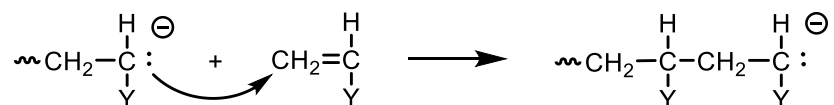


VII. ANIONIC POLYMERIZATION

A. Introduction to Anionic Polymerization

Anionic polymerization is defined as a chain-growth, addition polymerization of an unsaturated monomer, in which the propagating species is a carbanion, i.e., a negatively charged carbon possessing a bonding valence of three and carrying an unshared pair of electrons. The positive counterion is typically an alkali metal, such as lithium or sodium. Propagation consists of addition of the carbanion to an electrophilic olefin (a "Michael Reaction" in the terminology of organic chemistry).

Figure VII-1



Y = electron withdrawing group (inductive and/or by resonance)

The most significant feature of many anionic polymerizations is the absence of any kinetically significant termination reactions or chain transfer reactions. The term "living polymerization" was coined by Michael Szwarc to describe this behavior, and the profound scientific and technological significance of living polymerizations will be discussed throughout this course. It must be recognized, however, that living conditions can only be achieved for systems that have been rigorously purged of all acidic impurities, e.g., water, CO₂. Another feature observed for many anionic polymerizations is a rapid initiation rate compared to propagation rate. This is not strictly a necessary condition for a living polymerization, but it is characteristic of living anionic polymerizations and leads to narrow molecular weight distribution.

1. Initiators

Anionic polymerizations are initiated by,

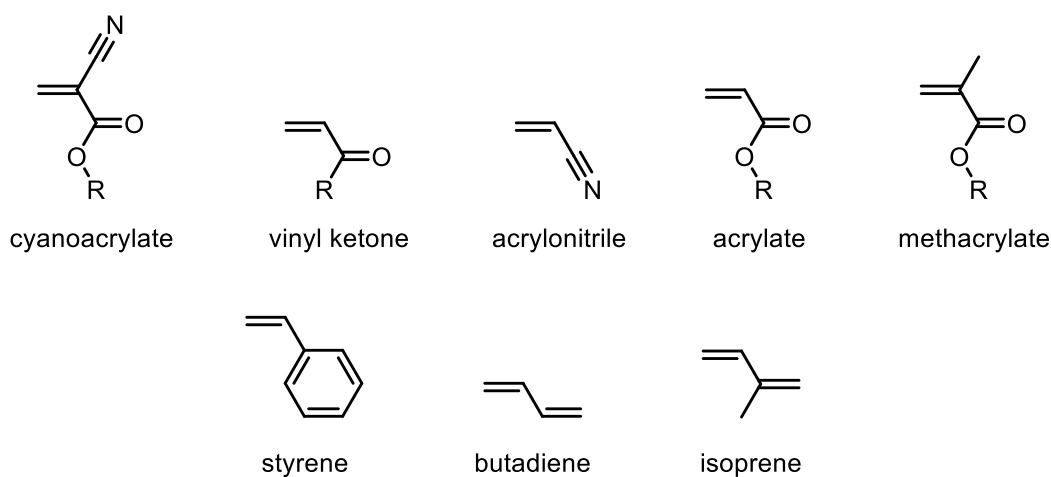
- nucleophiles (typically alkyl lithium compounds)
- products of electron transfer to π -electron systems

The growing chain ends consist of a carbon bearing a full (carbanion plus a metal cation) or partial negative charge (organometallic compound), depending on the states of association between carbon and metal. These different states, e.g., polar-covalent bond, contact ion pair, dissociated free ions, etc., are often in equilibrium with one another, and the position of the equilibrium depends on structure of the monomer, identity of the alkali metal, temperature, and reaction medium (solvent). These various equilibrium states represent the Winstein Spectrum discussed earlier.

2. Monomers

Suitable monomers for anionic polymerization are those possessing an electrophilic double bond and/or can stabilize a negative charge by resonance delocalization (Figure VII-2). The polar monomers in the top row are very reactive because the negative charge can be delocalized onto an electronegative heteroatom (oxygen and/or nitrogen); the top row monomers are ordered in descending reactivity moving from left to right. The hydrocarbon monomers in the bottom row (styrene and the dienes) are much less reactive, but also less prone to side reactions. These three monomers are most closely associated with classical living anionic polymerization.

Figure VII-2



3. Solvents

The range of suitable solvents for anionic polymerization is fairly narrow and limited mostly to aliphatic and aromatic hydrocarbons, ethers, and amines. Halogenated solvents undergo facile nucleophilic substitution reactions with carbanions; carbonyl-containing solvents such as ketones and esters also react quickly with carbanions. Any compounds with an acidic hydrogen atom, such as water or alcohols, usually will immediately terminate the growing carbanions by transfer of a proton; in fact, such compounds are commonly used to deliberately terminate polymerization. The following is a list of solvents commonly used in anionic polymerization. Propagation is markedly different in non-polar vs. polar solvents.

Non-polar:	<i>n</i> -alkanes:	<i>n</i> -hexane, <i>n</i> -heptane, etc.
	cycloparaffins:	cyclohexane
	aromatics:	benzene, toluene
Polar:	ethers:	tetrahydrofuran, dioxane, 1,2-dimethoxyethane, etc.
	amines:	triethylamine, liquid ammonia

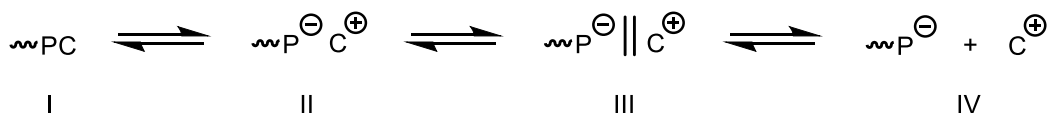
For living anionic polymerizations with fast initiation and no termination, the activation energy for the rate of polymerization is simply the activation energy for propagation, E_p . Values for E_p in anionic propagation are often strongly dependent on solvent; for styrene (sodium counterion) the value is relatively high in a non-polar solvent (dioxane) and relatively low in a polar solvent (THF):

$$E_p = 37.6 \frac{\text{kJ}}{\text{mole}} \quad \text{Dioxane} \quad \text{VII-1}$$

$$E_p = 4.2 \frac{\text{kJ}}{\text{mole}} \quad \text{THF} \quad \text{VII-2}$$

The higher value in dioxane results from the propagating chain ends being composed exclusively of contact ion pairs; dioxane is too poorly solvating (of the sodium counterions) to allow for solvent-separated ion pairs or free ions. The lower value in THF results from the fact that the propagating chain ends are distributed among contact pairs, solvent-separated pairs, and free ions. Increasing temperature causes this distribution to shift leftward along the Winstein spectrum (Figure VII-3), which tends to offset the increases in the various propagation rate constants (caused by increasing temperature).

Figure VII-3



In general, anionic polymerizations proceed at convenient rates at room temperature and slightly higher in non-polar solvents such as dioxane and hydrocarbons. In polar solvents such as THF they are usually run at low temperature, e.g., dry ice temperature, to avoid excessively fast rates.

B. Initiation of Anionic Polymerization

There are two modes of initiation of anionic polymerization:

- Nucleophilic - Leads to monofunctional chain growth reaction
- Electron transfer - Leads to difunctional chain growth reaction

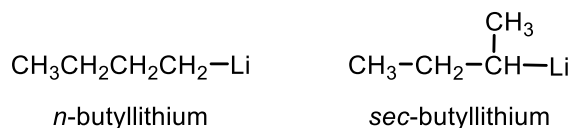
1. Nucleophilic Initiation

Nucleophilic initiation involves a direct attack of a nucleophile (almost always negatively charged) on the double bond of a monomer. The following compounds have all been used as anionic polymerization initiators (Table VII-1):

Table VII-1: Classes of Nucleophilic Initiators for Anionic Polymerization

Type	Example	Initiation Species	Counter Cation
Alkylolithiums	Butyllithium	Bu [⊖]	Li [⊕]
Metal amides	NaNH ₂	NH ₂ [⊖]	Na [⊕]
Grignard reagents	CH ₃ MgBr	CH ₃ [⊖]	MgBr [⊕]
Alkoxides	<i>t</i> -BuOK	<i>t</i> -BuO [⊖]	K [⊕]
Cyanides	KCN	CN [⊖]	K [⊕]

The two isomeric butyllithiums shown in Figure VII-4 are the most commonly used anionic initiators:

Figure VII-4

In general, the more stable the anion formed from the monomer, the more weakly nucleophilic may be the initiator (Table VII-2).

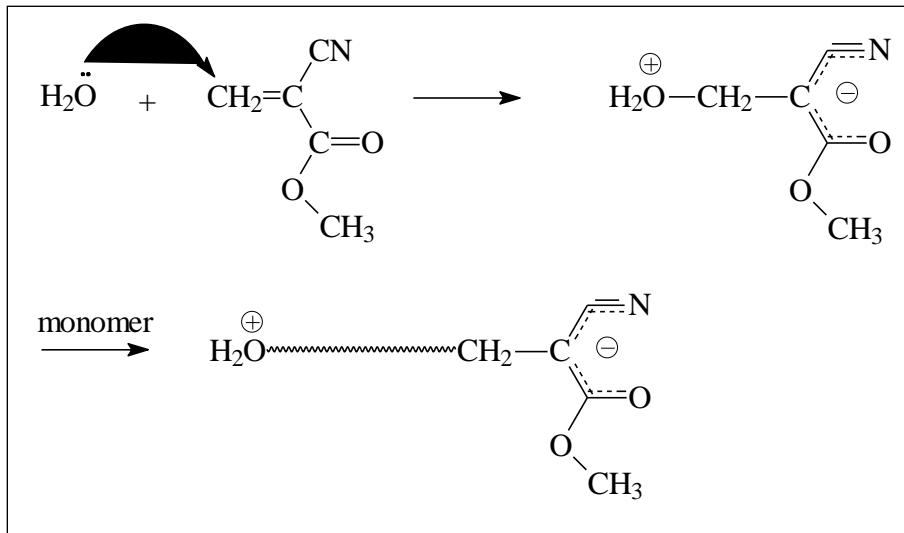
Table VII-2: Monomer Reactivity as a Function of Initiator Nucleophilicity

	Styrene	Dienes	(Meth)-acrylates	Acrylonitrile	Cyanoacrylate
Alkylolithium	+	+	+	+	+
Metal amide	+	+	+	+	+
Grignard	-	-	+	+	+
Alkoxide	-	-	+	+	+
Hydroxide	-	-	marginal	marginal	+
Cyanide	-	-	-	-	+
Water	-	-	-	-	+

The cyanoacrylates, the principle constituents of "Super Glue," are an excellent example of monomers that are extremely reactive toward anionic polymerization (Figure VII-5). The familiar auto-polymerization of these monomers upon exposure to air or surfaces is

believed to be due to water and to proceed via a zwitterionic intermediate. Very likely, the head group of one chain serves as the counterion for another.

Figure VII-5



a. Degree of polymerization

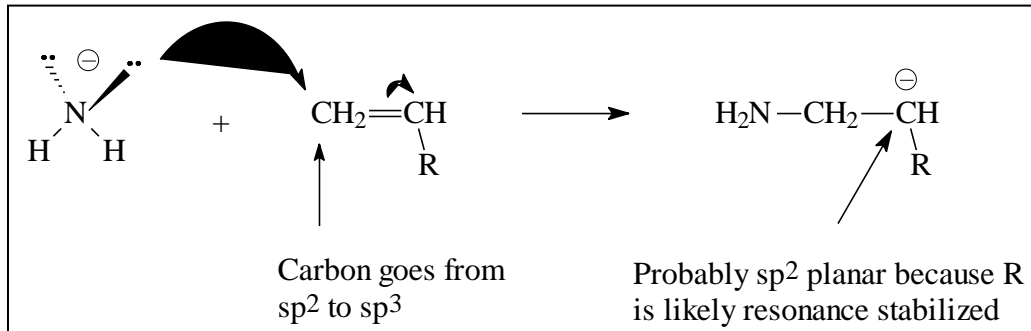
In the absence of chain transfer, nucleophilic initiation produces one mono-carbanionic chain per initiator moiety. If initiation is quantitative prior to complete conversion of the monomer, then the degree of polymerization of the formed polymer molecules will be determined by the mole ratio of consumed monomer to initiator:

$$\bar{X}_n = \frac{[M]_0 - [M]}{[I]_0} \quad \text{VII-3}$$

b. Mechanism of nucleophilic initiation

The mechanism for nucleophilic initiation involving a dissociated initiator species (a free-ion) is shown in Figure VII-6. It is a bimolecular, single-step, elementary process with a kinetic order of one with respect to both the initiator and monomer (eq VII-4).

Figure VII-6



$$r_i = k_i[\text{NH}_2^-][\text{M}]$$

VII-4

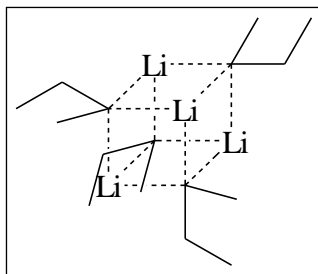
However, the most commonly used nucleophilic initiators are the alkyllithiums. These initiators are used for the commercial polymerization of 1,3-butadiene, isoprene, and styrene. Their great utility is largely due to their solubility in hydrocarbon solvents, which are the preferred solvents from the point of view of diene microstructure control, and due to the undesirably high rates of polymerization in ethers at room temperature. The mechanism of nucleophilic initiation by alkyllithiums in hydrocarbon solvents is more complex. The kinetics of nucleophilic initiation by alkyllithium compounds in hydrocarbon solvents are generally characterized by fractional orders with respect to the alkyllithium initiator (that is, the exponent "a" in eq VII-5 is not one, but rather a fraction, such as $\frac{1}{2}$, $\frac{1}{4}$, etc. (The order with respect to monomer, M, generally remains one.) Fractional orders are thought to be related to alkyllithium association.

$$r_i = k_i[\text{BuLi}]^a[\text{M}]^1$$

VII-5

Association refers to dipole-dipole interactions between two or more alkyllithium species. For example, shown in Figure VII-7 is a tetrameric association of *sec*-butyllithium as might be found in hydrocarbon solution. Note that each Li atom is "shared" among three alkyl groups, and that the structure is superficially similar to an inverse micelle.

Figure VII-7



The association number of various alkyllithium initiators in different solvents has been determined using colligative properties measurements (freezing point depression, boiling

point elevation, etc.) and discovered to be dependent on bulkiness of the alkyl group. For example, while *sec*-butyllithium preferentially forms tetramers, *n*-butyllithium, which is more slender and less bulky, preferentially forms hexamers.

c. *Effect of alkyl group on alkyllithium reactivity*

In decreasing order of reactivity with styrene and the dienes, the effect of the alkyl group of the initiator is as follows:

Styrene: *s*-butyl > *i*-propyl > *n*-butyl \approx ethyl > *t*-butyl
Dienes: *s*-butyl > *i*-propyl > *t*-butyl > *n*-butyl \approx ethyl

d. *Effect of hydrocarbon solvent on alkyllithium reactivity*

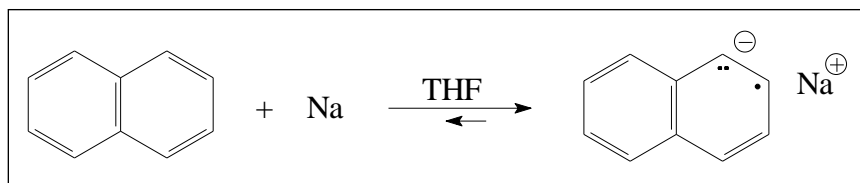
The order of alkyllithium reactivity induced by the common hydrocarbon solvents is as follows:

toluene > benzene > *n*-hexane > cyclohexane

2. Electron-Transfer Initiation

Alkali metals react with polynuclear aromatics such as naphthalene, in the presence of ether solvents, to form soluble products without the loss of hydrogen (Figure VII-8). The product is a brightly colored (dark blue-green) radical-anion in which the extra electron has been incorporated into the lowest-energy, unoccupied π orbital. The ether solvent is necessary to assist the transfer of the electron and to stabilize the alkali metal cation.

Figure VII-8



The following order of reactivity or electron affinity has been established:

anthracene > phenanthrene > naphthalene > biphenyl

In general, naphthalene is the most useful. For biphenyl, the equilibrium does not sufficiently favor the anion-radical. For anthracene the equilibrium lies well to the right, but the anion-radical is sluggish in reactivity with monomer.

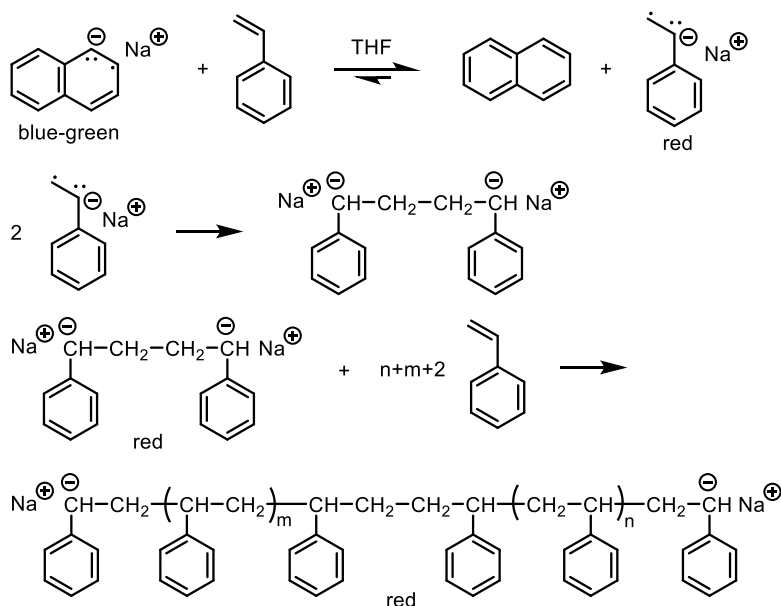
Sodium naphthalene is historically significant because Szwarc, Levy, and Milkovich used it in their famous 1956 paper in which they first demonstrated the living nature of the anionic polymerization of styrene. Using rigorously purified reagents, they were able to

show that termination and chain transfer reactions were completely undetectable, the molecular weight distributions were narrow, and number average degree of polymerization, \bar{X}_n , was predicted simply by the stoichiometry of the polymerization, as given by eq VII-6:

$$\bar{X}_n = \frac{[M]_0 - [M]}{0.5[I]_0} \quad \text{VII-6}$$

They found that the sequence shown in Figure VII-9 was virtually instantaneous as indicated by a change in color from blue-green to red:

Figure VII-9



The entire polymerization sequence shown in Figure VII-9 is very fast, being complete in several seconds. Note that the factor of 0.5 in the denominator of eq VII-6 accounts for the fact that coupling of styryl anion-radicals causes a doubling of the degree of polymerization.

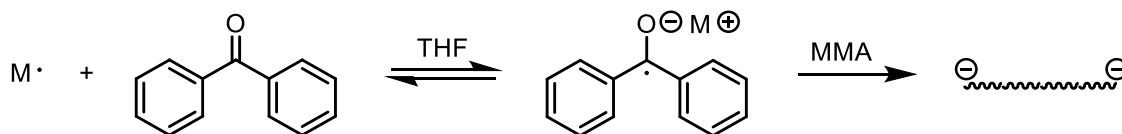
In addition to the Na naphthalene/THF system, several miscellaneous examples of electron transfer initiation have also been reported.

- Pure alkali metals initiate dienes in a heterogeneous reaction that is believed to consist of electron transfer, formation of a radical-anion, and coupling of the radical-anions followed by dianionic polymerization (discussed earlier).
- Lithium is soluble in liquid ammonia, without the loss of H_2 , forming a blue solution consisting of free solvated electrons and Li^{\oplus} counterions. The

resulting solution will initiate anionically polymerizable monomers via electron transfer, radical-anion coupling, and dianionic polymerization.

- Alkali metals will transfer an electron to a non-enolizable ketone (no hydrogens β to the carbonyl group). The resulting oxy radical-anion will transfer its extra electron to very reactive monomers such as acrylonitrile or methyl methacrylate; the resulting monomer radical-anion will then dimerize, followed by dianionic polymerization (see Figure VII-10).

Figure VII-10

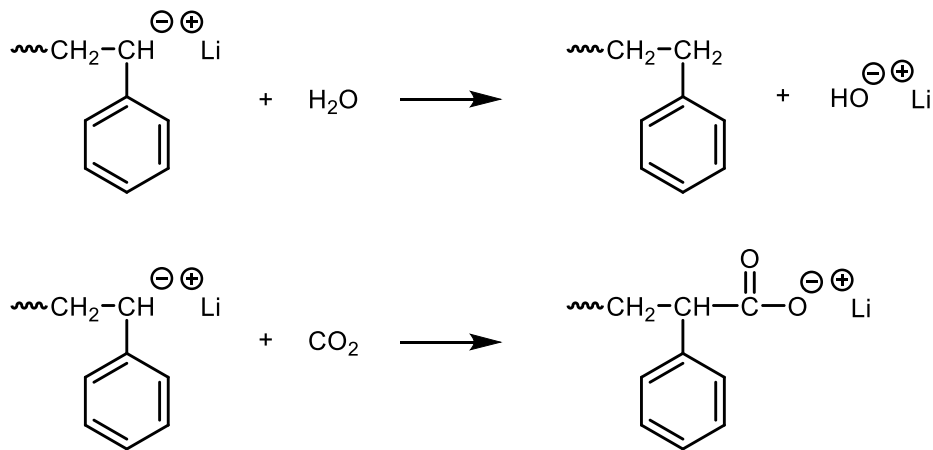


C. Termination and Transfer in Anionic Polymerization

1. Termination by Impurities and Deliberately Added Transfer Agents

Anionic polymerizations are usually carried out under an inert atmosphere or under high vacuum conditions where the “atmosphere” consists only of the vapors of monomer and solvent. The most common adventitious terminating/transfer agents are water and carbon dioxide:

Figure VII-11



The hydroxide ion generated through reaction of moisture is generally very inefficient at re-initiation, so it effectively terminates the chain. Moisture is particularly problematic because it is a very active transfer agent and it is difficult to completely remove. Moisture is typically removed from solvents and monomers by repeated distillations from exhaustive drying agents such as alkali metals or living polymers.

Moisture is removed from glassware by flaming under vacuum or by washing with a solution of living polymer.

Deliberate termination of a living anionic polymerization is most often carried out by the introduction of excess methanol or water.

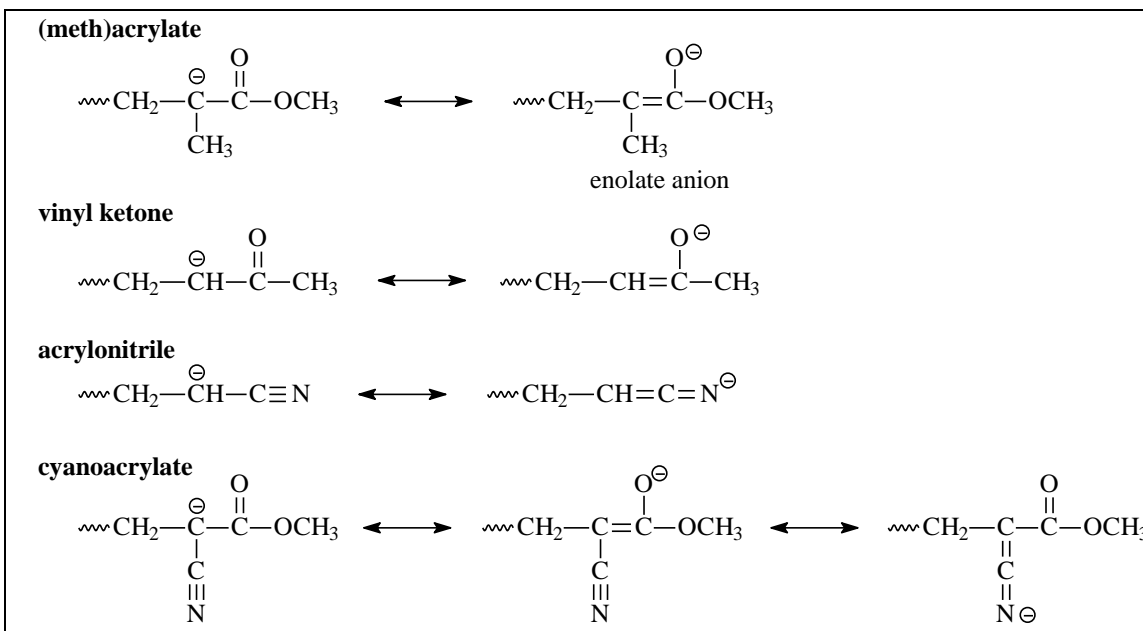
2. Termination and Side Reactions of Polar Monomers

The principle polar monomers in anionic polymerization include:

- alkyl acrylates and methacrylates
- methyl vinyl ketone
- acrylonitrile
- alkyl cyanoacrylates

These monomers are more reactive than styrene and the dienes in anionic polymerization because the polar substituent(s) stabilize the carbanion through resonance. This provides contributing resonance structures in which the negative charge is on an electronegative atom, i.e., oxygen or nitrogen.

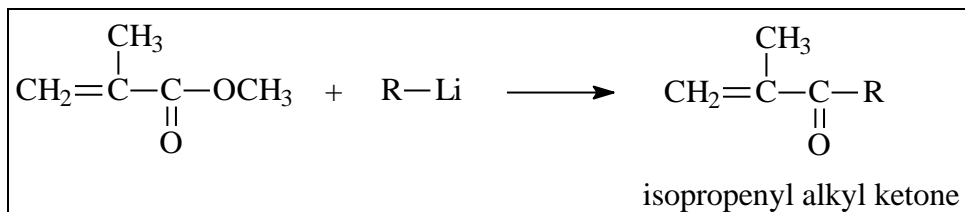
Figure VII-12



However, these polar substituents also provide additional sites for reaction with nucleophiles. This leads to termination and transfer reactions and reduces the livingness of the polymerizations. Most of our knowledge in the area comes from the study of methyl methacrylate, since it is the most commercially important member of this group. The important side reactions involve attack either by the alkyllithium initiator or the growing chain on the ester side group of either monomer or polymer. For example, attack by

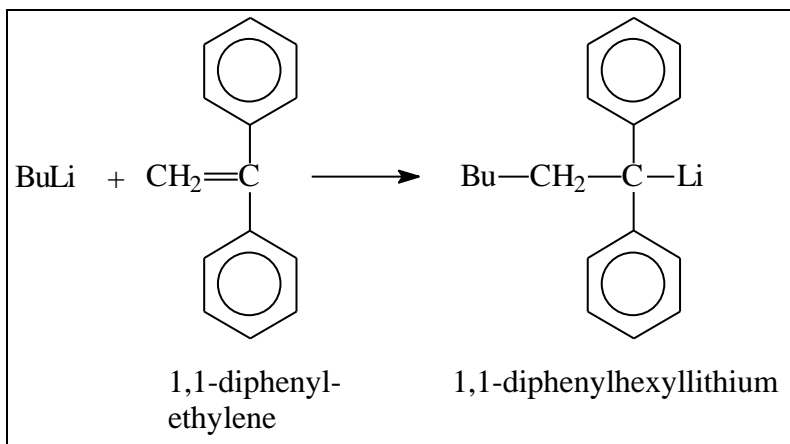
alkyllithium on the monomer creates isopropenyl alkyl ketone. This new monomer copolymerizes with methyl methacrylate, yielding a copolymer rather than the desired homo-poly(methyl methacrylate). Additionally, the carbanion derived from the ketone is less reactive (more stable) and tends to retard the rate of polymerization. Finally, the generated CH_3OLi is a significantly less efficient initiator than BuLi .

Figure VII-13



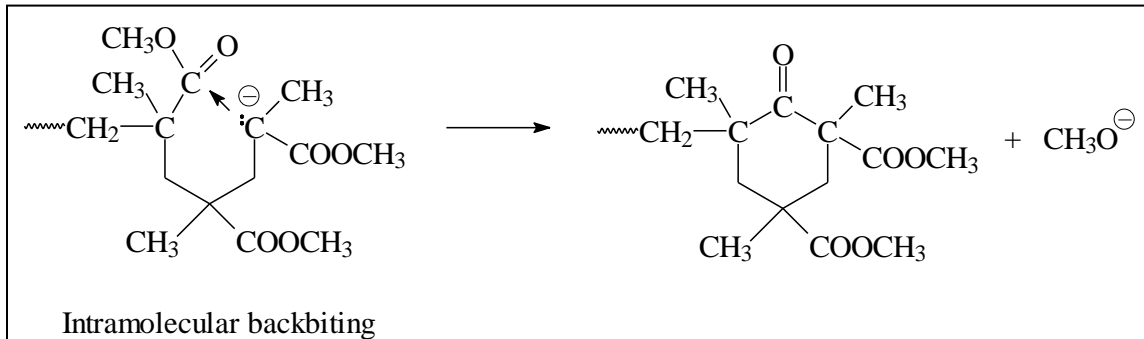
The reaction above is a major side reaction when the initiator is butyllithium (sterically unhindered), particularly in hydrocarbon solvents at room temperature. Lower temperatures and ether solvents help to reduce this reaction, but a sterically hindered initiator is generally required, as well. Examples include cumyl lithium, oligo(α -methylstyrene) or α -methylstyrene tetramer, and 1,1-diphenylhexyllithium, which is created by reaction of butyllithium with an equimolar quantity of 1,1-diphenylethylene.

Figure VII-14



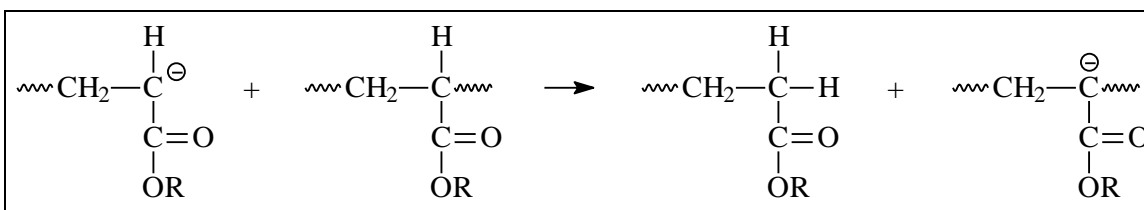
The most important side reaction in propagation is intramolecular attack of the terminal carbanion on the penultimate ester unit (backbiting) (Figure VII-15). This reaction represents a spontaneous (i.e., unimolecular) rate-retarding transfer process since the liberated alkoxide can re-initiate monomer, but very inefficiently. The reaction thus leads to poor molecular weight control, retarded rate, and gradual loss of living chain ends. It becomes increasingly problematic as monomer conversion rises.

Figure VII-15



For certain synthetic objectives, intramolecular backbiting can be sufficiently reduced (i.e., acceptable livingness can be achieved) with methacrylates through the use of low temperatures and polar solvents (THF). However, these remedies are insufficient for acrylates, which are more reactive generally, but also suffer from proton abstraction of enolizable protons along the polymer backbone.

Figure VII-16



A more recent strategy to achieve living anionic polymerization of methacrylates and acrylates involves the use of ligands that modify the reactivity of the carbanions and/or shift the equilibria among the various species along the Winstein Spectrum. Ligands that have proven effective include LiCl, Li alkoxide, aluminum alkyls, and crown ethers. For methacrylates and hindered acrylates (e.g. *t*-butyl acrylate) the use of an appropriate ligand has in some cases conferred acceptable synthetic control at moderate temperatures and/or hydrocarbon solvents, but lower temperatures (e.g. -78°C) and polar solvents still yield the best results. Unhindered acrylates represent the greatest challenge, and typically low temperatures and polar solvents are still required even in the presence of a ligand.

D. Propagation in Living Anionic Polymerization

For polymerizations without termination, propagation can be studied in isolation under the proper conditions (fast initiation). In the classical systems, e.g., styrene with an alkali metal counterion, all of the chains are active all of the time, meaning there is no significant concentration of dormant or covalent chain ends in the Winstein Spectrum.

Anionic chain propagation has been found to be:

- Independent of the mode of initiation as long as the metal counterion is the same, e.g., Li metal, lithium naphthalene, and butyllithium all lead to the same propagation rate at the same temperature and in the same solvent.
- Dependent on the identity of the counterion.
- Dependent on the solvent.

1. Kinetics of Anionic Propagation in Polar Solvents

The non-terminating nature of anionic polymerization simplifies the study of propagation kinetics, provided that the rate of initiation is greater than or equal to that of propagation. This requirement is generally met in polar solvents, but sometimes not in non-polar solvents. Thus, under conditions when propagation can truly be studied in isolation, it has consistently been found that the rate is first order with respect to the monomer concentration, but the order with respect to the growing chain end concentration depends on the system, particularly the nature of monomer and solvent, and is often less than one.

The rate of polymerization in a non-terminating system with rapid initiation can be expressed simply as the rate of propagation:

$$r_p = -\frac{d[M]}{dt} = k_p^{\text{app}}[M^\ominus][M] \quad \text{VII-7}$$

where, k_p^{app} = apparent second-order rate constant for propagation, which may include contributions from free and paired ions

$[M^\ominus]$ = total concentration of propagating anionic centers

In the first approximation, $[M^\ominus]$ can be assumed equal to the initiator concentration. It can be measured accurately by terminating the living chains, followed by analysis of the amount of terminating agent incorporated into the polymer.

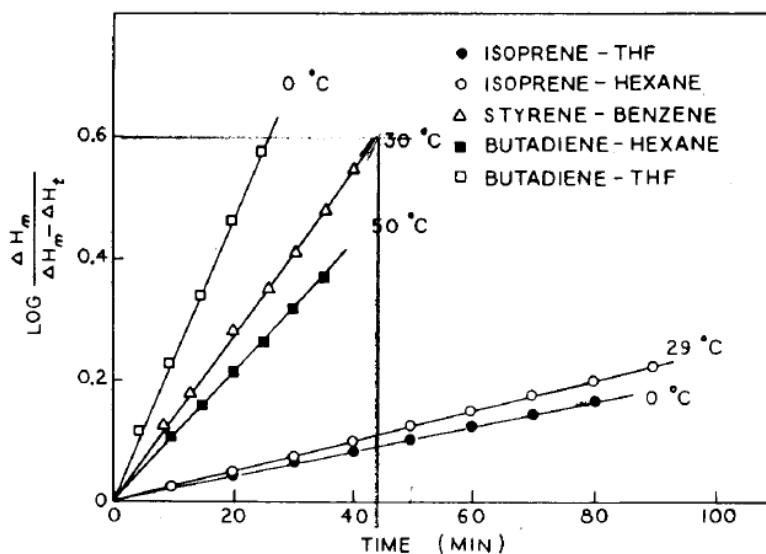
Since the concentration of living ends, $[M^\ominus]$, is constant for a given polymerization, eq 7 may be integrated to yield the following equation in which the $[M^\ominus]$ term may or may not be incorporated into an apparent first order rate constant, k_{app} :

$$\ln \frac{[M]_0}{[M]} = k_p^{\text{app}}[M^\ominus]t = k_{\text{app}}t \quad \text{VII-8}$$

Values for k_p^{app} for anionic polymerization are roughly similar to those of free radical polymerization; however, rates of anionic polymerization are generally much faster than free radical because the typical concentration of anions ($10^{-5} - 10^{-2}$ M) is much higher than

free radicals ($10^{-9} - 10^{-7}$ M). Typical first-order rate plots for anionic polymerization of styrene and the dienes are shown in Figure VII-17. Monomer concentration has been calculated from dilatometric data. The profound effect of solvent on rate can be appreciated from the data; for example, butadiene is faster at 0°C in THF than at 50°C in hexane. It is also clear that butadiene is faster than isoprene. It is difficult to make a conclusion concerning styrene, since it was measured in a different solvent.

Figure VII-17



In general, for hydrocarbon solvents,

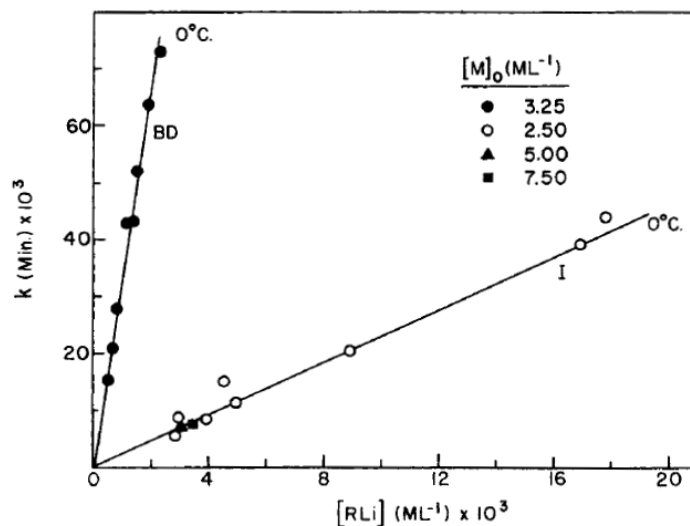
butadiene > isoprene > styrene

and in polar solvents such as THF:

styrene > butadiene > isoprene

Figure VII-18 shows the dependence of the apparent first-order rate constant for propagation (k_{app} in eq VII-8) of butadiene and isoprene in THF at 0°C on the concentration of butyllithium initiator, [RLi]. It is assumed that the butyllithium concentration is equal to the total concentration of propagating anionic centers, i.e. [RLi] = $[M^{\ominus}]$.

Figure VII-18



Since the relationships shown in the figure are linear and,

$$k_{app} = k_p^{app} [M^{\ominus}] \quad \text{VII-9}$$

it is clear that the value of k_p^{app} is independent of $[M^{\ominus}]$, and under these conditions in THF, diene polymerization proceeds via a simple bimolecular mechanism involving attack of unassociated (non-aggregated) paired ions (no dissociation to free ions) on monomer.

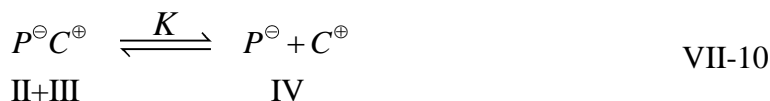
The situation for styrene polymerization in polar solvents is more complicated. As shown in Table VII-3, the apparent second-order rate constants for propagation of polystyrylsodium increase dramatically with increasing solvating power of the reaction medium: benzene < dioxane << THF < 1,2-dimethoxyethane. This is due mainly to an increasing fraction of free ions within the total $[M^{\ominus}]$.

Table VII-3: Effect of Solvent on the Rate of Anionic Polymerization of Styrene (Na Counterion) at 25°C

Solvent	Dielectric Constant (ϵ)	k_p^{app} (L/mole-sec)
Benzene	2.2	2
Dioxane	2.2	5
THF	7.6	550
1,2-Dimethoxyethane	5.5	3,800

In dioxane (and thus also in benzene, which is even more non-polar), the fraction of free ions is negligible; the kinetic behavior is found to be the same as discussed above for the

dienes in THF, i.e., k_p^{app} is independent of $[M^\ominus]$. However, in THF k_p^{app} has been observed to decrease with increasing $[M^\ominus]$. This is referred to as a “dilution effect” and is caused by the participation of free styryl carbanions, in addition to ion pairs, in the propagation reaction. This can be understood by considering the dissociation equilibrium in eq VII-10, which is a portion of the Winstein spectrum (here, contact and solvent-separated ion pairs have been combined):

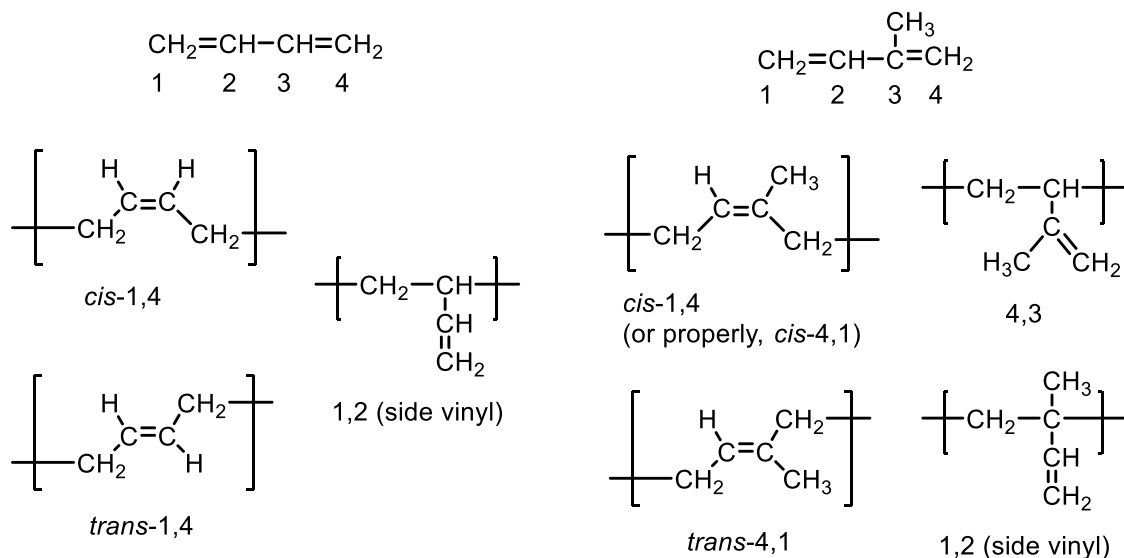


For 10^{-4} mol/L polystyryllithium at room temperature in THF, the fraction of free ions is about 4.6%. However, the forward reaction in eq VII-10 converts one particle into two, and thus Le Chatelier’s principle predicts that the fraction of free ions will decrease as the total concentration of living chain ends ($[M^\ominus]$) increases. For example, for 10^{-3} mol/L polystyryllithium at room temperature in THF, the fraction of free ions is only about 1.5%. Since the free ions propagate much faster than the pair ions (about 400 times faster at 25°C for polystyryllithium) increasing $[M^\ominus]$ causes a shift leftward in the equilibrium in eq VII-10, driving more of the propagating ends to the more sluggish paired ions. The causes k_p^{app} , which can be thought of as the frequency of monomer consumption per living chain end, to go down.

2. Chain microstructure in organolithium polymerization of dienes

The various possible isomeric enchainments (microstructures) of butadiene and isoprene are shown in Figure VII-19.

Figure VII-19



The best elastomeric properties from either diene are obtained from the *cis*-1,4 structure. Natural rubber is 100% pure *cis*-1,4-(polyisoprene). *Trans*-1,4 linkages lead to crystallinity, and 1,2 or 3,4 structures raise the glass transition temperature.

Both solvent and counterion greatly effect the chain microstructure of dienes:

- The proportion of 1,4 chain units is highest for lithium and decreases with increasing electropositive character of the alkali metal.
- Polar solvents lead to a higher side-vinyl structure in the polymer, especially for lithium.

The formation of side-vinyl units has been related to the ionic character of the carbon-metal bond at the growing chain end; polar solvents apparently increase ionicity (rightward shift along the Winstein spectrum) through better solvation of the positive metal. The effect is greatest for lithium since it is most readily solvated. In the absence of solvation effects, the more electropositive counterions also yield greater ionicity of the chain end.

Initiator and monomer concentration also effect diene chain microstructure:

- Aliphatic solvents lead to a slightly higher *cis*-1,4 content than aromatic solvents, without much effect on side-vinyl content.
- Undiluted monomer leads to the highest attainable *cis*-1,4 content for both polyisoprene and polybutadiene.
- A decrease in initiator concentration leads to a noticeable increase in *cis*-1,4 content for both dienes, without any notable change in side-vinyl content.
- Polymerization of isoprene and butadiene in the undiluted state, at initiator concentrations of about 10^{-5} M results in 96% *cis*-1,4-polyisoprene and 86% *cis*-1,4-polybutadiene.

E. Anionic Copolymerization

The most studied anionic copolymerization systems are between styrene and the dienes. Recall that in polar solvents, styrene homopolymerization is faster than that of either diene; however, in non-polar solvents styrene is slower. In light of this, it is not surprising that in non-polar solvents the diene is preferred in copolymerization.

Benzene

$$r_b = 10.8$$
$$r_s = 0.04$$

Cyclohexane

$$r_b = 15.5$$
$$r_s = 0.04$$

Addition of a polar cosolvent reverses this trend.

THF

$$r_b = 0.3$$

$$r_s = 4.0$$

Anionic copolymerizations often exhibit ideal behavior, i.e.,

$$r_1 r_2 = 1.0$$

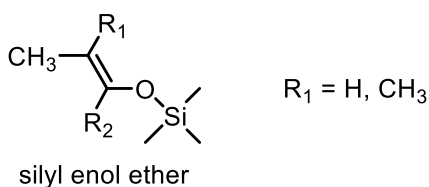
VII-11

This indicates that if one of the propagating carbanions exhibits a preference for one monomer over the other, then the other carbanion exhibits the same preference. For example, if M_1^\ominus reacts with M_1 twice as readily as with M_2 , then M_2^\ominus also reacts with M_1 twice as readily as with M_2 .

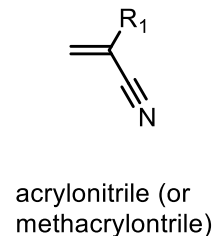
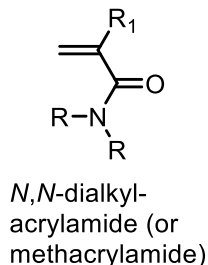
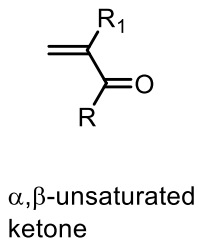
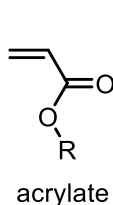
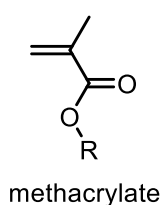
F. Group Transfer Polymerization

A modified anionic polymerization process, named group transfer polymerization (GTP), was introduced by DuPont scientists in the early 1980's and shown to yield living polymerization of methacrylates and acrylates at high temperatures, i.e., room temperature and slightly above. The process is similar to conventional anionic polymerization, except that the growing chain ends exist as an equilibrium between dormant silyl enol ethers (majority) and active carbanions (minority); in theory, any α,β -unsaturated carbonyl (or nitrile) compound should be polymerizable by this technique (Figure VII-20). The exchange mechanism between dormant and active states is of the degenerative-transfer type (similar to RAFT).

Figure VII-20

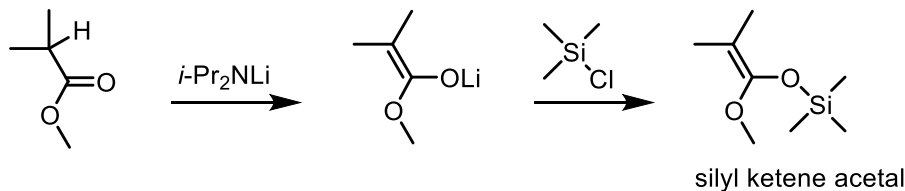


Monomers:



The most common initiator type for GTP is a silyl ketene acetal, usually synthesized from an ester enolate (Figure VII-21).

Figure VII-21



GTP requires a nucleophilic catalyst to create the initial population of active chains. Commonly used nucleophilic catalysts are tris(dimethylamino)sulfonium bifluoride and tetra-*n*-butylammonium fluoride, which are soluble in organic solvents. This represents another difference between GTP and conventional anionic polymerization. In GTP, the counterion is a large organic, onium ion rather than an alkali metal. The concentration of nucleophilic catalyst controls the concentration of active chains and hence the rate of polymerization and is typically <0.1 mole% relative to the initiator.

Typical reaction conditions for GTP are similar to conventional anionic polymerization, i.e., moisture and other active hydrogen compounds must be excluded. THF and toluene are the most commonly used solvents, although the range of possible solvents is broader than that possible with conventional anionic polymerization. The most commonly used monomer is methyl methacrylate, and polymerizations with it are typically carried out at room temperature. Acrylates generally require lower temperatures due to their higher reactivity.

DuPont scientists originally proposed a concerted mechanism, which led to the name “group transfer polymerization.” The concerted mechanism was later discredited and replaced by the now generally accepted degenerative-transfer mechanism, shown in Figure VII-22 (initiation) and Figure VII-23 (propagation).

Figure VII-22

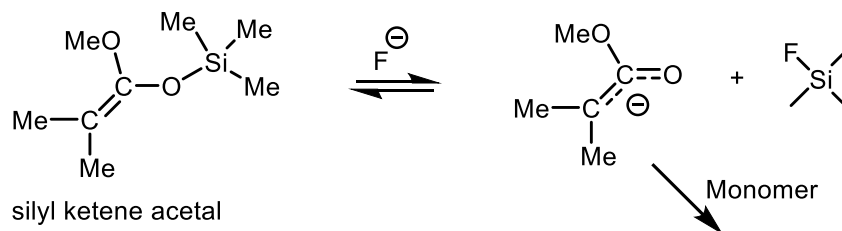
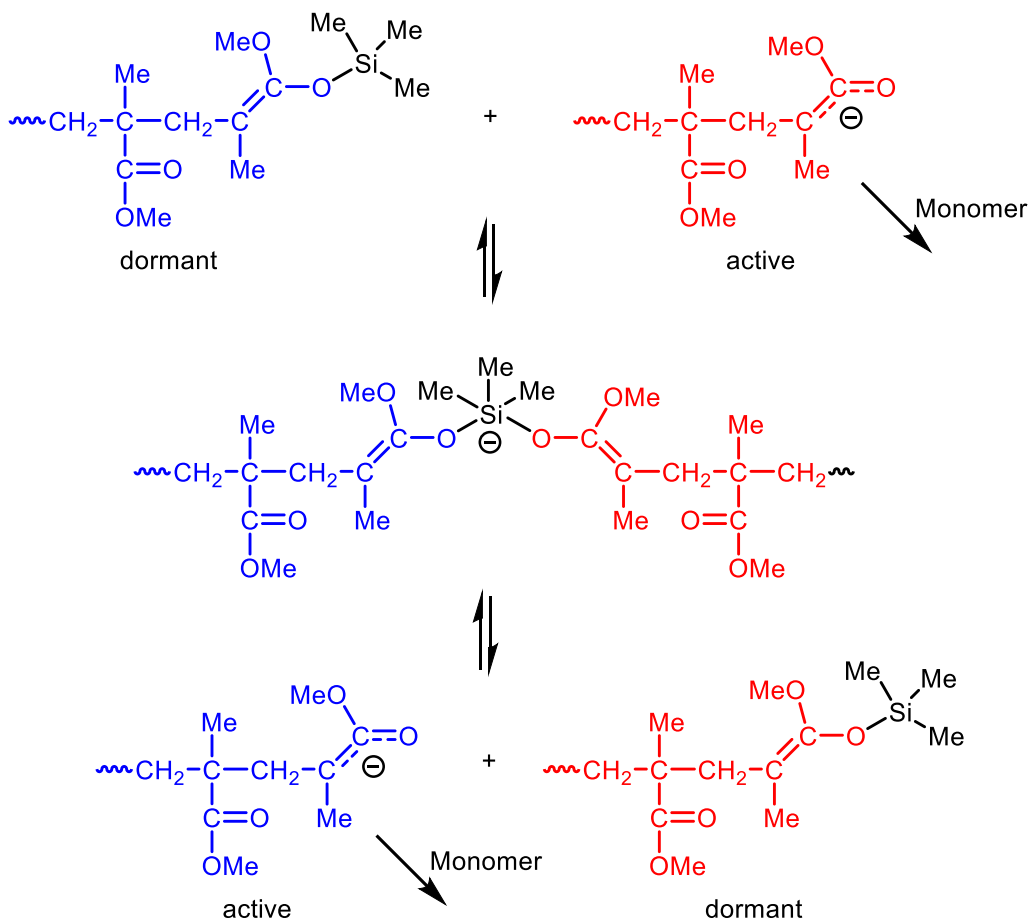


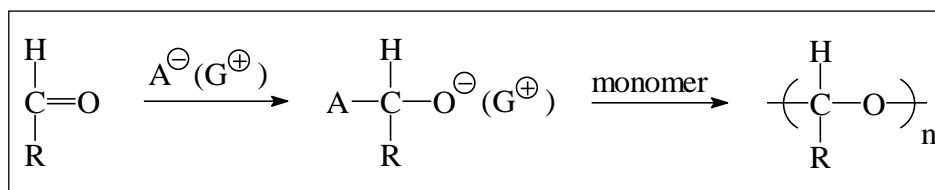
Figure VII-23



G. Anionic Polymerization of Carbonyl Monomers

Aldehydes will polymerize by addition to the C=O double bond to form polyacetals.

Figure VII-24



By far, the most important monomer is formaldehyde (R=H), which can be polymerized with almost any base including:

- metal alkyls (butyllithium, diethyl zinc, etc.)
- alkoxides
- phenolates
- hydrated alumina (surface polymerization)

tertiary amines (primary and secondary amines often form methylol derivatives)
 phosphines
 Grignard reagents

Two general characteristics of carbonyl polymerizations are their low ceiling temperatures and the often quite high degrees of crystallinity of the formed polymers. Table VII-4 lists the ceiling temperatures of some common aldehydes. Low T_c 's are due to the low enthalpy of polymerization, e.g., for acetaldehyde it is only about -29 kJ/mole vs. about -90 kJ/mole for a typical C=C double bond.

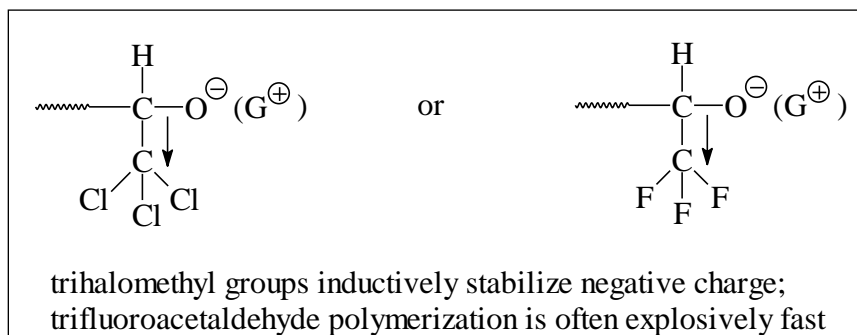
Table VII-4: Ceiling Temperatures of Aldehyde Monomers

Monomer	T_c ($^{\circ}\text{C}$)
Formaldehyde	119 ^a
Trifluoroacetaldehyde	81
Trichloroacetaldehyde	11
Propanal	-31
Acetaldehyde	-39
Pentanal	-42

^aMonomer concentration = 1 atm (gaseous); all other data are for neat liquid monomer.

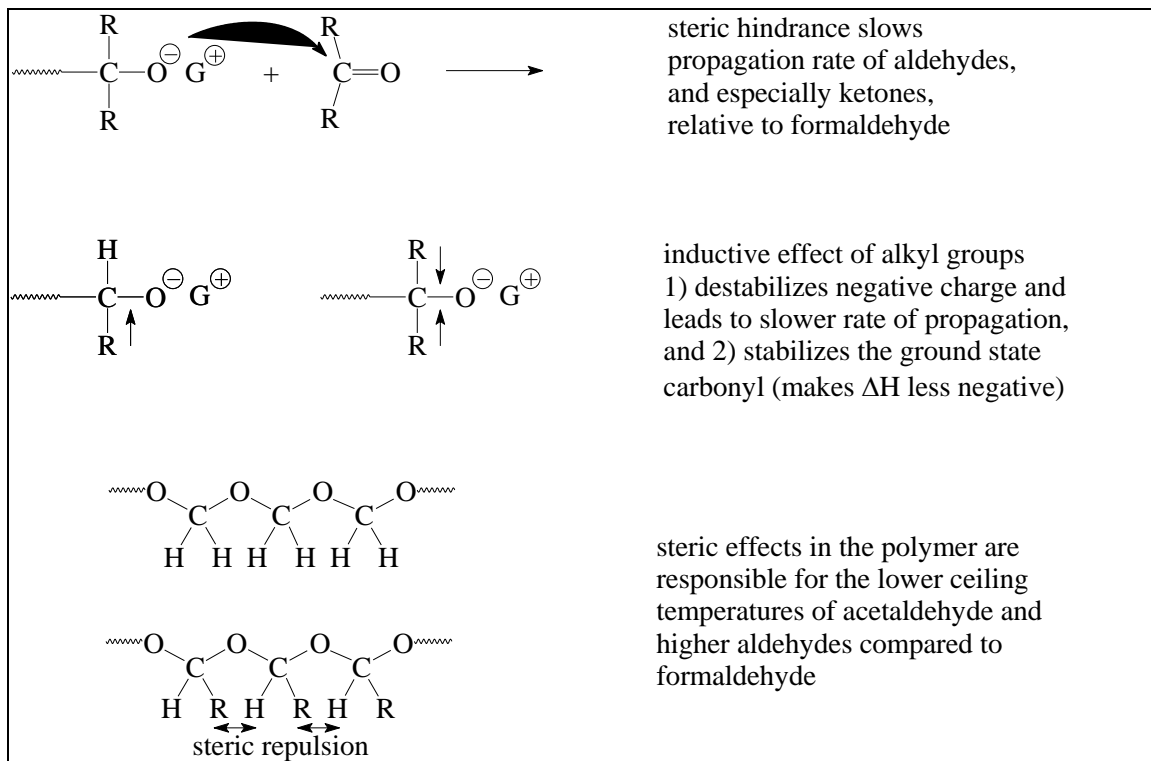
Electron withdrawing substituents on aldehydes, such as in trichloroacetaldehyde or trifluoroacetaldehyde, enhance polymerizability both kinetically and thermodynamically.

Figure VII-25



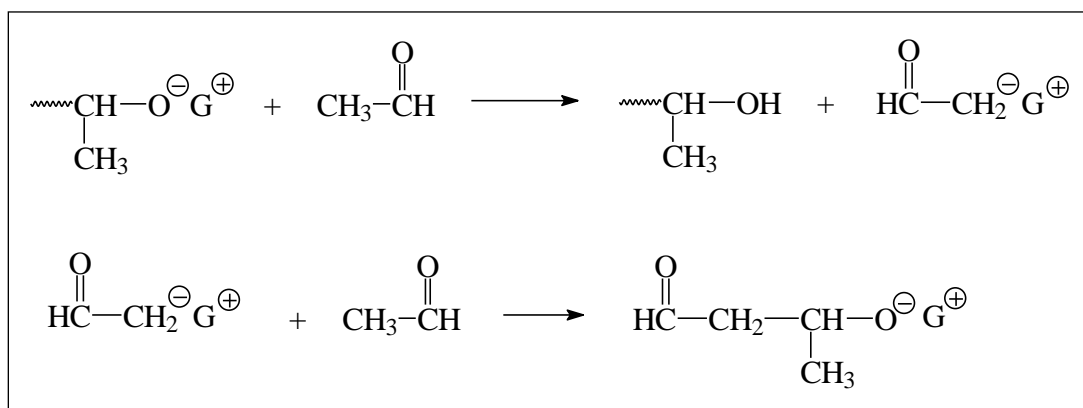
Acetaldehyde and higher aliphatic aldehydes generally require stronger bases, i.e., metal alkyls or alkoxides, for initiation compared to formaldehyde. Ketones and aromatic aldehydes are generally non-polymerizable due to steric and inductive effects:

Figure VII-26



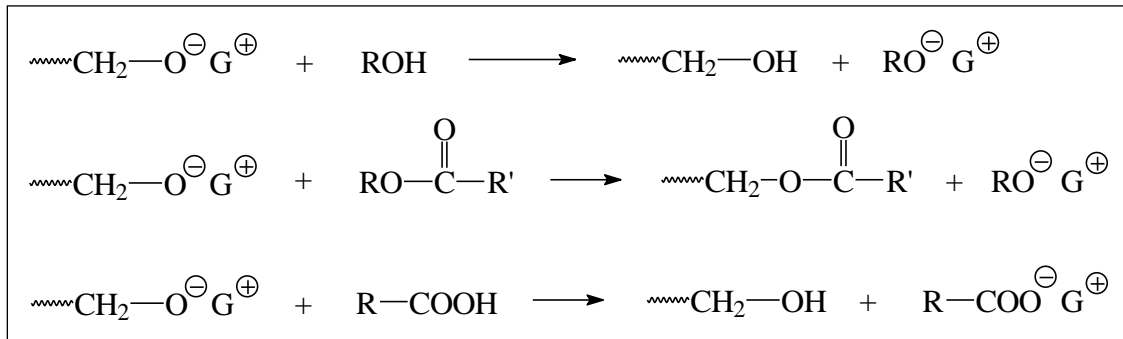
Aldol condensation (chain transfer to monomer) competes with polymerization of acetaldehyde and higher aliphatic aldehydes at room temperature and higher, but can be avoided at low temperatures:

Figure VII-27



Chain transfer occurs readily in carbonyl polymerizations, to compounds such as water, alcohols, carboxylic acids (formic acid), esters, and anhydrides.

Figure VII-28



In the first two examples in Figure VII-28, chain transfer has no effect on the rate of polymerization because the alkoxide formed is of similar reactivity to the propagating end group. In the third example, retardation or inhibition (depending on the monomer) occurs because the carboxylate formed is of lesser reactivity than the propagating chain end.

The polymerization of formaldehyde to produce polyoxymethylene (*Delrin*) is carried out on a commercial scale. The third reaction in Figure VII-28 can be a problem in the commercial process because formic acid is inevitably present as an impurity in formaldehyde. *Delrin* is stabilized against unzipping by end-capping with acetic anhydride. This replaces the very reactive hydroxyl end groups with less reactive ester groups.

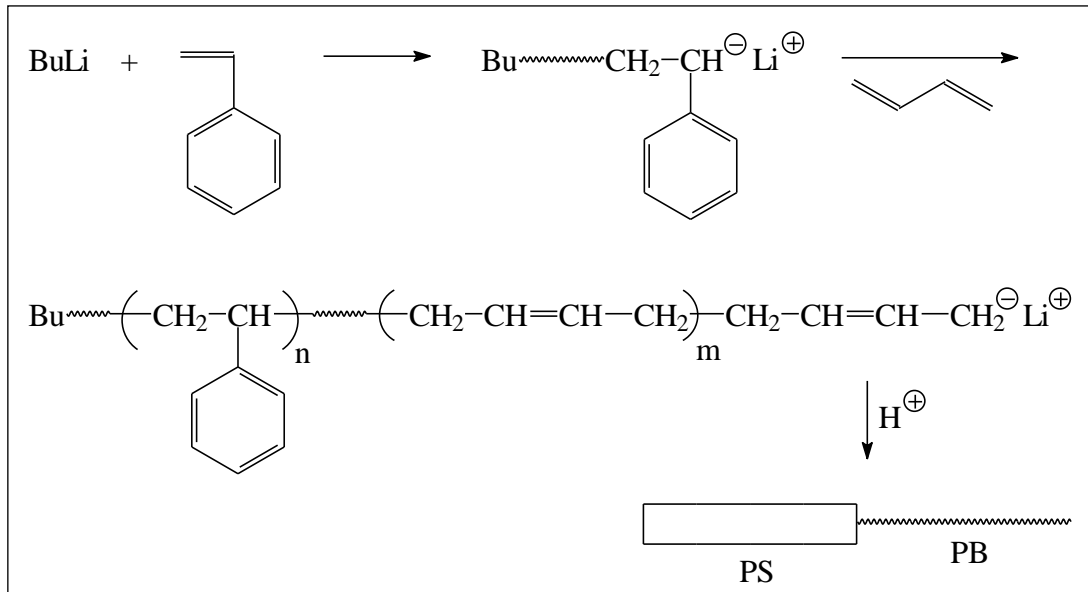
H. Synthesis Techniques Using Living Anionic Polymerization

- Block copolymers
- Graft copolymers
- Star branched polymers
- Functional and telechelic polymers
- Miscellaneous

1. Block copolymers

Living anionic polymerization is the most elegant, and often the best method for making block copolymers. The technique involves “sequential monomer addition.”

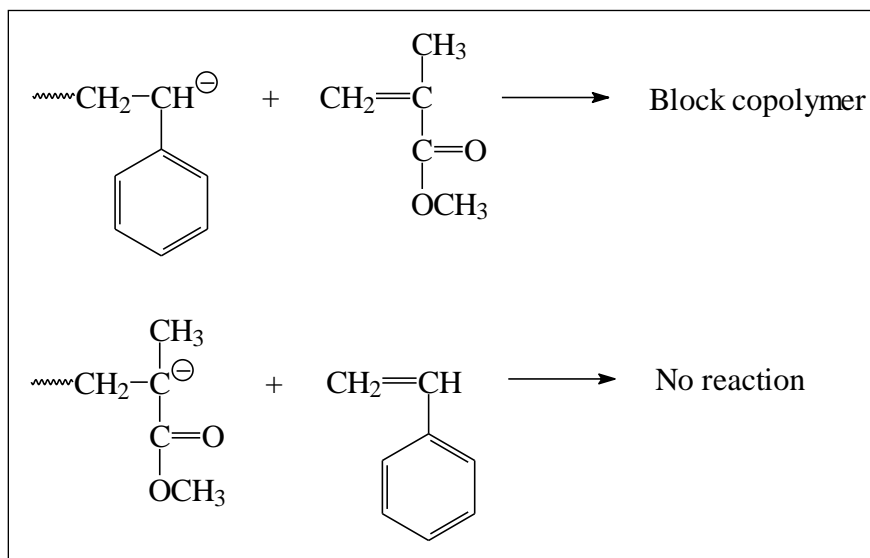
Figure VII-29



The principal limitation using anionic polymerization is that the monomer selection is somewhat limited. Most work has been done with styrene, dienes, vinyl pyridines, and methacrylates (and acrylates), with styrene-diene block copolymers by far the most studied and the most important.

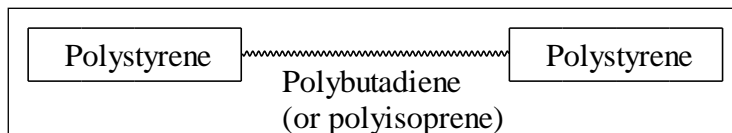
Proper sequencing of the monomers is critical if they are of unequal reactivity. Crossover can occur from the less reactive to the more reactive monomer but not vice-versa. Styrene and the dienes may be reacted in either direction.

Figure VII-30



Poly(styrene-*b*-diene-*b*-styrene) triblock copolymers are produced on a commercial scale for use as thermoplastic elastomers.

Figure VII-31



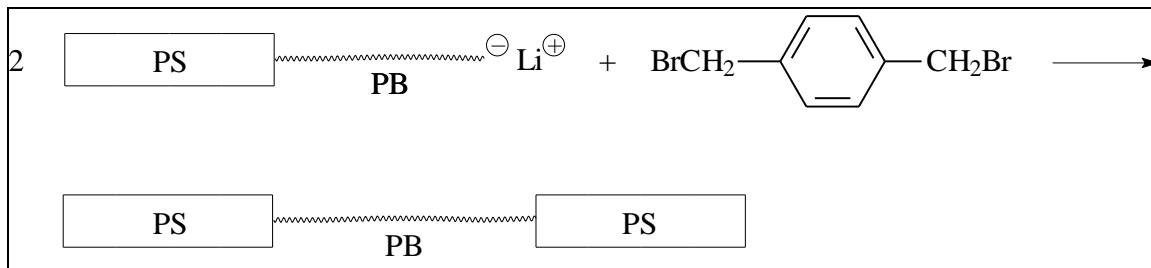
These polymers are micro-phase separated due to thermodynamic incompatibility between the two blocks. The resulting discontinuous polystyrene domains serve to physically crosslink the rubbery polydiene chains. They behave like crosslinked elastomers, but may be processed like thermoplastics. Often the diene center block is hydrogenated. Diblocks are not effective as TPE's; no significant advantage accrues from block numbers higher than three.

A triblock like that pictured above could be made by three possible methods:

- Simple sequencing process (styrene followed by diene followed by styrene)
- Use of a difunctional initiator with a polymerization sequence: 1) diene, 2) styrene.
- Coupling reaction between two diblocks produced using the polymerization sequence: 1) styrene, 2) diene.

The preferred commercial process is the coupling method, an example of which is shown in Figure VII-32. Silyl halides are more efficient coupling agents, but the commercial process uses a less-expensive carbon-based coupling agent such *p*-xylylene dibromide.

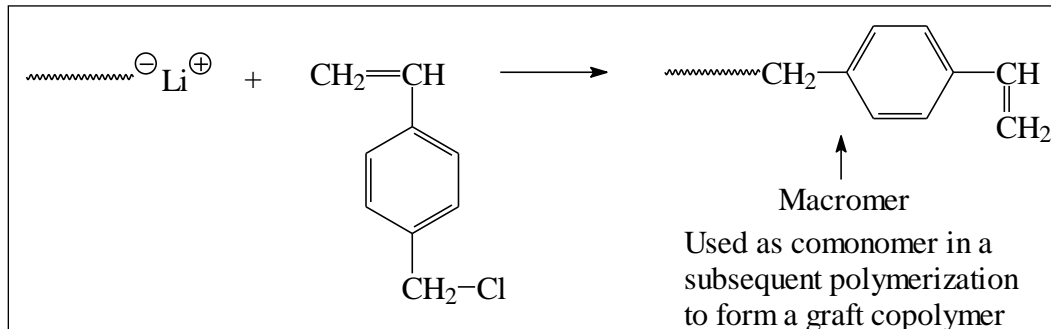
Figure VII-32



2. Graft copolymers

Living anionic polymerization techniques can be used to make graft copolymers via the macromer (macro-monomer) technique:

Figure VII-33



3. Star-branched polymers

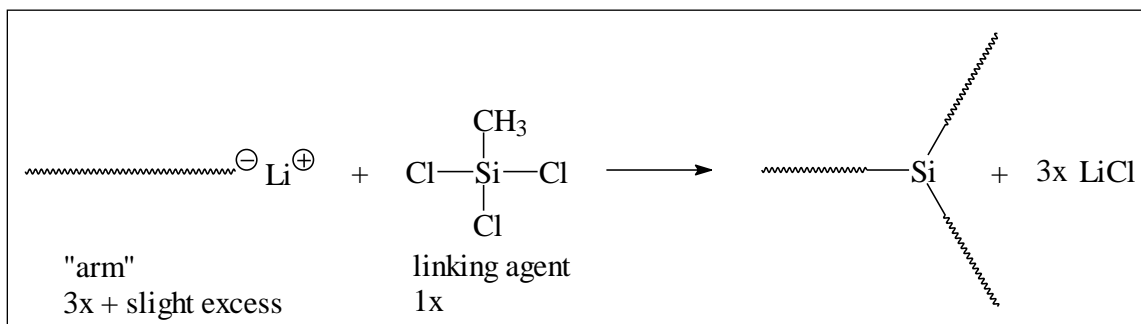
Star-branched polymers have been synthesized by a number of different methods:

- Linking method (arm-first, core last)
- Gel-core methods (arm-first, core last or core-first, arm last)
- Multi-functional initiator methods
- Hybrid methods

a. Linking method

This method involves reaction of living anionic chains with multi-functional linking agents, which are usually silyl halides. The latter are more efficient than carbon-based linkers (such as *p*-xylylene dibromide) because of much lower rates of metal-halogen exchange. Linking is also more efficient with sterically unhindered polydienyllithium chains compared to the relatively bulky polystyryllithium.

Figure VII-34



b. Gel-core methods

Figure VII-35

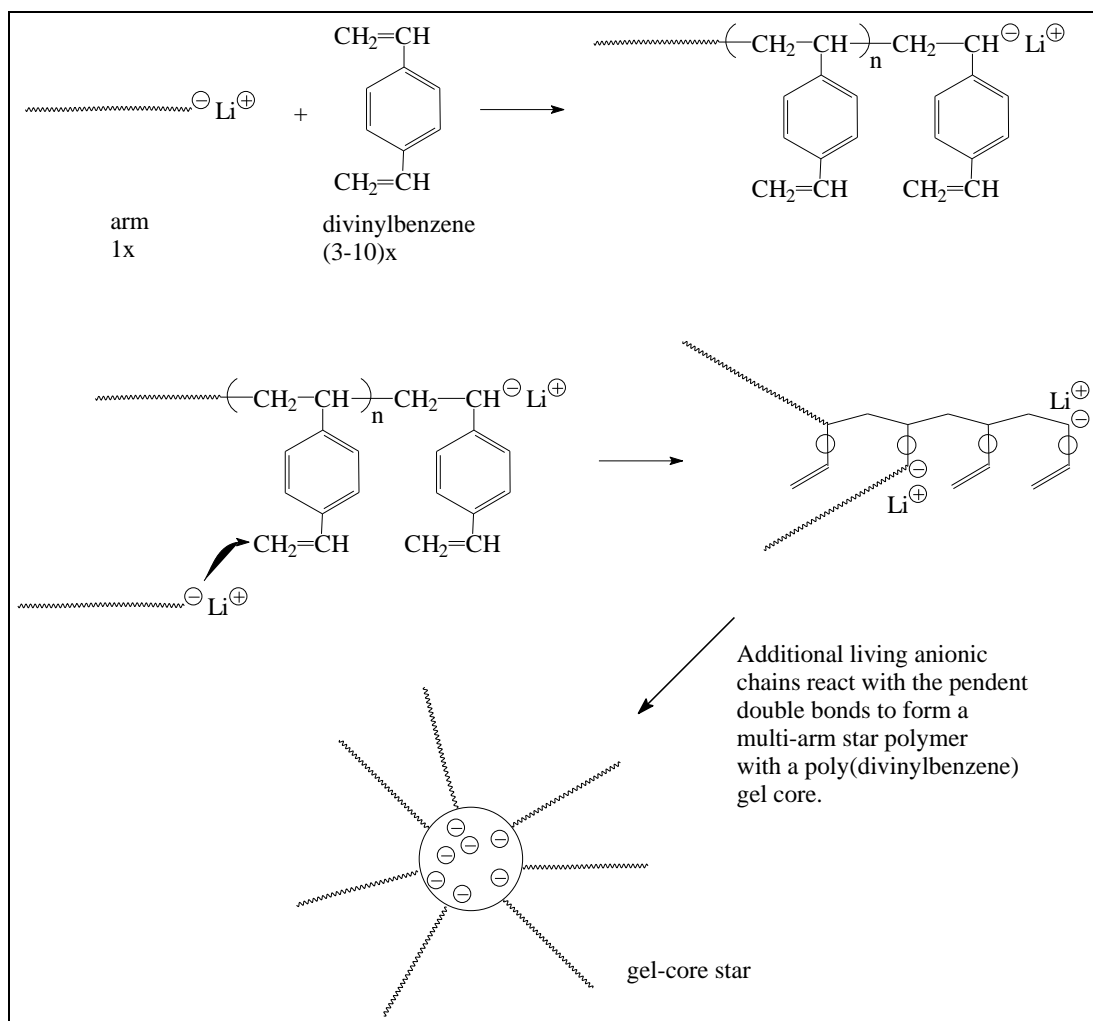
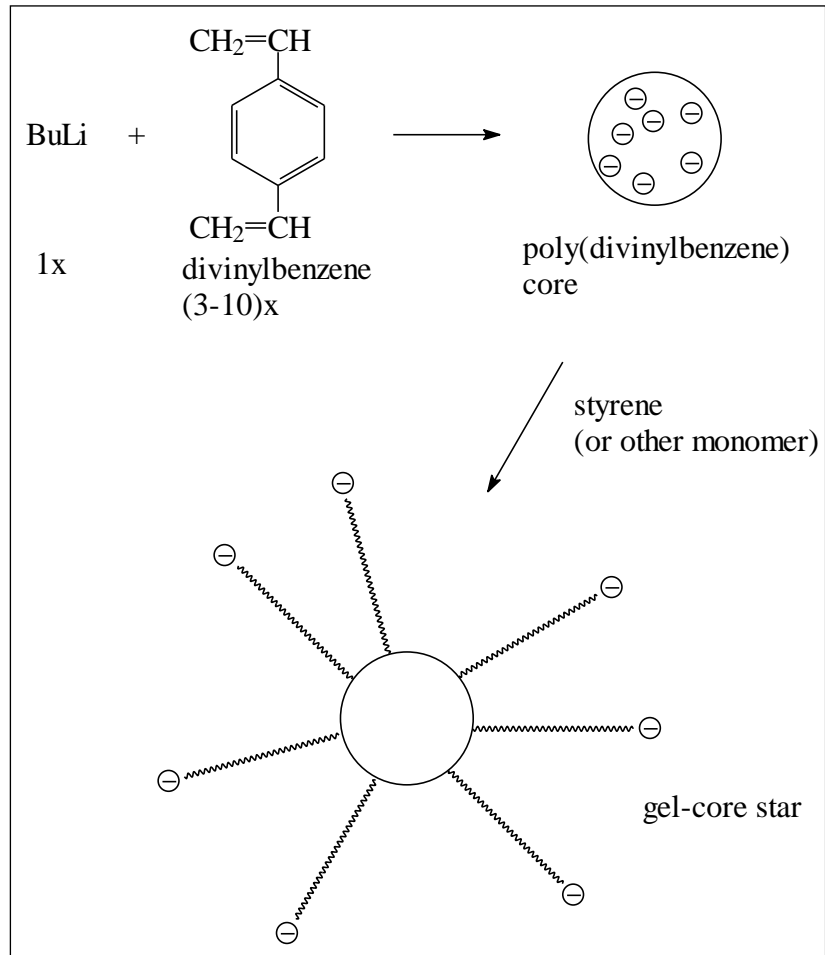


Figure VII-36

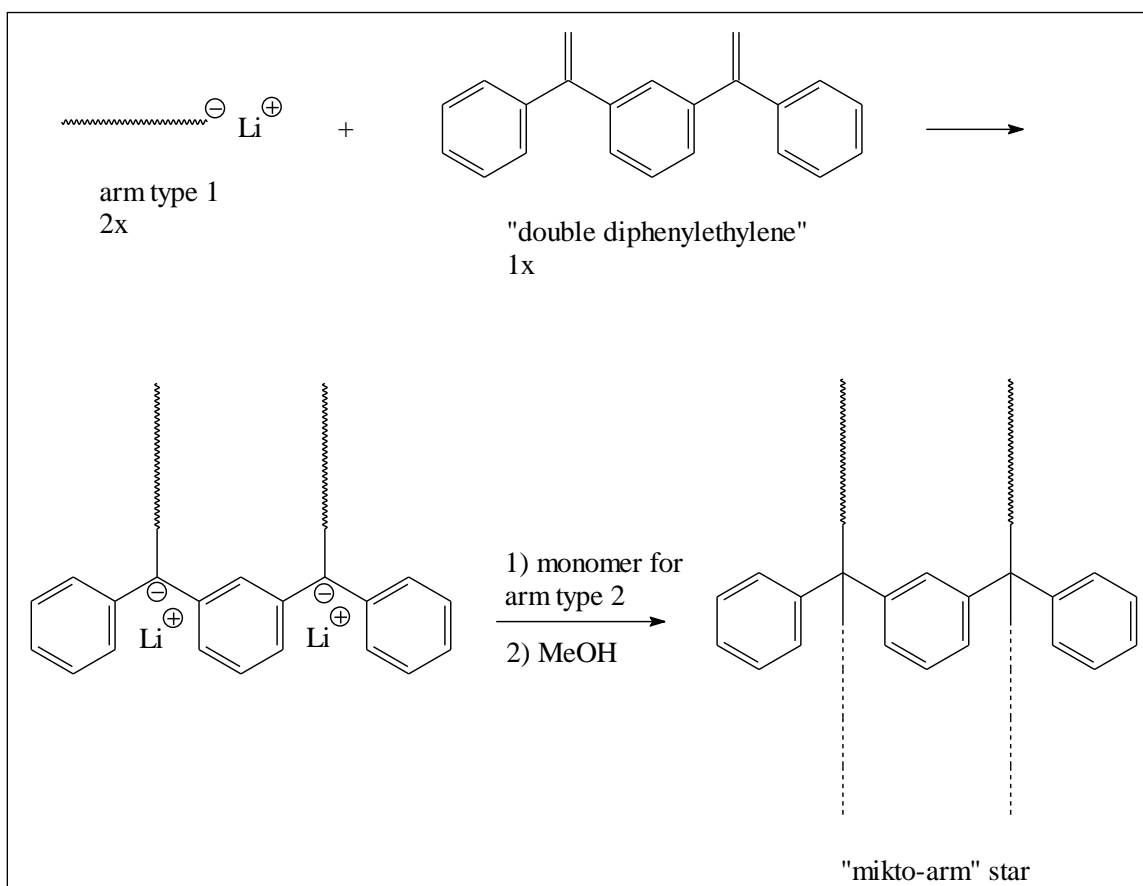


c. Multi-functional initiator methods

These are core-first, arm-last methods in which chains are grown outward from a common initiator molecule. This method has proven to be difficult with anionic polymerization due to poor solubility of multi-anionic species. Three-arm initiators, however, are quite common in cationic polymerization (to be studied later). The difference is that, for the anionic initiators, all of the sites are ionized all of the time, and the compounds are very polar; for the cationic initiators, only a small fraction of the sites are ionized at any given time, and the compounds are therefore much less polar and more soluble.

d. Hybrid methods

Figure VII-37



4. Functional and telechelic polymers

Figure VII-38

