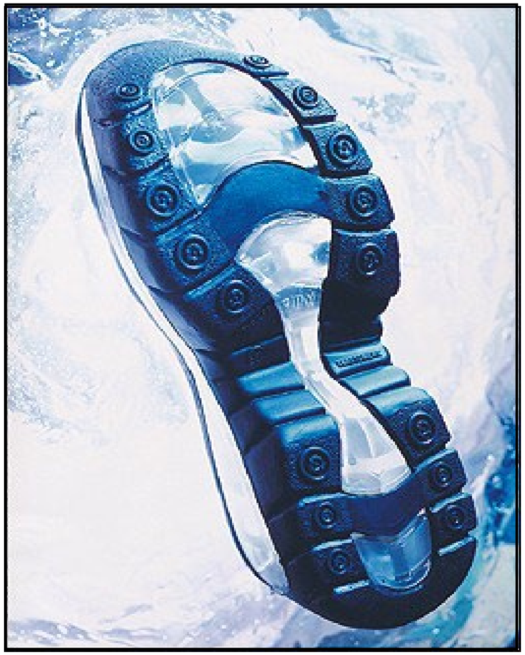
Thermoplastic Elastomers



Styrene-isoprene-styrene and styrene-1,2-butadiene-styrene ABA triblock copolymers with short styrene blocks are useful as thermoplastic elasomers (*Cariflex*, *Kraton*, *Soloprene*, *Stereon*)

Thermoplastic elastomers behave as elastomers at ambient temperatures but are thermoplastic at elevated temperatures ($T > T_{g,PS}$), where they can be molded and remolded





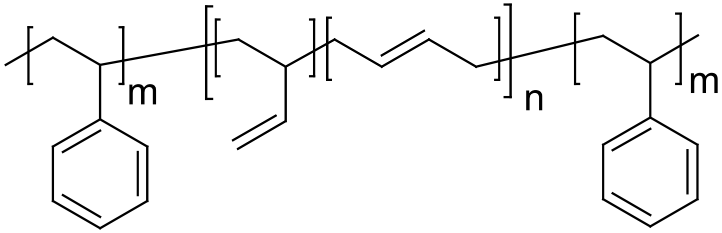
The polystyrene blocks aggregate to form glassy (hard) domains that physically crosslink the rubbery (soft) polydiene blocks

http://www.kraton.com/

How to Make These Polymers ?

Important requirement:

Control of block length, sequence and molecular weight (determines phase behaviour)



Conventional radical chain polymerization (styrene and butadiene):

- Initiation is slow compared to propagation and termination ($R_i < R_p, R_t$)
- Chains are very short-lived (< 1 s), due to high chain propagation rates and the existence of termination reactions

As a consequence:

- Relatively broad distribution of chain lengths
- Control over chain length is limited
- Difficult to control polymer composition, functionality and architecture

Alternatives:

- Controlled/Living radical polymerization: not very successfull so far. Distribution of chain lengths broader than what can be accomplished using living anionic polymerization
- **Anionic polymerization**

Anionic versus Cationic Polymerization

- The propagating species are anionic ion pairs and free ions with relative concentrations that depend on the reaction medium, as in cationic polymerization.
- Unlike cationic polymerization, there is a large difference between the reactivities of ion pairs and free ions in anionic polymerization.
- Although anionic polymerizations proceed well at low T, they are seldom as temperature sensitive as cationic polymerizations.
- Many anionic polymerizations are easier to understand since the identities of the initiating species and counterions are much better estabilished.
- Solvents useful for anionic polymerizations are limited to aliphatic and aromatic hydrocarbons and ethers. Halogenated solvents (nucleophilic substitution reactions!) and other polar solvents such as esters and ketones cannot be used since they can react with anions.
- Termination of anionic polymerization occurs by transfer of a positive fragment (usually H^+) from the solvent or a deliberately added agent.
- Many anionic polymerizations are living polymerizations when the reaction conditions are appropriately chosen.

Living and Controlled Polymerization

M. Szwarc:
Living Polymerization: Chain growth process without chain breaking reactions (transfer and termination) (1)

End-group control
Block copolymer synthesis via sequential monomer addition

To allow MW control and narrow MWD, additional requirements need to be fullfilled:

- Fast initiation and complete consumption of the initiator in the early stages of the polymerization process (2)
- Exchange between species of various reactivities should be at least as fast as propagation (3)

It was suggested to use the term „controlled“ for polymerizations which fullfill (2) and (3), but which are not free of chain breaking reactions. Problem: what does controlled refer to? What is and what is not controlled?? Alternatives: „living“ polymerization, „apparently living“ ....

Living Polymerizations & Macromolecular Engineering

1. Fast and quantitative initiation

All chains start to grow at the same time and $X_n = \Delta[M] / [I]_0$

Consequences:
- Narrow molecular weight distribution
- Precise control of X_n

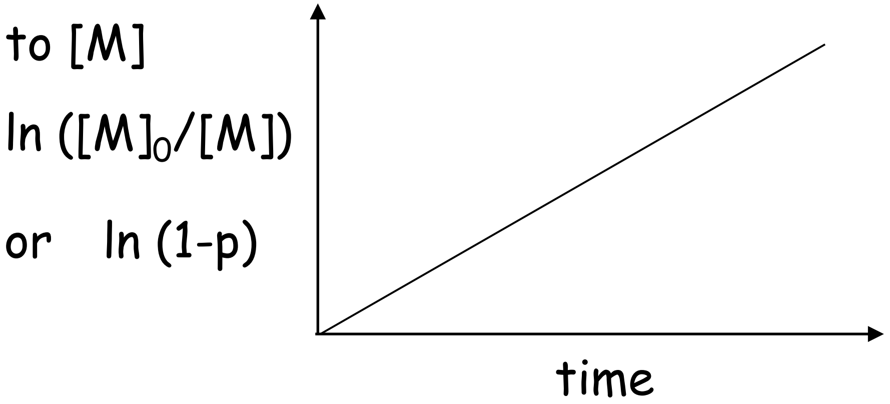
2. Long-lived polymer chains

Consequences: Control of end group functionality and polymer architecture

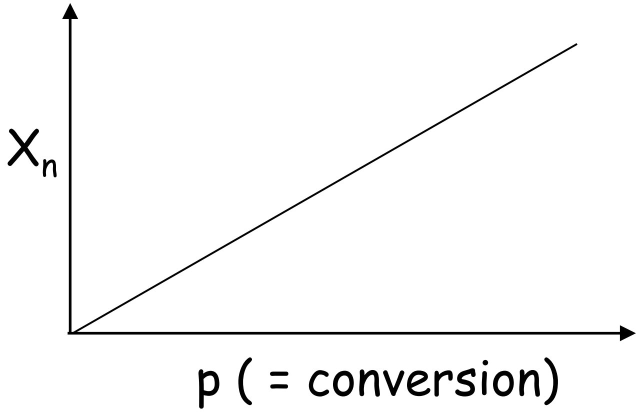
Increasing the lifetime of a polymer chain means reducing the probability for termination to occur.

Mechanistic Characteristics of Living Polymerizations

1. R_p is first order with respect to [M]



2. $X_n = ([M]_0 - [M])/[I]_0 = p[M]_0/[I]_0$



3. Narrow polydispersity (M_w/M_n)

$$M_w/M_n = 1 + 1/X_n$$

Outline

Anionic Polymerization:

- Initiation
    - Nucleophilic initiators
    - Electron transfer
- Termination
- Kinetics
- Macromolecular engineering

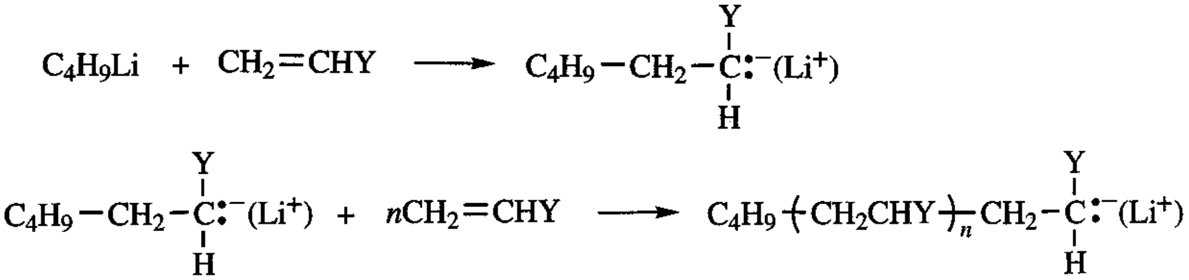
Initiation of Anionic Polymerization

Nucleophilic initiators

- Include covalent or ionic metal amides ($NaNH_2$, $LiN(C_2H_5)_2$), alkoxides, hydroxides, cyanides, phosphines, amines and organometallic compounds (e.g. n-C_4H_9Li, ΦMgBr)
- Initiation involves the addition to monomer of a nucleophile, either as neutral (B:) or negative ($B:^-$) species
- The initiator required for a particular monomer depends on its reactivity towards nucleophilic attack: monomer reactivity increases with increasing ability to stabilize the carbanion charge

Alkyl derivatives of alkali metals

Most important:
Alkyllithium derivatives; due to their solubility in hydrocarbon solvents



$$C_4H_9Li + CH_2{=}CHY \longrightarrow C_4H_9{-}CH_2{-}\overset{Y}{\underset{H}{C}}{:}^{-}(Li^{+})$$

Initiation

$$C_4H_9{-}CH_2{-}\overset{Y}{\underset{H}{C}}{:}^{-}(Li^{+}) + nCH_2{=}CHY \longrightarrow C_4H_9{(}CH_2CHY{)}_n CH_2{-}\overset{Y}{\underset{H}{C}}{:}^{-}(Li^{+})$$

Propagation

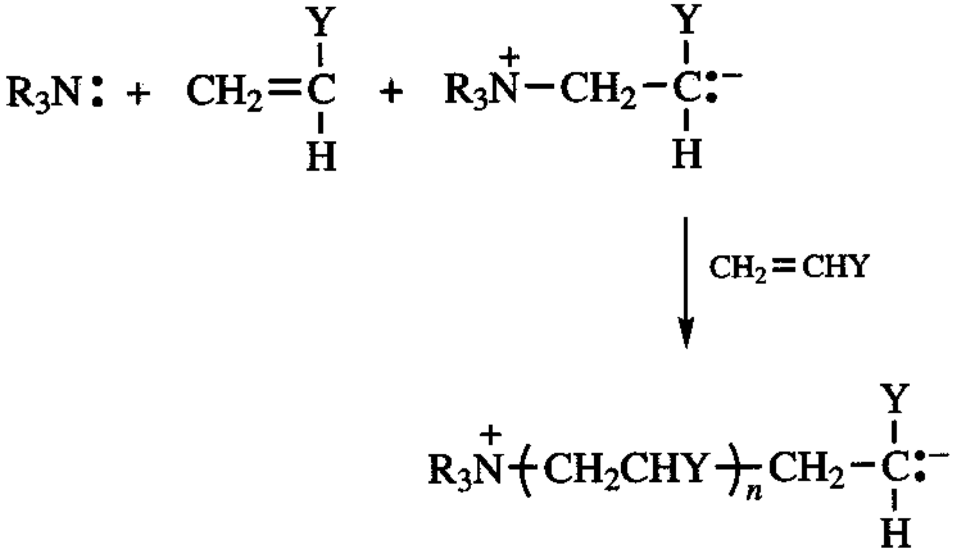
Alkyls or aryls of heavier alkali metals are poorly soluble in hydrocarbon solvents, but can be dissolved in ethers

Alkyl derivatives of alkaline-earth metals

E.g. Organomagnesium compounds: considerably less reactive than organolithiums due to the much less polarized metal-carbon bond. They can only initiate polymerization of monomers more reactive than styrene and 1,3-dienes, such as 2- and 4-vinylpyridine

Neutral nucleophiles

For example: tertiary amines and phosphines
The propagating species is a zwitterion



$$R_3N\!: + CH_2{=}\overset{\displaystyle Y}{\underset{\displaystyle H}{C}} + R_3\overset{+}{N}{-}CH_2{-}\overset{\displaystyle Y}{\underset{\displaystyle H}{C}}\!:^- \xrightarrow{CH_2=CHY} R_3\overset{+}{N}\!\left(CH_2CHY\right)_n CH_2{-}\overset{\displaystyle Y}{\underset{\displaystyle H}{C}}\!:^-$$

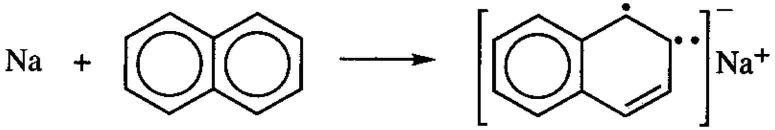
Initiation of Anionic Polymerization

Electron transfer

Aromatic radical-anions, such as e.g. sodium naphthalene

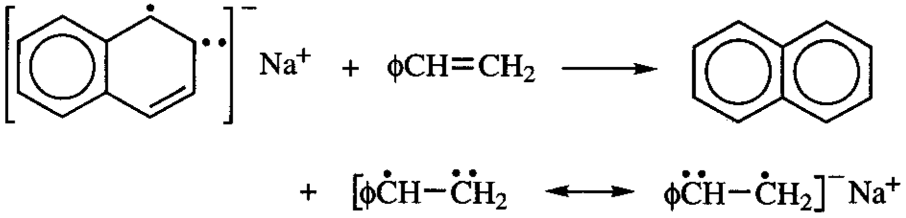
- Initiation consists of 3 steps:

1. Formation of a naphthalene radical-anion

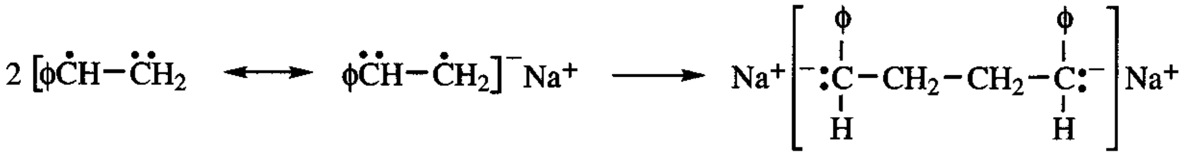


- Transfer of an electron from the alkali metal to naphthalene
- Polar solvents (e.g. THF) are needed to stabilize the radical anion

2. Electron transfer to monomer to form e.g. a styryl radical anion

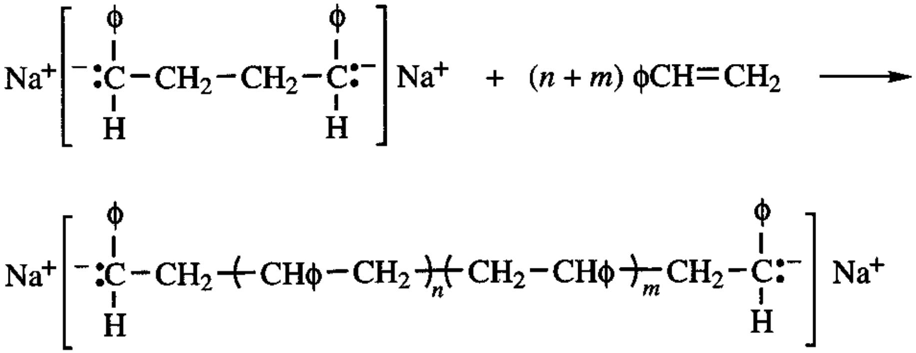


3. Dimerization of the styryl radical-anion to form a dicarbanion



$$2\left[\phi\dot{C}H-\ddot{C}H_2 \longleftrightarrow \phi\ddot{C}H-\dot{C}H_2\right]^- Na^+ \longrightarrow Na^+\left[{}^-{:}\overset{\phi}{\underset{H}{C}}-CH_2-CH_2-\overset{\phi}{\underset{H}{C}}{:}^-\right]Na^+$$

- Propagation:



$$Na^+\left[{}^-{:}\overset{\phi}{\underset{H}{C}}-CH_2-CH_2-\overset{\phi}{\underset{H}{C}}{:}^-\right]Na^+ + (n+m)\,\phi CH{=}CH_2 \longrightarrow$$

$$Na^+\left[{}^-{:}\overset{\phi}{\underset{H}{C}}-CH_2\left(CH\phi-CH_2\right)_n\left(CH_2-CH\phi\right)_m CH_2-\overset{\phi}{\underset{H}{C}}{:}^-\right]Na^+$$

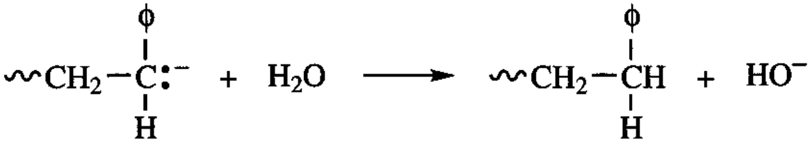
Termination of Anionic Polymerization

Polymerizations without termination

- Termination by combination of the anion with a metal counterion does not take place
- Many anionic polymerizations, especially of nonpolar monomers such as styrene and 1,3-butadiene, take place under conditions in which there are no effective termination reactions (i.e. „living anionic polymerization“)

Termination by impurities and deliberately added transfer agents

- Oxygen and CO_2 lead to –OH and –COOH groups (via the corresponding peroxy and carboxyl anions and the addition of a proton donor)
- Moisture terminates propagating carbanions via proton transfer:



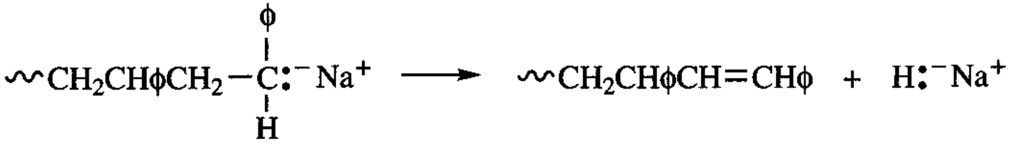
$$\sim CH_2-\overset{\phi}{\underset{H}{C}}:^- \; + \; H_2O \longrightarrow \sim CH_2-\overset{\phi}{\underset{H}{C}}H \; + \; HO^-$$

- Living polymers are terminated by deliberate addition of chain transfer agents such as water or alcohol after all of the monomer has been consumed

Spontaneous termination

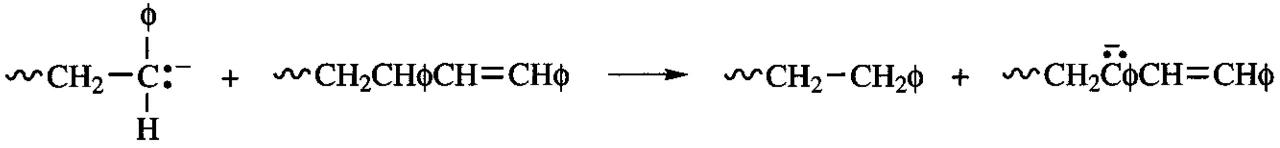
- Living polymers do not live forever; even in absence of terminating agents the concentration of carbanion centers decays with time („spontaneous termination“)
- Polystyryl carbanions, one of the most stable living anionic systems, remain living for weeks in hydrocarbon solvents at RT

Mechanism for polystyryl anions:



$$\sim CH_2CH\phi CH_2-\overset{\phi}{\underset{H}{C}}{:}^-\,Na^+ \longrightarrow \sim CH_2CH\phi CH{=}CH\phi + H{:}^-\,Na^+$$

hydride elimination

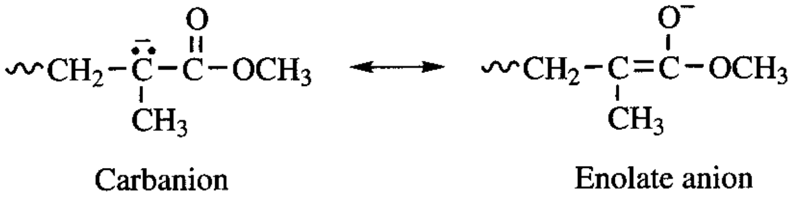


$$\sim CH_2-\overset{\phi}{\underset{H}{C}}{:}^- + \sim CH_2CH\phi CH{=}CH\phi \longrightarrow \sim CH_2-CH_2\phi + \sim CH_2\ddot{C}\phi CH{=}CH\phi$$

abstraction of an allylic hydrogen

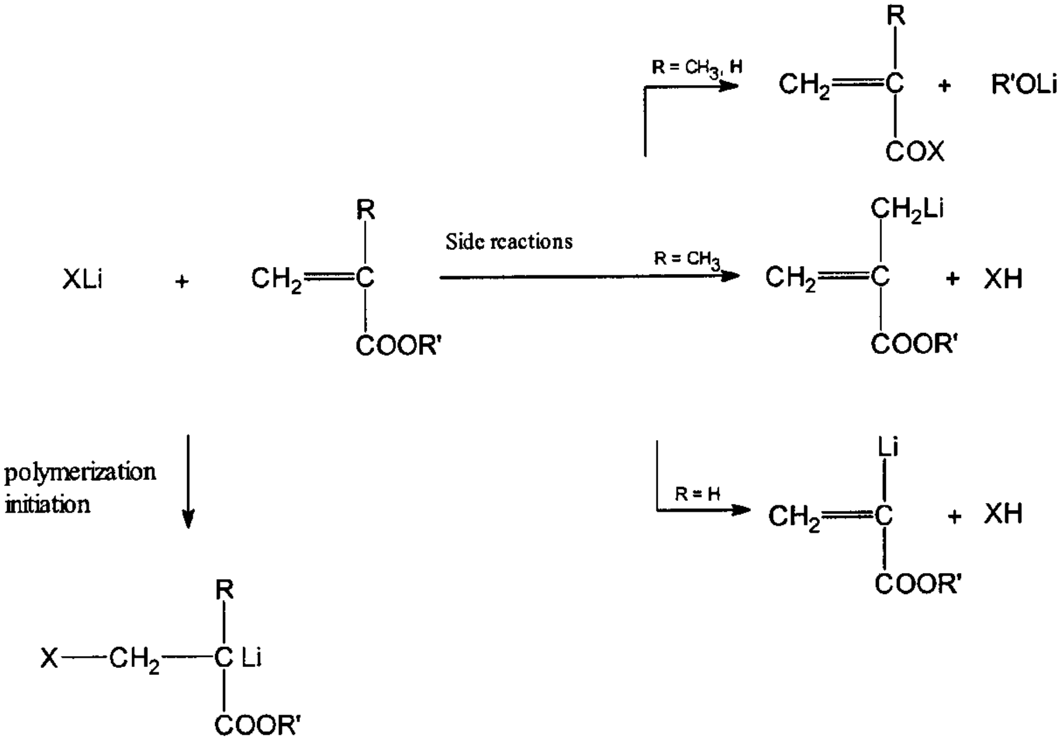
Termination and side-reactions of polar monomers

- Polar monomers such as methyl (meth)acrylate, methyl vinyl ketone and acrylonitrile are more reactive than e.g. styrene and 1,3-dienes because the polar substituent stabilizes the carbanion propagating center by resonance interaction to form the enolate anion

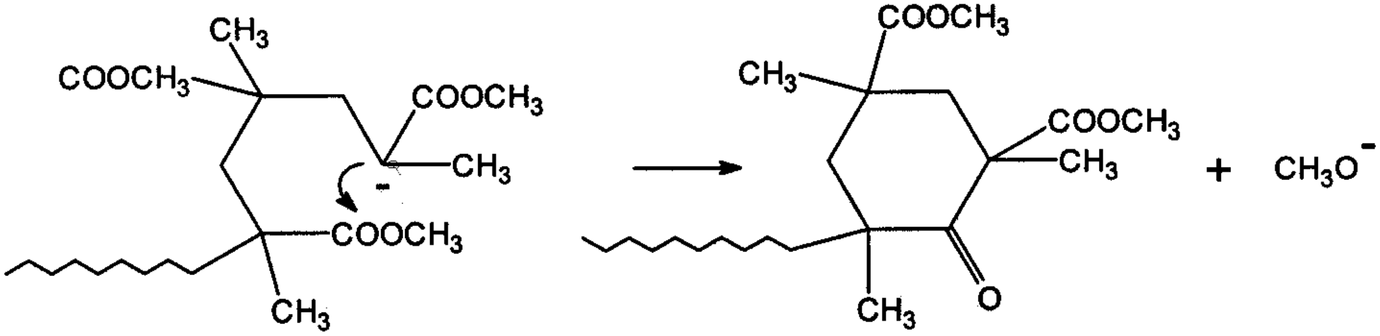


- However, several termination and side reactions compete with initiation and propagation, which makes it diffult to achieve living anionic polymerization

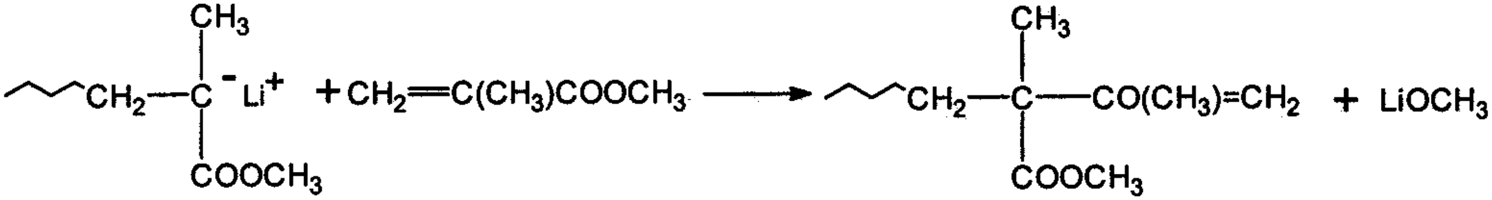
Side reactions competing with initiation:



Side reactions competing with propagation:

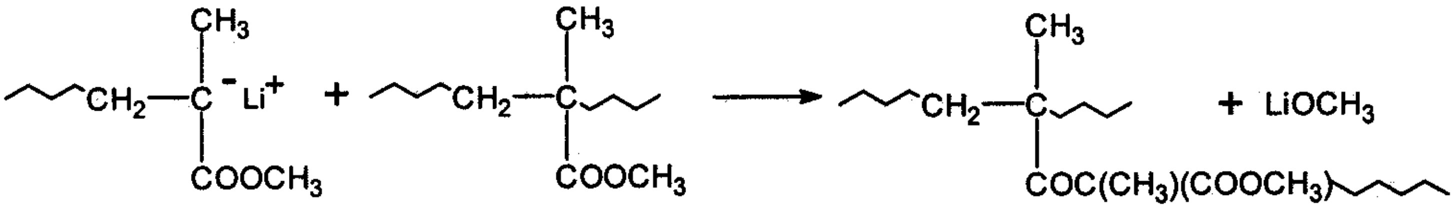


Back-biting cyclization.



$$\sim\!CH_2-\overset{\displaystyle CH_3}{\underset{\displaystyle COOCH_3}{C^-}}\,Li^+ + CH_2{=}C(CH_3)COOCH_3 \longrightarrow \sim\!CH_2-\overset{\displaystyle CH_3}{\underset{\displaystyle COOCH_3}{C}}-CO(CH_3){=}CH_2 + LiOCH_3$$

1,4 monomer addition.



$$\sim\!CH_2-\overset{\displaystyle CH_3}{\underset{\displaystyle COOCH_3}{C^-}}\,Li^+ + \sim\!CH_2-\overset{\displaystyle CH_3}{\underset{\displaystyle COOCH_3}{C}}\!\sim \longrightarrow \sim\!CH_2-\overset{\displaystyle CH_3}{\underset{\displaystyle COC(CH_3)(COOCH_3)\sim}{C}}\!\sim + LiOCH_3$$

Polymer branching

Living Anionic Polymerization of (Meth)Acrylates

- Control of temperature, solvent and the addition of ligands
- Side reactions are minimized by altering the reactivities of the propagating species (free ions and/or ion pairs) so that there is greater selectivity in favor of normal propagation
- To achieve living polymerization requires fast initiation and fast exchange among free-ion and ion-pair-propagating species and dormant (and associated) covalent species
- Side reactions dominate over normal polymerization in hydrocarbon solvents

Successful and alternative approaches:

1. Living anionic polymerization of methacrylates (not acrylates) can be realized in polar solvents (THF) at low temperature (-20°C - -70°C)

2. Ligated Anionic Polymerization: uses ligands to enhance the reactivity of the propagating species and equilibria among the different active and dormant species. Efficient ligands include: metal alkoxides (LiOR), inorganic salts (LiCl), aluminium alkyls (R_3Al) and crown ethers. The ligands alter the propagating species by coordinating with either the propagating anionic center or its counterion, or both.

3. Controlled Radical Polymerization

   Often experimentally easier to achieve than living anionic polymerization due to the less stringent requirements with regards to the exclusion of moisture and oxygen

Kinetics of Living Anionic Polymerization

The rate of polymerization in nonterminating systems can be expressed as the rate of propagation:

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

$[M^-]$: total concentration of all types of propagating centers (free ions and ion pairs)
Note: since free ions usually constitute a very small percentage of $[M^-]$, $[M^-]$ often can be set equal to the concentration of ion pairs

The above equation is only valid if initiation is rapid compared to propagation, which is true for polymerizations in polar solvents, but often not for polymerizations in nonpolar solvent systems

Living Anionic versus Radical Polymerization

Living anionic polymerization:

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

Radical polymerization:

$$R_p = k_p[\mathrm{M}\bullet][\mathrm{M}]$$

- Depending on the solvent anionic k_p^{app} values may be 10-100 times smaller (hydrocarbon solvents) or larger (ether solvents) than the k_p values for radical polymerization
- The concentration of propagating radicals is ~ 10^{-9} – 10^{-7}M, versus 10^{-4} – 10^{-2}M for the propagating anions

Anionic polymerization rates are much higher than radical rates due to the difference in the concentrations of the propagating species

Living Anionic Polymerization: The Reaction Medium

The propagation rate constant and the polymerization rate for anionic polymerization are strongly dependent on the nature of the solvent and the counterion

Polymerization of styrene by sodium naphthalene (3×10^{-3} M at 25°C)

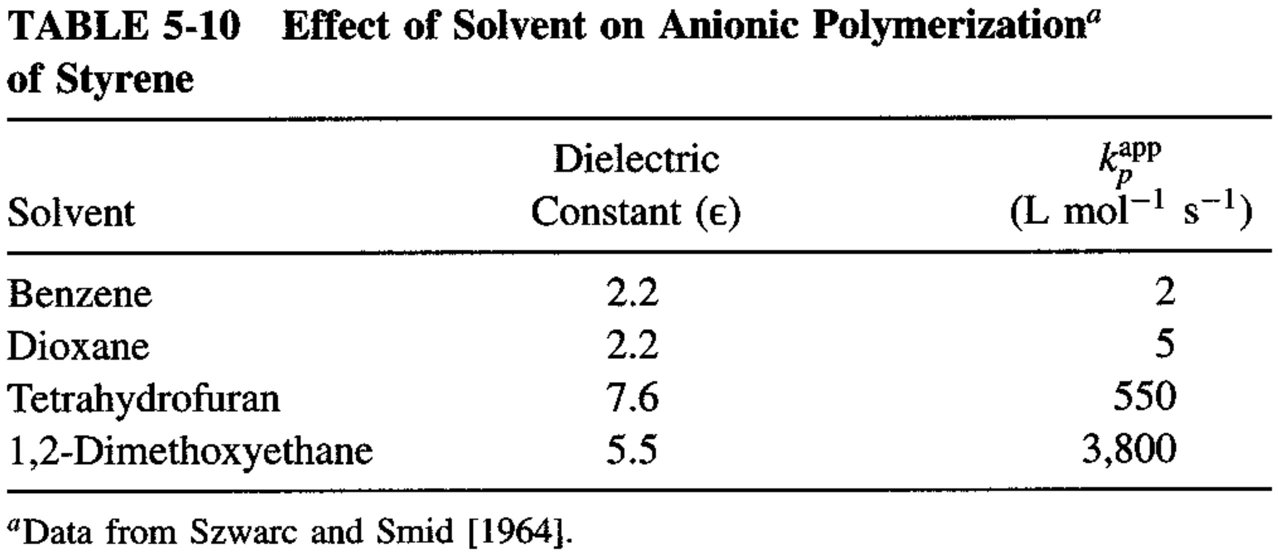


TABLE 5-10 Effect of Solvent on Anionic Polymerization[a] of Styrene

Solvent	Dielectric Constant (ϵ)	k_p^{app} (L mol^{-1} s^{-1})
Benzene	2.2	2
Dioxane	2.2	5
Tetrahydrofuran	7.6	550
1,2-Dimethoxyethane	5.5	3,800

[a] Data from Szwarc and Smid [1964].

The increase in k_p^{app} with increasing solvating power of the reaction medium is mainly due to the increased fraction of free ions relative to ion pairs

Determining Individual Propagation Rate Constants

$$\left.\begin{aligned} R_p &= k_p^{-}[\mathrm{P}^-][\mathrm{M}] + k_p^{\mp}[\mathrm{P}^-(\mathrm{C}^+)][\mathrm{M}] \\ R_p &= k_p^{\mathrm{app}}[\mathrm{M}^-][\mathrm{M}] \end{aligned}\right\} \Rightarrow \qquad k_p^{\mathrm{app}} = \frac{k_p^{-}[\mathrm{P}^-] + k_p^{\mp}[\mathrm{P}^-(\mathrm{C}^+)]}{[\mathrm{M}^-]} \quad \text{[i]}$$

$$\mathrm{P}^-(\mathrm{C}^+) \overset{K}{\rightleftharpoons} \mathrm{P}^- + \mathrm{C}^+ \qquad\qquad K = \frac{[\mathrm{P}^-][\mathrm{C}^+]}{[\mathrm{P}^-(\mathrm{C}^+)]}$$

- if $[P^-] = [C^+]$,
  i.e. there is no source of either ion other than $P^-(C^+)$, then $[\mathrm{P}^-] = (K[\mathrm{P}^-(\mathrm{C}^+)])^{1/2}$

Under most conditions, the extent of dissociation is small and the concentration of ion pairs is close to the total concentration of living ends:

$$[\mathrm{P}^-] = (K[\mathrm{M}^-])^{1/2} \quad \text{[ii]}$$

and the concentration of ion pairs:

$$[\mathrm{P}^-(\mathrm{C}^+)] = [\mathrm{M}^-] - (K[\mathrm{M}^-])^{1/2} \quad \text{[iii]}$$

Cont'd from 23

Substitution of [ii] and [iii] in [i] gives:

$$\boxed{k_p^{\mathrm{app}} = k_p^{\mp} + \frac{(k_p^{-} - k_p^{\mp})K^{1/2}}{[\mathrm{M}^{-}]^{1/2}}}$$

- Polymerization can also be carried out in the presence of excess counterion by adding a strongly dissociating salt (e.g. $\mathrm{NaB\phi_4}$ to supply excess $\mathrm{Na^+}$). The concentration of free ions, depressed by the common ion effect is given by:

$$K = \frac{[\mathrm{P}^{-}][\mathrm{C}^{+}]}{[\mathrm{P}^{-}(\mathrm{C}^{+})]} \qquad \Rightarrow \qquad [\mathrm{P}^{-}] = \frac{\mathrm{K}[\mathrm{M}^{-}]}{[\mathrm{C}^{+}]}$$

When the added salt is strongly dissociated and the ion pairs slightly dissociated, the counterion concentration is very close to that of the added salt [CZ]: $[\mathrm{C}^+] \approx [\mathrm{CZ}]$ and the $[\mathrm{P}^-]$ and $[\mathrm{P}^-(\mathrm{C}^+)]$ are given by:

$$[\mathrm{P}^{-}] = \frac{\mathrm{K}[\mathrm{M}^{-}]}{[\mathrm{CZ}]} \quad [\mathrm{iv}] \qquad \& \qquad [\mathrm{P}^{-}(\mathrm{C}^{+})] = [\mathrm{M}^{-}] - \frac{K[\mathrm{M}^{-}]}{[\mathrm{CZ}]} \quad [\mathrm{v}]$$

And, by combining [i], [iv] and [v]: $\boxed{k_p^{\mathrm{app}} = k_p^{\mp} + \frac{(k_p^{-} - k_p^{\mp})K}{[\mathrm{CZ}]}}$

$$k_p^{\mathrm{app}} = k_p^{\mp} + \frac{(k_p^- - k_p^{\mp})K^{1/2}}{[\mathrm{M}^-]^{1/2}}$$

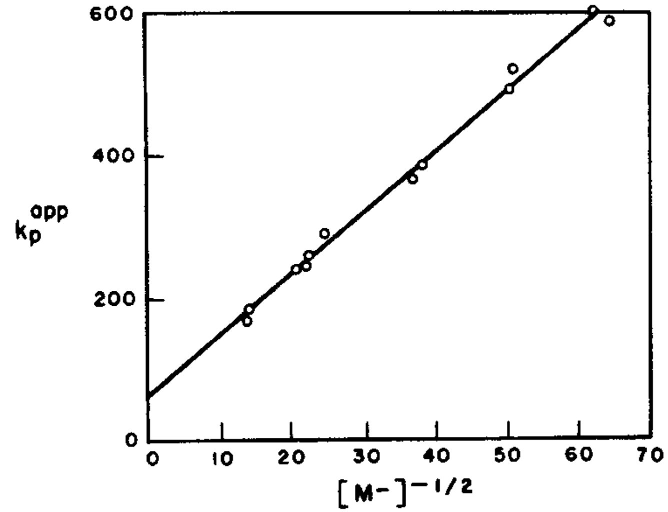


Fig. 5-5 Polymerization of styrene by sodium naphthalene in 3-methyltetrahydrofuran at 20°C. After Schmitt and Schulz [1975] (by permission of Pergamon Press and Elsevier, Oxford).

$$k_p^{\mathrm{app}} = k_p^{\mp} + \frac{(k_p^- - k_p^{\mp})K}{[\mathrm{CZ}]}$$

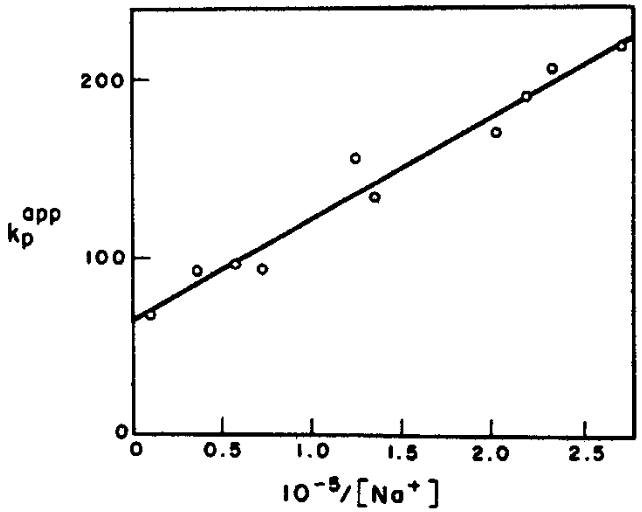


Fig. 5-6 Polymerization of styrene by sodium naphthalene in 3-methyltetrahydrofuran at 20°C in the presence of sodium tetraphenylborate. After Schmitt and Schulz [1975] (by permission of Pergamon Press and Elsevier, Oxford).

The combination of two slopes and two intercepts allows the individual calculation of k_p^-, $k_p^{\pm}$ and K

Reactivity in Anionic Polymerization

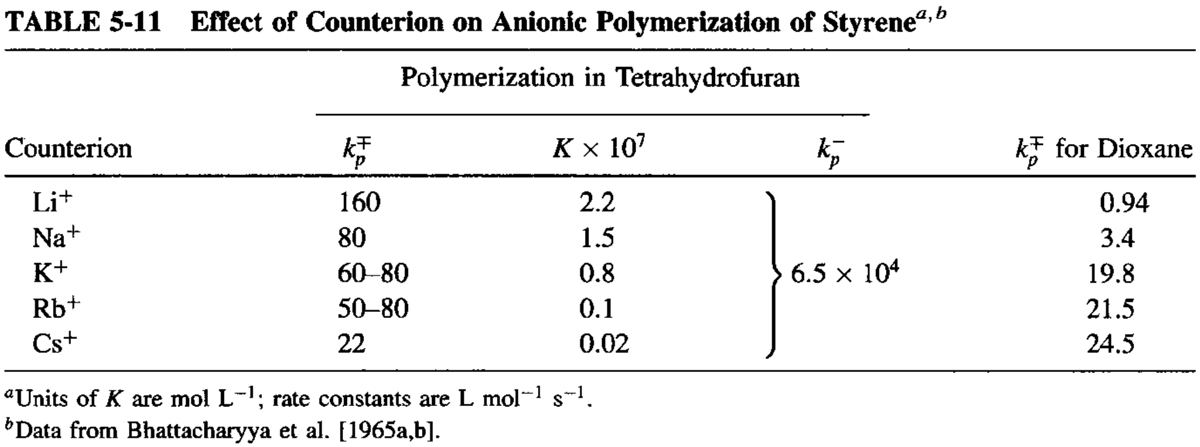


TABLE 5-11 Effect of Counterion on Anionic Polymerization of Styrene[a, b]

	Polymerization in Tetrahydrofuran			
Counterion	$k_p^{\mp}$	$K \times 10^7$	k_p^-	$k_p^{\mp}$ for Dioxane
Li^+	160	2.2	6.5×10^4	0.94
Na^+	80	1.5		3.4
K^+	60–80	0.8		19.8
Rb^+	50–80	0.1		21.5
Cs^+	22	0.02		24.5

[a] Units of K are mol L^{-1}; rate constants are L mol^{-1} s^{-1}.

[b] Data from Bhattacharyya et al. [1965a,b].

$\varepsilon_{dioxane} = 2.2$
$\varepsilon_{THF} = 7.6$

Note: in dioxane no detectable dissociation of ion pairs to free ions could be measured

Increasing solvating power affects the reaction rate through an increase in the concentration of free ions (larger K). Free ions are much more reactive than ion pairs, and have a very large effect on R_p. The majority of propagation (~90%) involves ion pairs.

The dissociation constant K decreases with decreasing solvation of the counterion; the small Li^+ is solvated to a greater extent than the larger Cs^+

The reactivities of the ion pairs increase in the same order as K; the fraction of ion pairs that are of the solvent separated type increases with increasing solvation of the counter ion. Solvent separated ion pairs are much more reactive than contact ion pairs

The lower values of $k_p^{\pm}$ in dioxane are due to the presence of a smaller fraction of solvent-separated ion pairs. The order of reactivity in dioxane is the reverse of that in THF; solvation is not important in dioxane. The ion pair with the highest reactivity is that with the weakest bond between carbanion and counterion. Bond strength decreases and reactivity increases with increasing size of counterion

Degree of Polymerization

For living anionic polymerization:

$$\overline{X}_n = \frac{\text{Concentration of reacted monomer}}{\text{Concentration of living ends}}$$

$$\overline{X}_n = \frac{p[\mathrm{M}]_0}{[\mathrm{ZY}]_0} \quad \Rightarrow \quad \overline{X}_n = \frac{2p[\mathrm{M}]_0}{[\mathrm{I}]_0}$$

Initiation via electron transfer

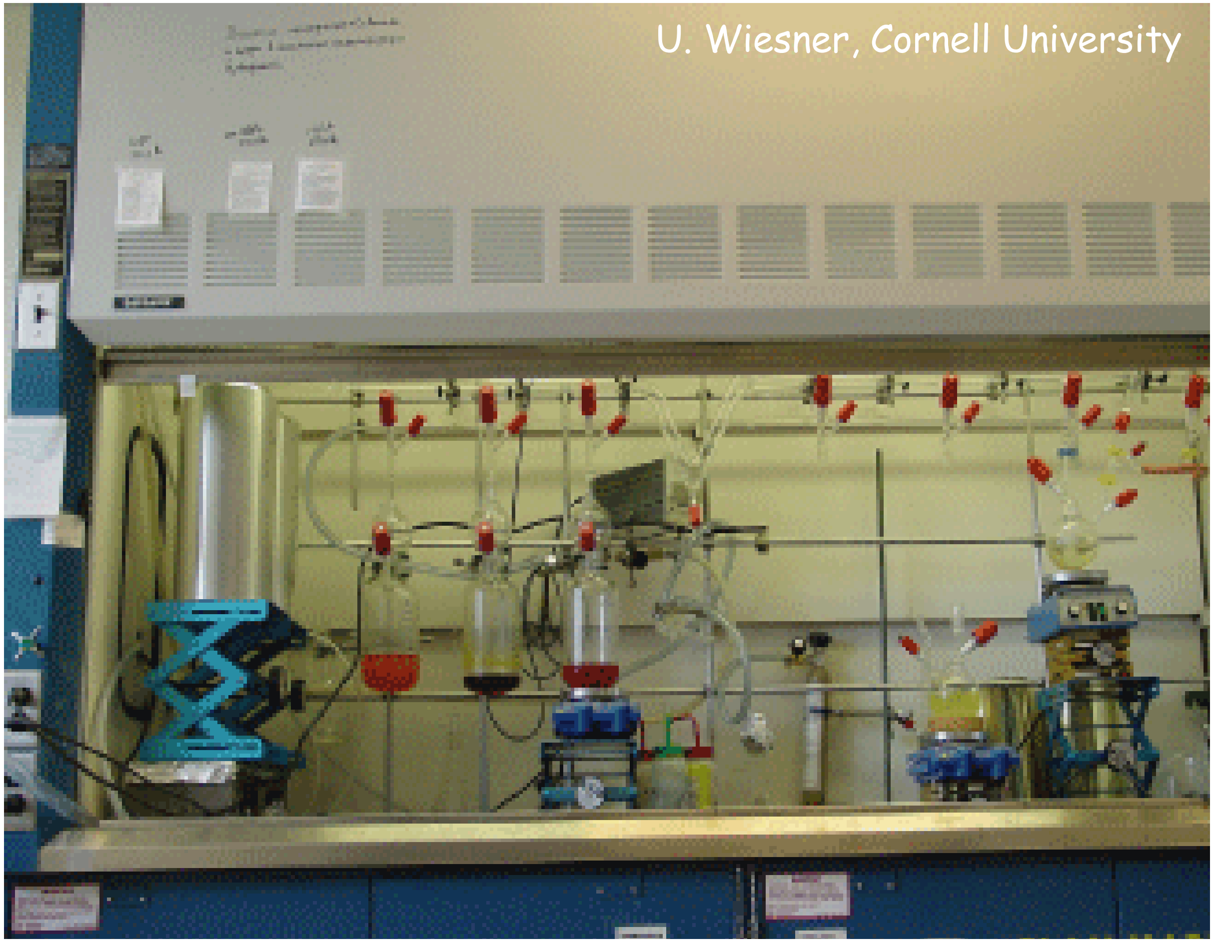
$$\overline{X}_n = \frac{p[\mathrm{M}]_0}{[\mathrm{I}]_0}$$

Initiation using e.g. RLi

- Prerequisite: all the initiator I is converted to propagating chain ends
- Living polymerization can be achieved for systems with fast initiation and efficient mixing in absence of depropagation, termination and transfer reactions

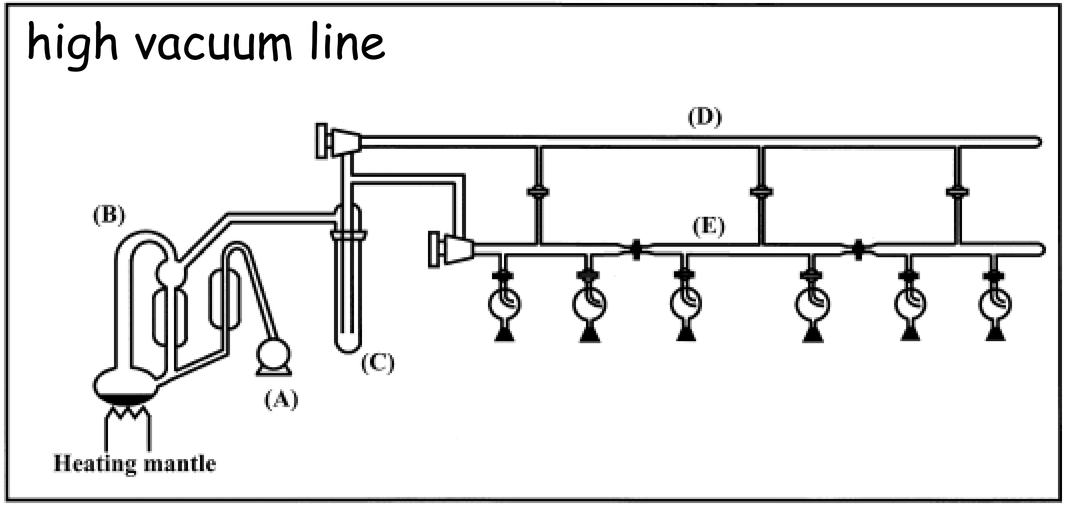
Anionic Polymerization: Practical Aspects

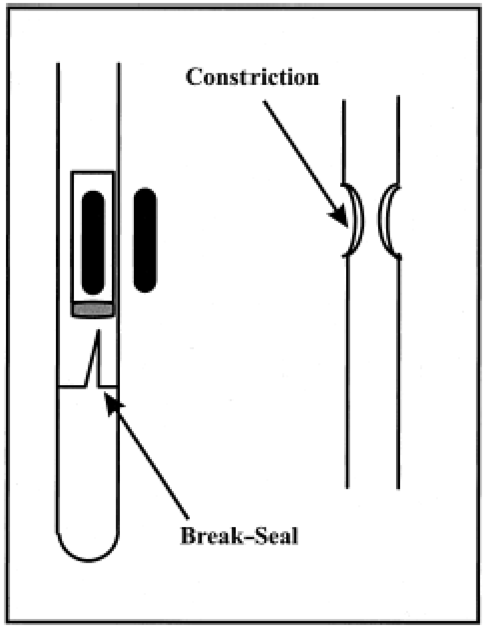
High vacuum conditions:



U. Wiesner, Cornell University

high vacuum line





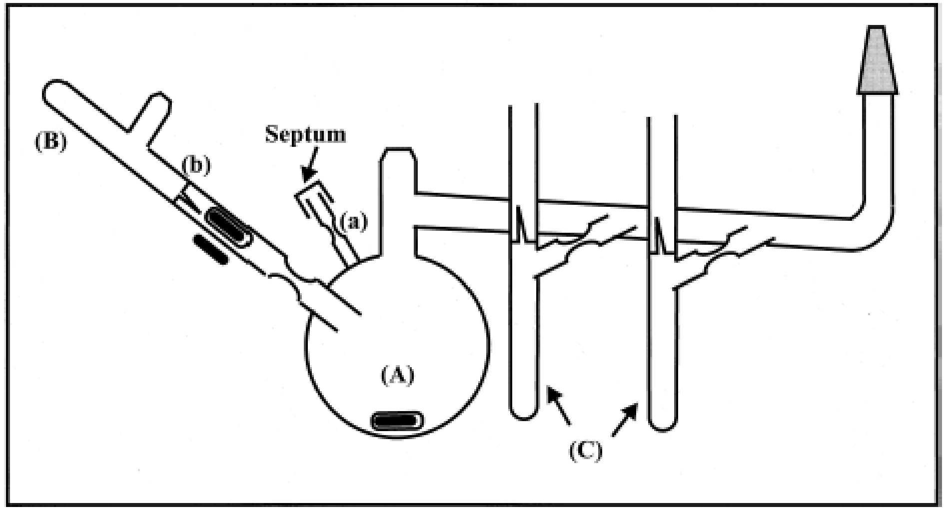


Figure 3. Apparatus for short-path distillation of high-boiling point substances.

N. Hadjichristidis et al. *J. Polym. Sci. Part A Polym. Chem.* **2000**, *38*, 3211

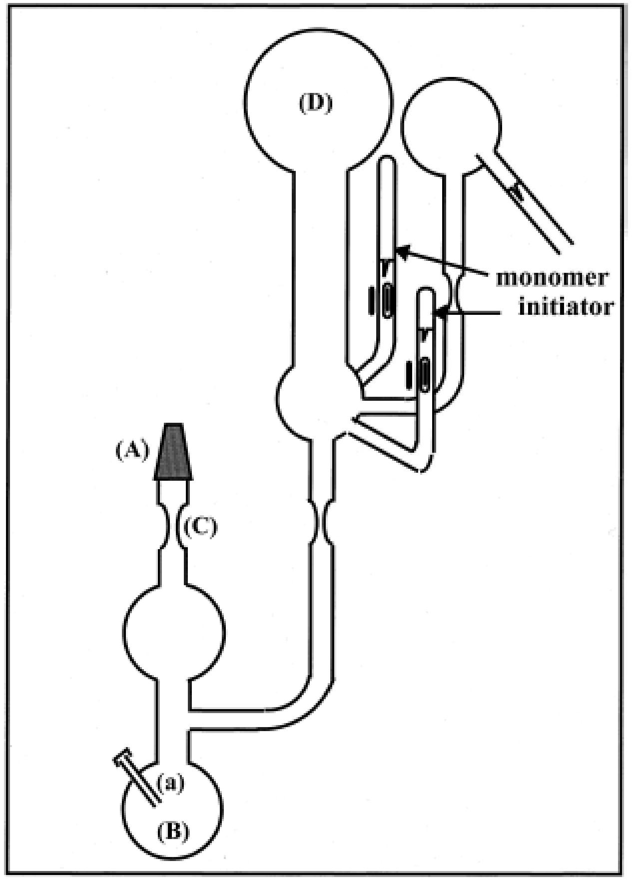


Figure 9. Apparatus for the preparation of linear homo- and copolymers, along with symmetric star homopolymers and star-block copolymers, consisting of the purge section and the main polymerization reactor.

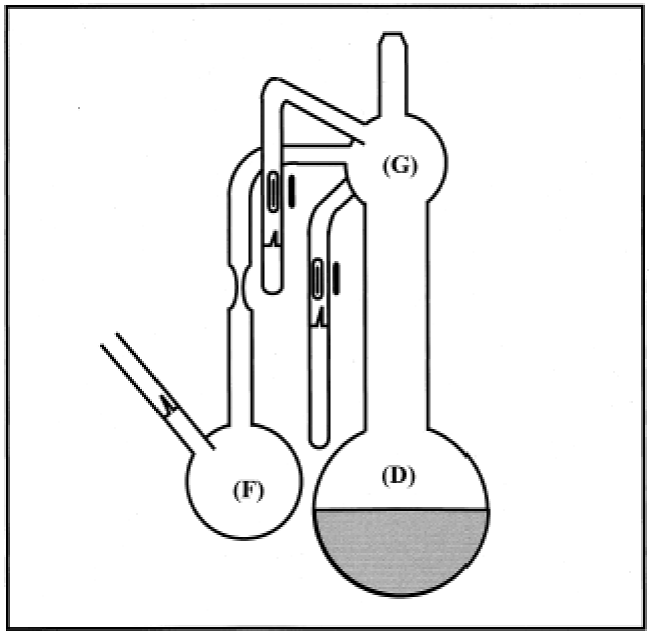


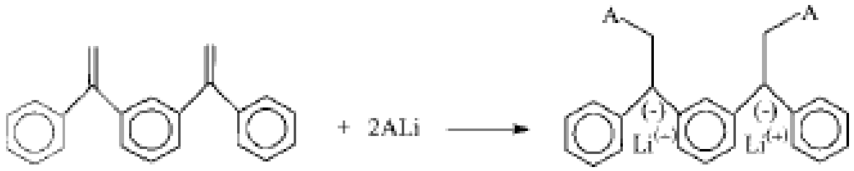
Figure 11. The main polymerization apparatus.

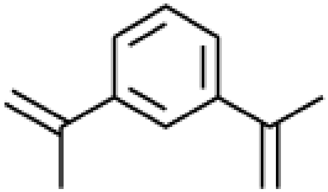
Macromolecular Engineering

- Sequential monomer addition works well in anionic polymerization to produce well-defined block copolymers:

Sequence of monomers is important: polystyryl carbanion initiates polymerization of methyl methacrylate, but the reverse does not occur. Poly(methyl methacrylate) carbanion is more stable than polystyryl carbanion

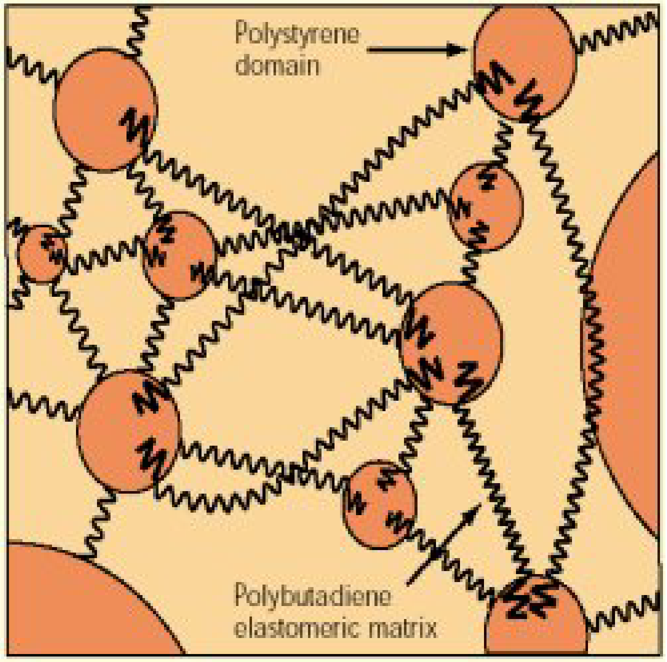
Difunctional initiators allow the preparation of ABA, BABAB, CABAC and other symmetric block copolymers. Difunctional initiators can be prepared by reacting dienes such as m-diisopropenylbenzene or 1,3-bis(1-phenylethenyl)benzene with 2 eq. BuLi



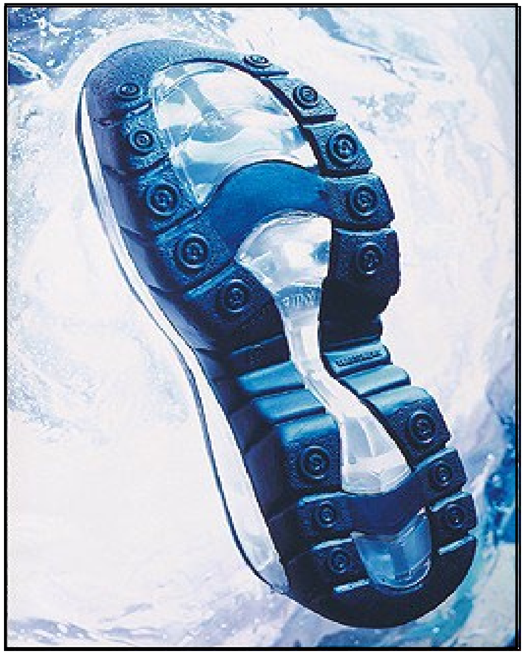


Styrene-isoprene-styrene and styrene-1,2-butadiene-styrene ABA triblock copolymers with short styrene blocks are useful as thermoplastic elasomers (*Cariflex, Kraton, Soloprene, Stereon*)

Thermoplastic elastomers behave as elastomers at ambient temperatures but are thermoplastic at elevated temperatures ($T > T_{g,PS}$), where they can be molded and remolded



The polystyrene blocks aggregate to form glassy (hard) domains that physically crosslink the rubbery (soft) polydiene blocks



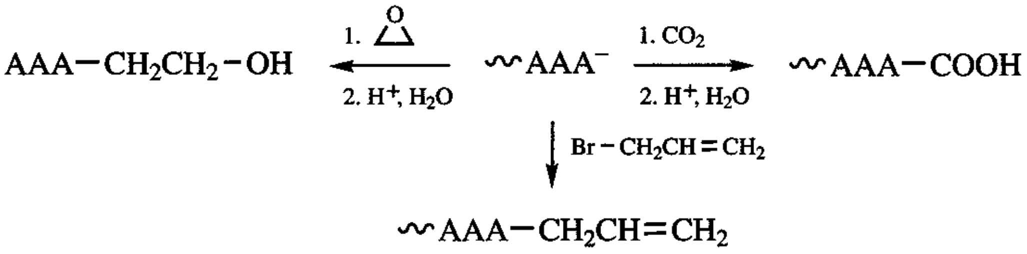
http://www.kraton.com/

- Telechelic (end-functionalized) polymers
  - Telechelic polymers contain one or more end groups with the capacity to undergo further reactions
  - If the end group is a polymerizable unit, the telechelic is also called a macromonomer

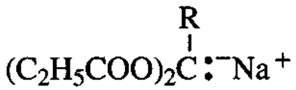
Two strategies:

1. Termination with a suitable reagent:

   - Living anionic polymers can be terminated with various electrophiles:



   - Living cationic polymers can be terminated with suitable nucleophiles:

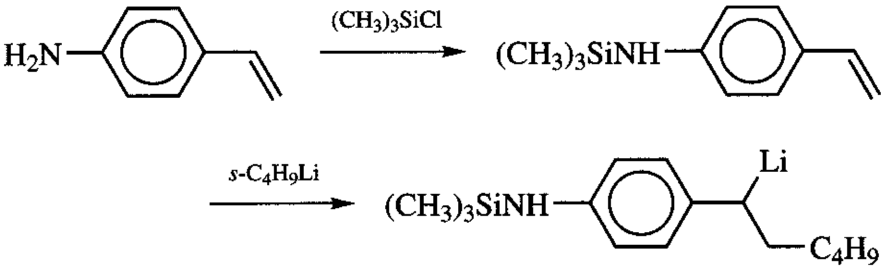


$(C_2H_5COO)_2\overset{R}{C}\!:^{-}Na^{+}$

sodiomalonate

2. Using functional initiators:

- Anionic polymerization:



- Cationic polymerization

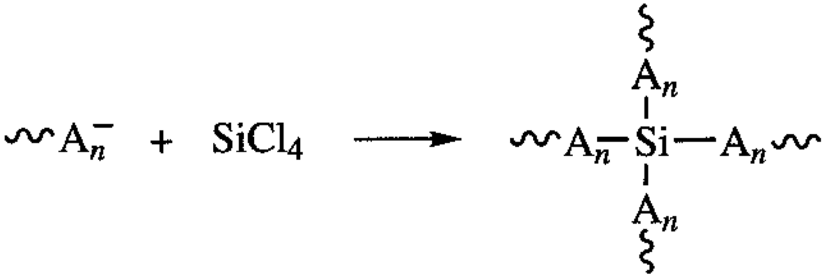
$$CH_2{=}CH{-}COOCH_2CH_2O\overset{CH_3}{\overset{|}{C}}H{-}I$$

- Coupling Reactions

Block copolymers

$$\sim A_nB_m^- \xrightarrow{Br(CH_2)_6Br} \sim A_nB_m(CH_2)_6B_mA_n \sim$$

Star polymers



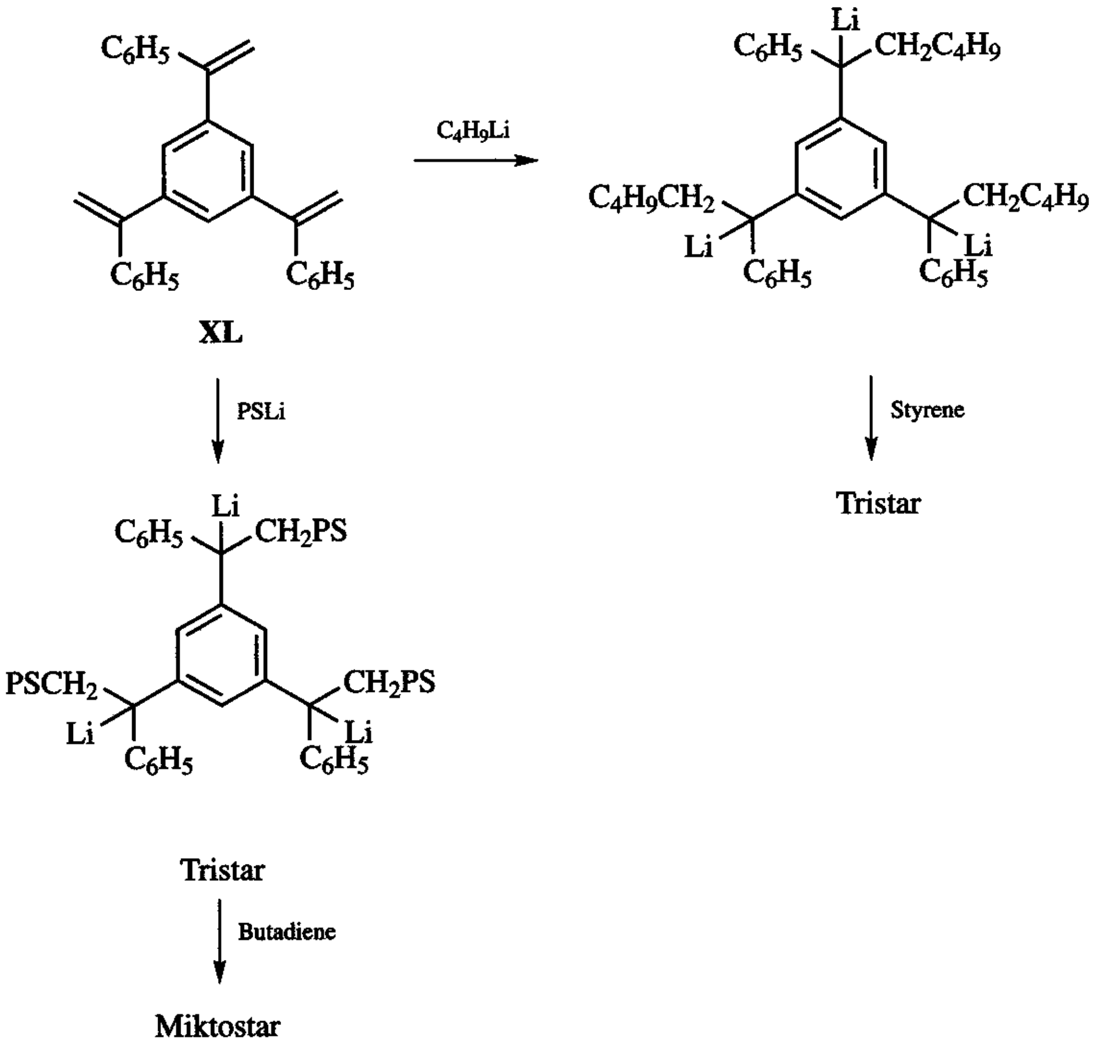
$$\sim A_n^- + SiCl_4 \longrightarrow \sim A_n-\underset{\underset{\sim}{A_n}}{\overset{\overset{\sim}{A_n}}{Si}}-A_n\sim$$

Miktoarm star / μstar / hetero arm or mixed-arm star polymers

$$PILi \xrightarrow[CH_3SiCl_3]{excess} PISi(CH_3)Cl_2 \xrightarrow{PSLi} PISi(CH_3)(PS)_2$$

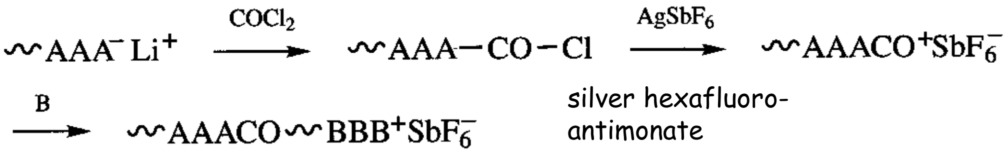
Alternative approach to miktoarm star polymers

1,3,5-tris(1-phenylethenyl)benzene



- Transformation Reactions

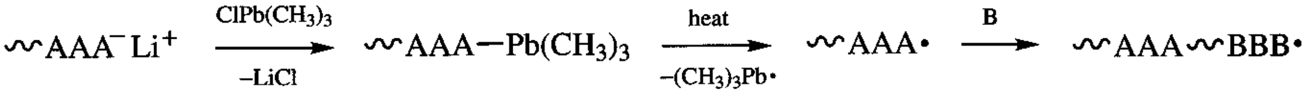
Anionic ⇒ cationic:



$$\sim AAA^{-}Li^{+} \xrightarrow{COCl_2} \sim AAA{-}CO{-}Cl \xrightarrow{AgSbF_6} \sim AAACO^{+}SbF_6^{-} \xrightarrow{B} \sim AAACO\sim BBB^{+}SbF_6^{-}$$

silver hexafluoro-antimonate

Anionic ⇒ radical:



$$\sim AAA^{-}Li^{+} \xrightarrow[-LiCl]{ClPb(CH_3)_3} \sim AAA{-}Pb(CH_3)_3 \xrightarrow[-(CH_3)_3Pb\bullet]{heat} \sim AAA\bullet \xrightarrow{B} \sim AAA\sim BBB\bullet$$

trimethyl lead chloride

Radical versus Ionic Chain Polymerization

1. Ionic polymerizations usually proceed at lower temperatures than radical polymerizations. Although ionic reaction temperatures are usually below 0°C, there are numerous ionic polymerizations that proceed at temperatures somewhat above 0°C. Radical polymerizations, on the other hand, almost always proceed at temperatures appreciably above approximately 50°C. Furthermore, ionic polymerizations invariably have lower activation energies than their radical counterparts and, in some cases, they may actually possess negative activation energies.
2. Ionic polymerizations are distinguished by their marked sensitivity to changes in the polarity and solvating ability of the reaction media and counterion effects. Radical polymerizations do not show such effects.
3. The addition of known radical scavengers such as the DPPH radical to a polymerizing system will halt polymerization if it is a radical reaction. Ionic polymerizations will be unaffected by such additions. One must be careful, however, not to use a radical scavengers that also affects ionic polymerization. Thus, benzoquinone would be a poor choice as a radical scavenger, since it can also act as an inhibitor in ionic polymerization.
4. The chain transfer constant for an additive or solvent in the polymerization can be determined. This value can then be compared with the transfer constants for the same substance in the polymerization of the same monomer by known radical, cationic, and anionic initiators.
5. Copolymerization behavior can also be used to distinguish between radical and ionic polymerizations (see Chap. 6).