# 7

# ANIONIC POLYMERIZATION

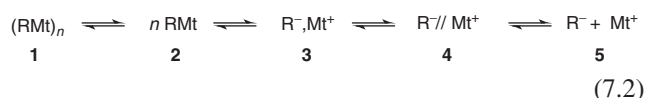RODERIC QUIRK

## 7.1 INTRODUCTION

This chapter describes the general aspects of anionic polymerization of vinyl, carbonyl, and heterocyclic monomers, with emphasis on alkyllithium-initiated polymerization of vinyl monomers. Anionic polymerization is defined as a chain reaction polymerization in which the active centers for propagation are anions, which can be in the form of free ions, paired ions, or aggregated species [1]. The term "anion" will be considered as an atom or group of atoms with a negative charge and an unshared pair of electrons. Anions can be considered to be the conjugate bases of the corresponding Bronsted acids, as shown in Equation 7.1.

$$\overset{|}{\underset{|}{C}}\!\!-\!\!H \;\rightleftharpoons\; \overset{|}{\underset{|}{C}}\!:^{\ominus} \;+\; H^{\oplus} \qquad (7.1)$$
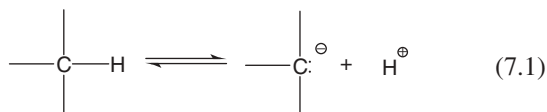
The stability and reactivity of anionic species can be deduced from $pK_a$ values for the equilibria depicted in Equation 7.1 [2, 3]. The more acidic conjugate acids (lower $pK_a$ values) are associated with a correspondingly more stable anionic species.

In general, these anions are associated with a counterion, typically an alkali metal cation. The exact nature of the anion can be quite varied depending on the structure of the anion, counterion, solvent, and temperature [3–5]. The range of possible propagating species in anionic polymerization is depicted in terms of a Winstein spectrum of structures as shown in Equation 7.2 for a carbanionic chain end (R$^-$) [3, 6]. In addition to the aggregated (associated) (**1**) and unaggregated (unassociated) (**2**) species, it is necessary to consider the intervention of free ions (**5**), contact ion pairs (**3**), and solvent-separated ion pairs (**4**); Mt$^+$ represents a metallic counterion such as an alkali metal cation. In hydrocarbon media, species (**1–3**) would be expected to predominate. Polar solvents tend to shift the Winstein spectrum to the right, that is, toward more reactive, less associated, more ionic species. With respect to the nature of the bonding in organoalkali metal compounds, it is generally agreed that the carbon–alkali metal bond is ionic for sodium, potassium, rubidium, and cesium. In contrast, experimental evidence and theoretical studies indicate that the carbon–lithium bond includes some covalent character, that is, it is a semipolar bond [3, 7]; however, there is disagreement about the relative amounts of covalent versus ionic bonding [8].

$$(RMt)_n \;\rightleftharpoons\; n\,RMt \;\rightleftharpoons\; R^-,Mt^+ \;\rightleftharpoons\; R^- /\!/ Mt^+ \;\rightleftharpoons\; R^- + Mt^+$$
$$\mathbf{1} \qquad\qquad \mathbf{2} \qquad\qquad \mathbf{3} \qquad\qquad \mathbf{4} \qquad\qquad \mathbf{5}$$
$$(7.2)$$

One unique aspect of anionic polymerization is that the reactive propagating species are not transient intermediates. Carbanions and organometallic species can be prepared and investigated independently of the polymerization process. These species can also be characterized and monitored during the polymerization.

## 7.2 LIVING ANIONIC POLYMERIZATION

One of the most important advances in the science and technology of anionic polymerization was the report in 1956 by Michael Szwarc and coworkers delineating the characteristics of living anionic polymerizations, that is, that they proceed in the absence of the kinetic steps of chain transfer

and chain termination [9, 10]. The most recent IUPAC definition of a living polymerization is a chain polymerization in which chain termination and irreversible intermolecular chain transfer are absent [1]; it should be noted that chain termination is defined as a chemical reaction in which a chain carrier is converted *irreversibly* into a nonpropagating species without the formation of a new chain carrier. The importance of living polymerizations is that they provide methodologies for the synthesis of polymers with control of the major variables that affect polymer properties including molecular weight, molecular weight distribution, copolymer composition and microstructure, stereochemistry, chain-end functionality, and molecular architecture [3, 11]. This inherent control aspect of living anionic polymerization stimulated tremendous industrial research activity which led to the development of numerous technologies for the preparation of important commodity and specialty materials [3]. Today, anionic polymerization is used for the commercial production of more than three million tons of polymers annually, including polybutadiene, polyisoprene, styrene-butadiene rubber (SBR), and styrene-diene-styrene triblock copolymers plus their hydrogenated analogs [12].

A general mechanism for living anionic polymerization of a vinyl monomer is illustrated in Scheme 7.1, encompassing only initiation and propagation steps; chains are terminated only by the deliberate addition of a Bronsted acid or an electrophile. Important aspects of this mechanism, and that of any living polymerization, are that one initiator generates one polymer chain and that the product after all of the monomer has been consumed is a polymer with an active anionic chain end. With this mechanism, the defining characteristics of living polymerizations with respect to the synthesis of a wide variety of polymers with low degrees of compositional heterogeneity can be understood.

### 7.2.1    Molecular Weight Control

Molecular weight is one of the most important variables affecting polymer properties. The number average molecular weight ($M_n$) in living anionic polymerization is a simple function of the stoichiometry and the degree of monomer conversion, since one polymer is formed for each initiator molecule. The expected $M_n$ can be calculated as shown in Equation 7.3 as a function of monomer conversion. From a practical point of view, polymers can be prepared with predictable molecular weights ranging from $\approx 10^3$ to $> 10^6$ g/mol using living anionic polymerizations.

$$M_n = \frac{\text{Grams of monomer consumed}}{\text{Moles of initiator}} \quad (7.3)$$

The ability to predict and control molecular weight depends critically on the absence of significant amounts of terminating species that react with the initiator, decrease the effective number of initiator molecules, and thus increase the observed molecular weight relative to the calculated molecular weight. In many cases, the impurities react quickly with initiators, especially alkyllithium initiators, so that molecular weight control can still be achieved by determining the impurity level and compensating for this
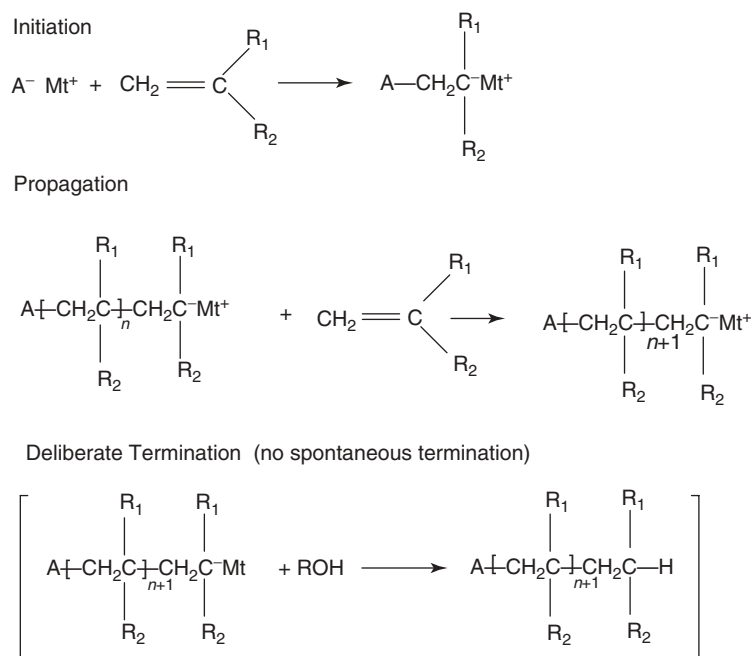


**Scheme 7.1**    General mechanism for a living anionic polymerization.

by the addition of more initiator than the stoichiometric amount, Equation 7.3.

### 7.2.2 Molecular Weight Distribution

In principle, it is possible to prepare a polymer with a narrow molecular weight distribution (Poisson distribution) using living polymerization when the rate of initiation is competitive with or faster than the rate of propagation and monomer addition is irreversible [14, 15]. This condition ensures that all of the chains grow for essentially the same period of time. The relationship between the polydispersity and the degree of polymerization for a living polymerization is shown in Equation 7.4; the second approximation is valid for high molecular weights [13]. The Poisson distribution represents the ideal limit for termination-free polymerizations. Thus, it is predicted that the molecular weight distribution will decrease with increasing molecular weight for a living polymerization system. Broader molecular weight distributions are obtained using less active initiators, with mixtures of initiators, or with continuous addition of initiator as involved in a continuous-flow stirred-tank reactor. Thus, living polymerizations can form polymers with broader molecular weight distributions. It has been proposed that a narrow molecular weight distribution (monodisperse) polymer should exhibit $M_w/M_n \leq 1.1$ [16]. Molecular weight distribution affects melt viscosity and processing characteristics of polymers [17].

$$\frac{X_w}{X_n} = 1 + \left[ \frac{X_n}{(X_n + 1)^2} \right] \approx 1 + \left[ \frac{1}{X_n} \right] \qquad (7.4)$$

## 7.3 GENERAL CONSIDERATIONS

### 7.3.1 Monomers

Two broad types of monomers can be polymerized anionically: vinyl, diene, and carbonyl-type monomers with difunctionality provided by one or more double bonds; and cyclic (e.g., heterocyclic) monomers with difunctionality provided by a ring that can open by reaction with nucleophiles. For vinyl monomers, it is generally considered that there must be substituents on the double bond that can stabilize the negative charge that develops in the transition state for monomer addition as shown in Equation 7.5. These substituents must also be stable to the anionic chain ends; thus, relatively acidic, proton-donating groups (e.g., amino, hydroxyl, carboxyl, acetylene functional groups) or strongly electrophilic functional groups (e.g., cyano, carbonyl, nitro, sulfonyl) that can react with bases and nucleophiles must not be present or must be protected by conversion to a suitable derivative. In general, substituents that stabilize negative charge by anionic charge

delocalization render vinyl monomers polymerizable by an anionic mechanism. Such substituents include aromatic rings, double bonds, as well as carbonyl, ester, cyano, sulfoxide, sulfone, and nitro groups. The general types of monomers that can be polymerized anionically without the incursion of termination and chain transfer reactions include styrenes, styrenes with stable or protected functional groups [14, 18–20], vinylaromatics, dienes (e.g., 1,3-butadiene and isoprene), alkyl methacrylates, vinylpyridines, aldehydes, epoxides, episulfides (thiiranes), cyclic siloxanes, lactones, and lactams. Monomers with polar substituents such as carbonyl, cyano, and nitro groups often undergo side reactions with initiators and propagating anions; therefore, controlled anionic polymerization to provide high molecular weight polymers is generally not possible. Many types of polar monomers can be polymerized anionically, but do not produce living, stable, carbanionic chain ends. These types of polar monomers include acrylonitriles, propylene oxide, vinyl ketones, acrolein, vinyl sulfones, vinyl sulfoxides, vinyl silanes, halogenated monomers, ketenes, nitroalkenes, and isocyanates.



$$(7.5)$$
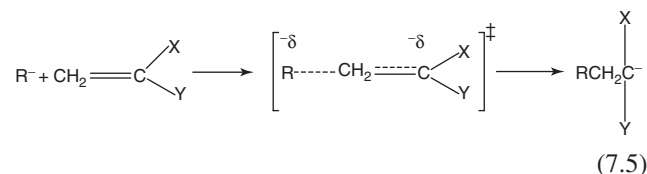
The simplest vinyl monomer, ethylene, although it has no stabilizing moiety, can be polymerized by an anionic mechanism using butyllithium complexed with $N,N,N',N'$-tetramethylethylenediamine (TMEDA) as a complexing ligand [20, 21]. The conversion of a double bond to two single bonds provides the energetic driving force for this reaction. Because of the insolubility of the crystalline high density polyethylene formed by anionic polymerization, the polymer precipitates from solution during the polymerization.

Although cyclopropane itself is not anionically polymerizable, cyclopropanes with two electron-withdrawing groups on one of the ring carbons, for example, -$CO_2R$ or -CN substitution, undergo anionic polymerization [22, 23]. Another anionically reactive monomer is trimethylvinylsilane [$CH_2$=$CHSi(CH_3)_3$] in which the silicon atom with available d orbitals can stabilize the resulting carbanion [24]. 4-Vinyltriphenylamine undergoes living alkyllithium-initiated polymerization to form a polymer of interest as a hole transport layer in light-emitting diodes [25]. The living polymerization of 4-vinylbenzocyclobutene using $sec$-butyllithium in benzene has been reported [26]. For some styrene monomers with potentially reactive functional groups, anionic polymerization can be effected in polar media (tetrahydrofuran (THF) [27] or THF/$N,N$-dimethylacetamide [28])

at low temperatures ($-78\,^{\circ}$C), for example, 4-(4-(2-isopropenylphenoxy)butyl)styrene [27] and 4-cyanostyrene [28]. There has been renewed interest in the anionic polymerization of 1,3-cyclohexadiene, even though chain transfer and chain termination reactions can occur [29–33]. 1,3,5-Trienes such as *trans*-1,3,5-hexatriene can be polymerized by alkyllithium-initiated anionic polymerization, but it was not possible to eliminate branching reactions [34]. Monoaddition to poly(styryl)lithium was effected by addition of 1.2 equivalents of *trans*-1,3,5-hexatriene at $-10\,^{\circ}$C in toluene to form the corresponding diene-functionalized macromonomer [35].

### 7.3.2    Solvents

The range of useful solvents for anionic polymerization is limited by the high reactivity (basicity and nucleophilicity) of the initiators and propagating carbanionic chain ends. For styrene and diene monomers, the solvents of choice are alkanes, cycloalkanes, aromatic hydrocarbons, and ethers [3, 36–38]; the use of alkenes has also been described, although some chain transfer can occur, especially at elevated temperatures and in the presence of Lewis bases [39]. Aromatic hydrocarbon solvents such as benzene and toluene provide enhanced rates of initiation and propagation relative to the alkanes [40]; however, chain transfer reactions can occur with alkylated aromatic solvents, for example, toluene and ethylbenzene [41, 42]. A useful alternative is *t*-butylbenzene which has no reactive benzylic hydrogens and has a much lower freezing point ($-58\,^{\circ}$C), making it useful for low temperature processes [43].

Polar solvents such as ethers and amines react with organometallic initiators, as well as propagating polystyryl and polydienyl carbanions, to decrease the concentration of active centers [3, 44, 45]. The rate of reaction with ethers decreases in the order Li > Na > K. For example, dilute solutions of poly(styryl)lithium in THF at room temperature decompose at the rate of a few percent each minute. Alkyllithium initiators also react relatively rapidly with ethers; the order of reactivity of organolithium compounds with ethers is tertiary RLi > secondary RLi > primary RLi > phenyllithium > methyllithium > benzyllithium [44]. An approximate order of reactivity of ethers toward alkyllithium compounds is dimethoxyethane, THF > tetrahydropyran > diethyl ether > diisopropyl ether. Tertiary amines can also react with alkyllithium compounds. The importance of these reactions can be minimized by working at lower temperatures (e.g., <0 $^{\circ}$C); it is also advisable to use only the minimum amounts of ethers and other Lewis bases required as additives.

For less reactive anionic chain ends such as those involved in propagation of heterocyclic monomers, a wider range of solvents can be utilized. For example, dipolar aprotic solvents such as dimethylsulfoxide (DMSO), *N*,*N*-dimethylformamide (DMF), and hexamethylphosphoramide (HMPA) can be used for polymerizations of epoxides.
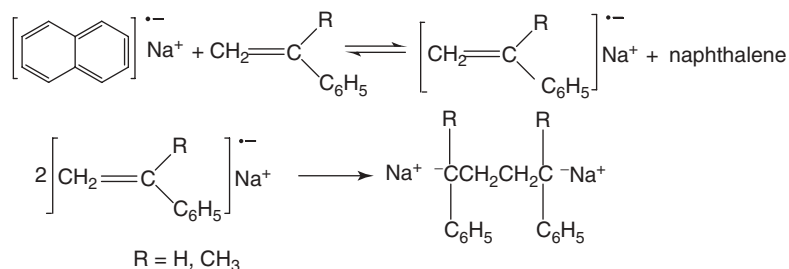
### 7.3.3    Initiators

The choice of a suitable initiator is essential for the preparation of polymers with well-defined structures and low degrees of compositional heterogeneity. A useful guide to choose an appropriate initiator for anionic polymerization of a given monomer is that the initiator should have a reactivity (stability) similar to that of the propagating anionic species, that is, the p$K_a$ of the conjugate acid of the propagating anion should correspond closely to the p$K_a$ of the conjugate acid of the initiating species [3, 46]. If the initiator is too reactive, then side reactions are promoted. If the initiator is relatively unreactive, the initiation reaction may be slow or inefficient. For example, the p$K_a$ values for the propagating carbanions in styrene and diene monomers are 43–44 [2]. Thus alkyl organometallic compounds with p$K_a$ values >56 are generally used as initiators for polymerizations of these monomers [3]. Initiators can be classified in terms of their mechanisms of initiation: (i) initiation by electron transfer (alkali and alkaline-earth metals and radical anions) and (ii) nucleophilic addition. The following sections discuss each of these initiator types.
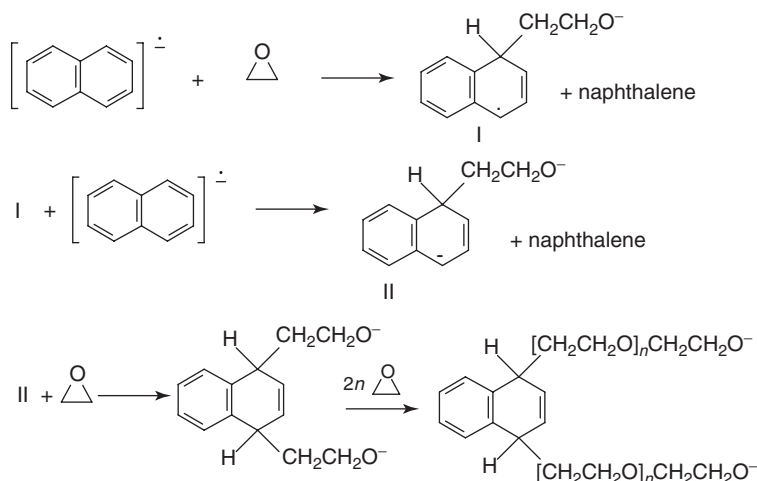
#### 7.3.3.1    Initiation by Electron Transfer

*Alkali Metals*    The direct use alkali metals and alkaline-earth metals as initiators for anionic polymerization of diene monomers as first reported in 1910 is primarily of historical interest because these are uncontrolled, heterogeneous processes [4]. One of the most significant developments in anionic vinyl polymerization was the discovery reported in 1956 by Stavely and coworkers at Firestone Tire and Rubber Company that polymerization of neat isoprene with lithium dispersion produced high *cis*-1,4-polyisoprene, similar in structure and properties to *Hevea* natural rubber [47]. This discovery led to development of commercial anionic solution polymerization processes using alkyllithium initiators.

The mechanism of the anionic polymerization of styrenes and 1,3-dienes initiated by alkali metals has been described in detail by Szwarc [48]. Initiation is a heterogeneous process occurring on the surface of the metal (Mt) by reversible transfer of an electron to adsorbed monomer (M) as shown in Scheme 7.2. The initially formed radical anions (M$^-$) rapidly dimerize to form dianions. Monomer addition to these dianions forms adsorbed oligomers that desorb and continue chain growth in solution. This heterogeneous initiation reaction continues to generate new active chain ends during the course of the subsequent propagation reactions. Consequently, there is little control of molecular weight, and relatively broad molecular weight distributions

Mt + M $\rightleftharpoons$ Mt$^+$, M$^{\cdot-}$

2 Mt$^+$, M$^{\cdot-}$ $\rightleftharpoons$ Mt$^+$, $^-$M—M$^-$, Mt$^+$

Mt$^+$, $^-$M—M$^-$, Mt$^+$ + $n$M $\longrightarrow$ Mt$^+$, $^-$M—[M]$_n$—M$^-$, Mt$^+$

**Scheme 7.2**

have been reported for the soluble polymer obtained from these bulk polymerizations ($M_w/M_n = 3$–$10$) [47]; formation of a high degree of branching and gel content (45%) has also been reported for these processes [47, 49].

Alkali metals can dissolve in solvating media such as ethers and amines to form blue solutions of solvated electrons. In the presence of strongly complexing ligands such as crown ethers or cryptands, electrides (complexed alkali cation and electron), or nuclides (complexed alkali cation and alkali metal anion) can be formed as shown in Scheme 7.3 [50]. Nuclides have been shown to react with monomers such as styrene and methyl methacrylate (MMA) to form intermediate dianions that are rapidly protonated by the solvent THF to form the monoanion initiating species as shown in Scheme 7.4 [51, 52]. For the nuclide-initiated polymerization of MMA, although there was good agreement between calculated and observed molecular weights, the molecular weight distributions were broad ($M_w/M_n = 1.2$–$1.6$) [52].

*Radical Anions* Many aromatic hydrocarbons react reversibly with alkali metals in polar aprotic solvents to form

stable, homogeneous solutions of the corresponding radical anions as shown in Equation 7.6 [4, 48]. Radical anions can be formed efficiently only in polar aprotic solvents such as THF and glymes. Aromatic radical anions such as sodium naphthalene react with monomers such as styrene by reversible electron transfer to form the corresponding monomer radical anions as shown in Scheme 7.5 (R = H).

$$Mt + Ar \rightleftharpoons Ar^{\bullet-}Mt^+, \quad Mt = Li, Na, K, Rb, Cs \quad (7.6)$$

Although the equilibrium between the radical anion of the monomer and the aromatic radical anion lies far to the left because of the low electron affinity of the monomer, this is an efficient initiation process because the resulting monomer radical anions rapidly undergo head-to-head dimerization reactions with rate constants that approach diffusion control [53].

The reactions of monomers with aromatic radical anions or directly with alkali metals can be used to prepare oligomeric dianionic initiators from monomers such as α-methylstyrene which have accessible ceiling temperatures ($T_c = 61\,°C$) as shown in Scheme 7.5 (R$=$CH$_3$) [54]. Dimers or tetramers can be formed depending on the alkali metal system, temperature, and concentration.

Monomers that can be polymerized with aromatic radical anions include styrenes, dienes, epoxides, thiiranes, and cyclosiloxanes. For epoxides and cyclosiloxanes, the mechanism of initiation involves nucleophilic addition of the radical anion to these monomers as shown in Scheme 7.6, in contrast to the electron transfer mechanism occurring for hydrocarbon monomers (Scheme 7.5) [45].

### 7.3.3.2 Initiation by Nucleophilic Addition
*Alkyllithium Compounds* Although anionic polymerization of vinyl monomers can be effected with a variety of organometallic compounds, alkyllithium compounds are the most useful class of initiators [3, 44, 46, 45, 55]. A variety of simple alkyllithium compounds are readily available commercially in hydrocarbon solvents such as hexane and

Crown ether or cryptand

2 Mt $\rightleftharpoons$ [Mt$^+$] Mt$^-$  (nuclide)

Crown ether or cryptand

Mt $\rightleftharpoons$ [Mt$^+$] e$^-$  (electride)

**Scheme 7.3** Mechanism of metal-initiated anionic polymerization.

K$^-$(K$^+$) + CH$_2$=CH | C$_6$H$_5$ $\longrightarrow$ [CH$_2$=CH]$^{\cdot-}$ | C$_6$H$_5$ K$^o$(K$^+$)

[CH$_2$=CH]$^{\cdot-}$ | C$_6$H$_5$ K$^o$(K$^+$) $\longrightarrow$ K$^+$ $^-$CH$_2$CH$^-$ | C$_6$H$_5$ K$^+$

K$^+$ $^-$CH$_2$CH$^-$ | C$_6$H$_5$ K$^+$ + [THF] $\longrightarrow$ CH$_3$CH$^-$ | C$_6$H$_5$ K$^+$ + CH$_2$=CHO$^-$ K$^+$ + CH$_2$=CH$_2$

**Scheme 7.4**

**Scheme 7.5**  Initiation mechanism with aromatic radical anions by electron transfer.



**Scheme 7.6**  Radical anion initiation by addition.

cyclohexane. They can be prepared by reaction of the corresponding alkyl chlorides with lithium metal.

Alkyllithium compounds are generally associated into dimers, tetramers, or hexamers in hydrocarbon solution [3, 44]. The degree of association is related to the steric requirements of the alkyl group, that is, the degree of association decreases as the steric requirements of the alkyl group increase.

The relative reactivities of alkyllithiums as polymerization initiators are intimately linked to their degree of association as shown below with the average degree of association in hydrocarbon solution, where known, indicated in parentheses after the alkyllithium compound [44, 55, 56]:

*Styrene Polymerization*  Menthyllithium (2) > *sec*-BuLi (4) > *i*-PrLi (4–6) > *i*-BuLi > *n*-BuLi (6) > *t*-BuLi (4)

*Diene Polymerization*  Menthyllithium (2) > *sec*-BuLi (4) > *i*-PrLi (4–6) > *t*-BuLi (4) > *i*-BuLi > *n*-BuLi (6)

In general, the less associated alkyllithiums are more reactive as initiators than the more highly associated species.

Alkyllithium initiators are primarily used as initiators for polymerizations of styrenes and dienes. They effect quantitative living polymerization of styrenes and dienes in hydrocarbon solution. In general, these alkyllithium initiators are too reactive for alkyl methacrylates and vinylpyridines. *n*-Butyllithium is used commercially to initiate anionic homopolymerization and copolymerization of butadiene, isoprene, and styrene with linear and branched structures. Because of its high degree of association (hexameric), *n*-butyllithium-initiated polymerizations are often effected at elevated temperatures (>50 °C) and in the presence of small amounts of Lewis base to increase the rate of initiation relative to propagation and thus obtain polymers with narrower molecular weight distributions [55, 57].

*sec*-Butyllithium is used commercially to prepare styrene-diene block copolymers because it can initiate styrene polymerization rapidly compared to propagation so that even polystyrene blocks with relatively low molecular weights (10,000–15,000 g/mol) can be prepared with stoichiometric control and narrow molecular weight distributions.

Alkyllithiums react quite differently with cyclic sulfides compared to the normal nucleophilic ring-opening

reaction with epoxides [58, 59]. Ethyllithium reacts with 2-methylthiacyclopropane to generate propylene and lithium ethanethiolate, Equation 7.7. The resulting lithium ethanethiolate is capable of initiating polymerization of 2-methylthiacyclopropane. In contrast, ethyllithium reacts with



$$(7.7)$$
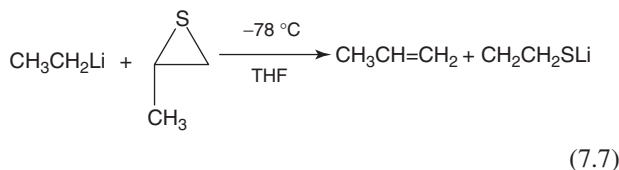
2-methylthiacyclobutane, Equation 7.8, to form an alkyllithium product that is capable of initiating polymerization of styrene.



$$(7.8)$$
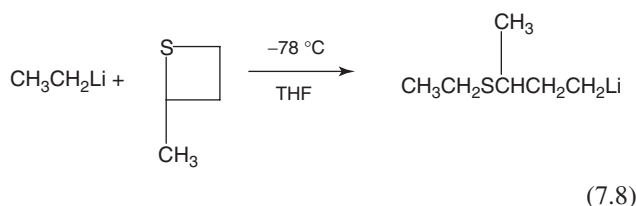
*Organoalkali Initiators*   In general, the simple organoalkali metal derivatives other than lithium are not soluble in hydrocarbon media. However, higher homologs of branched hydrocarbons are soluble in hydrocarbon media. The reaction of 2-ethylhexyl chloride and sodium metal in heptane produces soluble 2-ethylhexylsodium [60]. This initiator copolymerizes mixtures of styrene and butadiene to form styrene-butadiene copolymers with high (55–60%) vinyl microstructure [61, 62].

Cumyl potassium ($pK_a \approx 43$ based on toluene) [2] is a useful initiator for anionic polymerization of a variety of monomers, including styrenes, dienes, methacrylates, and epoxides. This carbanion is readily prepared from cumyl methyl ether as shown in Equation 7.9, and is generally used at low temperatures in polar solvents such as THF [63].



$$(7.9)$$
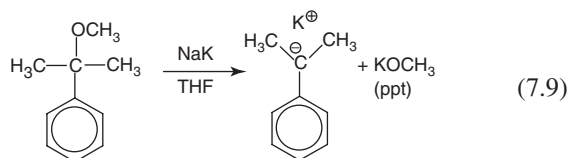
*Organoalkaline-Earth Initiators*   Both styrene and 1,3-dienes can be polymerized by organoalkaline-earth metal compounds, specifically those of magnesium, calcium, barium, and strontium. In general, hydrocarbon-soluble benzyl, 1,1-diphenylalkyl and triphenylmethyl derivatives have been investigated. For example, the adduct of 1,1-diphenylethylene (DPE) with dibenzylbarium, that is, bis(1,1,3-triphenylpropyl)barium, is hexane-soluble and polymerizes styrene with controlled molecular

weight , but the molecular weight distribution was broad ($M_w/M_n = 1.20$) [64]. Broad molecular weight distributions are typical for these initiators for both styrene and butadiene polymerizations and has been ascribed to slow rates of initiation relative to propagation [65]. Hydrocarbon-soluble *n*,*s*-dibutylmagnesium is not an active initiator for styrenes and dienes in cyclohexane.

*Ate Complexes*   Alkyllithium compounds interact with organometallic compounds of different metals ($MtR'_n$), most notably those of groups I, II, and II which behave like Lewis acids, to form mixed organometallic compounds, referred to as "ate" complexes, schematically represented in Equation 7.10 [66]. However, X-ray and nuclear magnetic resonance (NMR) investigations indicate the formation of more complex, stoichiometry-dependent types of structures involving bridging alkyl groups between the two types of metal centers for aluminum, magnesium, and zinc systems [67, 68]. The importance of these mixed organometallic species is that they dramatically attenuate the reactivity of the chain ends so that controlled polymerizations can be effected at higher temperatures and with higher monomer concentrations, that is, "retarded" polymerizations [69].

$$RLi + MtR'_n \rightarrow Li^+ \left[ RMtR'_n \right]^- \qquad (7.10)$$

*Difunctional Initiators*   The methodology for preparation of hydrocarbon-soluble dilithium initiators is generally based on the reaction of an aromatic divinyl precursor with two mol of butyllithium. Unfortunately, because of the tendency of organolithium chain ends in hydrocarbon solution to associate and form electron-deficient dimeric, tetrameric, or hexameric aggregates, most attempts to prepare dilithium initiators in hydrocarbon media have generally resulted in the formation of insoluble three-dimensionally associated species [70]. The reaction of *meta*-diisoprenylbenzene with 2 mol of *t*-butyllithium in the presence of 1 equivalent of triethylamine in cyclohexane at −20 °C has been reported to form pure diadduct without oligomerization, Equation 7.11 [71]. This initiator in the presence of 5 vol% of diethyl ether for the butadiene block has been used to prepare well-defined poly(methyl methacrylate)-*b*-polybutadiene-*b*-poly(methyl methacrylate).



$$(7.11)$$
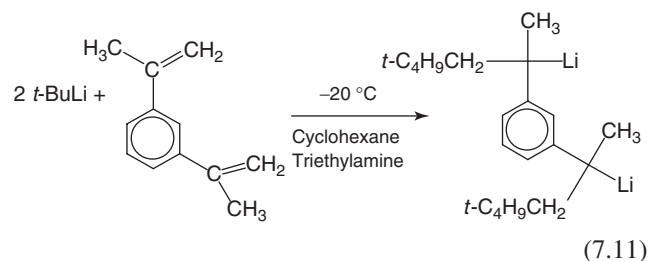
The reaction of pure *m*-divinylbenzene (DVB) with *sec*-butyllithium in toluene at −49 °C in the presence of triethylamine ([Et$_3$N]/[Li] = 0.1) has been reported to produce the corresponding dilithium initiator in quantitative yield [72]. Polymerization of butadiene with this initiator in toluene at −78 °C produced well-defined polybutadiene with high 1,4-microstructure (87%).

The addition reaction of 2 mol of *sec*-butyllithium with 1,3-bis(1-phenylethenyl)benzene, Equation 7.12, proceeds rapidly and efficiently to produce the corresponding dilithium species that is soluble in toluene or in cyclohexane [46, 73]. Although this dilithium initiator is useful for the preparation of homopolymers and triblock copolymers with relatively narrow molecular weight distributions, it is necessary to add a small amount of Lewis base or 2 or more equivalents of lithium alkoxide (e.g., lithium *sec*-butoxide) to produce narrow, monomodal molecular weight distributions.



(7.12)
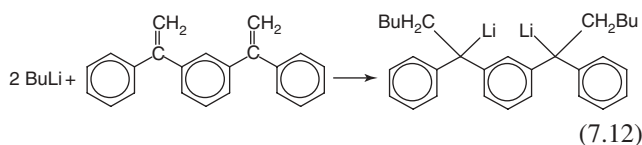
The reaction of multifunctional aryl bromides with several equivalents of *sec*-butyllithium has been reported to form multifunctional organolithium initiators that are soluble in hydrocarbon solvent as shown in Scheme 7.7 [74, 75]. It should be noted that this procedure requires 2 extra equivalents of *sec*-butyllithium to react with the 2 mol of *sec*-butyl bromide that is formed by lithium–halogen exchange. This initiator was used to prepare triblock copolymers containing polybutadiene center blocks with high 1,4-microstructure and which exhibited good tensile properties (>900% elongation, circa 30 MPa tensile strength at break). [74]

*Functionalized Initiators* Alkyllithium initiators that contain functional groups provide versatile methods for the preparation of end-functionalized polymers and macromonomers [76–78]. For a living anionic polymerization, each functionalized initiator molecule will produce one macromolecule with the functional group from the initiator residue at one chain end and the active anionic propagating species at the other chain end. However, many functional groups such as hydroxyl, carboxyl, phenol, and primary amine are not stable in the presence of reactive dienyllithium and styryllithium chain ends. Therefore, it is necessary to convert these functional groups into suitable derivatives, that is, protected groups, that are stable to the carbanionic chain ends and that can be removed readily after the polymerization. Examples of protected functional initiators include the hydroxyl-protected initiators, 6-lithiohexyl acetaldehyde acetal, 6-(*t*-butyldimethylsiloxy)-hexyllithiium, and 3-(*t*-butyldimethylsiloxy)propyllithium

as well as a primary amine-protected initiator, 4-bis(trimethylsily)aminophenyllithium [76].

*1,1-Diphenylmethyl Carbanions* The carbanions based on diphenylmethane (p$K_a$ = 32) [2] are useful initiators for vinyl and heterocyclic monomers, especially alkyl methacrylates at low temperatures [78]. 1,1-Diphenylalkyllithiums can also efficiently initiate the polymerization of styrene and diene monomers that form less stable carbanions. Diphenylmethyllithium can be prepared by the metallation reaction of diphenylmethane with butyllithium or by the addition of butyllithium to DPE as shown in Equation 7.13. This reaction can also be utilized to prepare functionalized initiators by reacting butyllithium with a substituted DPE derivative [78]. Addition of lithium salts such as lithium chloride, lithium *tert*-butoxide, or lithium 2-(2-methoxyethoxy)ethoxide with 1,1-diphenylmethylcarbanions and other organolithium initiators has been shown to narrow the molecular weight distributions and to improve the stability of active centers for anionic polymerization of both alkyl methacrylates, *tert*-butyl acrylate, and 2-vinylpyridine [79–81].



(7.13)
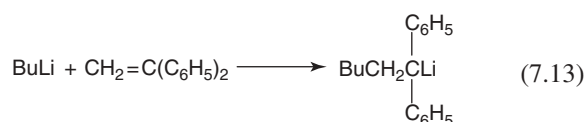
## 7.4 KINETICS AND MECHANISM OF POLYMERIZATION

### 7.4.1 Styrene and Diene Monomers

#### 7.4.1.1 Hydrocarbon Solvents
*Initiation* The mechanism of initiation of anionic polymerization of vinyl monomers with alkyllithium compounds and other organometallic compounds is complicated by association and cross-association phenomena in hydrocarbon solvents and by the presence of a variety of ionic species in polar media [3, 4, 45, 48, 55, 56]. The kinetics of initiation is complicated by competing propagation and the occurrence of cross-association of the alkyllithium initiator with the propagating organolithium [55]. Thus, only the initial rates provide reliable kinetic data.

Typical kinetics of the initiation reaction of *n*-butyllithium with styrene in benzene exhibits a first-order dependence on styrene concentration and approximately a one-sixth order dependence on *n*-butyllithium concentration as shown in Equation 7.14.

$$R_i = k_i \left( \frac{K_d}{6} \right)^{1/6} [\text{BuLi}]_o^{1/6} [\text{M}]$$  (7.14)
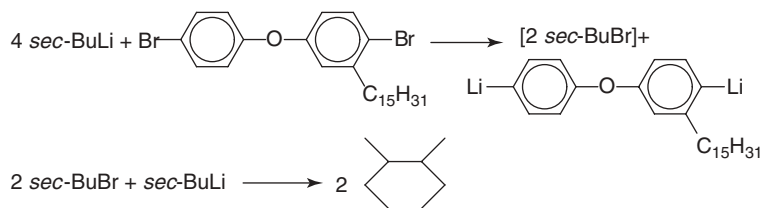
**Scheme 7.7**  Synthesis of diaryllithium-based difunctional initiator.
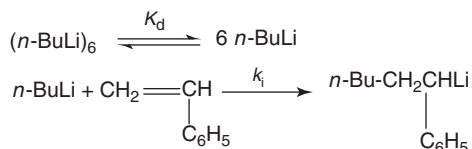
**Scheme 7.8**  Mechanism of styrene initiation with *n*-butyllithium in hydrocarbon solution.

Since *n*-butyllithium is aggregated predominantly into hexamers in hydrocarbon solution [44], the fractional kinetic order dependency of the initiation process on the total concentration of initiator has been rationalized on the basis that unassociated *n*-butyllithium is the initiating species and that it is formed by the equilibrium dissociation of the hexamer as shown in Scheme 7.8.

The kinetic order for *sec*-butyllithium-initiated polymerization of styrene is close to 0.25 in benzene solution; this result is also consistent with initiation by unassociated *sec*-butyllithium, since *sec*-butyllithium is associated predominantly into tetramers in benzene solution [44]. The experimentally observed energy of activation (18 kcal/mol) for *n*-BuLi/styrene initiation [56] appears to be too low to include the enthalpy of complete dissociation of the aggregates, estimated to be 108 kcal/mol [82]. An alternative mechanism is the incomplete or stepwise dissociation of the aggregate [3].

The observed inverse correlation between reaction order dependence for alkyllithium and degree of alkyllithium aggregation is not observed in aliphatic solvents. The use of aliphatic solvents leads to decreased rates of initiation and pronounced induction periods. In fact, a different reaction mechanism involving the direct addition of monomer with aggregated organolithium species has been proposed for aliphatic solvents [3, 56].

The actual complexity of these initiation events has been documented by combined $^1$H NMR and small-angle neutron scattering studies of the *t*-butyllithium-initiated polymerization of butadiene in heptanes at 8 °C, which revealed the presence of coexisting large-scale aggregates ($n \approx 100$; $\leq 1$ wt%) and smaller aggregates during all stages of the polymerization, that is, initiation and propagation [83, 84]. The average degree of aggregation decreased from $n \approx 140$ at the beginning of initiation/polymerization process and leveled off at circa 4 with increasing chain

length. It was stated that for the lower aggregation numbers (circa 4) the structure of the aggregates is star-like and in agreement with the traditional mechanism (see diene propagation section) [83].

*Propagation*  The anionic propagation kinetics for styrene (S) polymerization with lithium as counterion is relatively unambiguous. The reaction in monomer concentration is first order, as it is for polymerization of all styrene and diene monomers in heptane, cyclohexane, benzene, and toluene [3, 55, 56]. The reaction order dependence on total chain-end concentration, $[PSLi]_o$, is one-half as shown in Equation 7.15. The observed one-half kinetic order dependence on chain-end concentration is consistent with the fact that poly(styryl)lithium is predominantly associated into dimers in hydrocarbon solution [85, 86]. If the unassociated poly(styryl)lithium is the reactive entity for

$$R_p = -\frac{d[S]}{dt} = k_{obs}[PSLi]_o^{1/2}[S] \qquad (7.15)$$

monomer addition, assuming that the aggregate is a dormant species, a simple dissociative mechanism can be invoked, Scheme 7.9. This mechanism leads to the kinetic equation (Eq. 7.15).

Elucidation of the mechanism of propagation for isoprene and butadiene in hydrocarbon solution with lithium as counterion in the past has been complicated by disagreement in the literature regarding both the kinetic order dependence on chain-end concentration and the degree of association of the chain ends, as well as by apparent changes in kinetic reaction orders with chain-end concentration [3, 56]. For butadiene and isoprene propagation, reported reaction order dependencies on the concentration of poly(dienyl)lithium chain ends include 0.5, 0.33, 0.25, and 0.167. Kinetic studies of isoprene propagation with lithium as counterion in hydrocarbon solvents showed
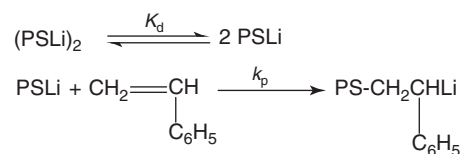
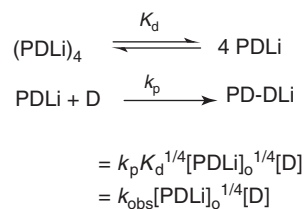**Scheme 7.9**  Mechanism of styrene propagation for poly(styryl) lithium.

that the kinetic order dependence on chain-end concentration changed from 0.5 to either 0.25 or 0.17 as the chain-end concentration was varied from $10^{-2}$ to $10^{-6}$ mol/l [3, 87, 88]. Comparison of these kinetic orders with the degrees of association of the poly(dienyl)lithium chain ends had been complicated by the lack of agreement regarding the predominant degree of association of these species in hydrocarbon solution. However, recent evaluation of the association states of poly(dienyl)lithium chain ends in benzene by small-angle neutron scattering, as well as by dynamic and static light scattering, indicates that predominantly tetrameric aggregates are in equilibrium with small amounts of higher order aggregates ($n > 100$) [83, 89–94]. Thus, the 0.25 kinetic order dependence on poly(dienyl)lithium chain-end concentration can be interpreted in terms of the predominantly tetrameric degree of aggregation as shown by the mechanism in Scheme 7.10.

The observation of concentration dependence of the reaction order (increasing from 0.25 to 0.5 (when [PILi] $<5 \times 10^{-5}$ mol/l) with decreasing concentration of poly(isoprenyl)lithium in benzene can be explained in terms of the intermediacy of a dimeric association state as shown in Equation 7.16 [87].

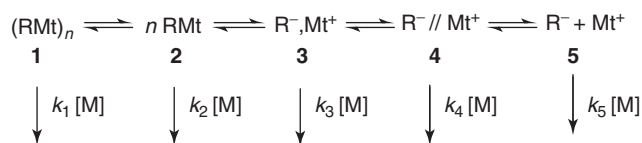$$(PILi)_4 \rightleftharpoons 2(PILi)_2 \rightleftharpoons 4PILi \qquad (7.16)$$
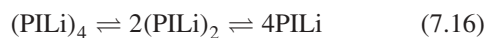
### 7.4.1.2 Polar Solvents
A change in the reaction medium from hydrocarbon to polar solvents causes changes in the nature of the alkali metal carbanions, which can be interpreted in terms of the Winstein spectrum of ionic species as shown in Scheme 7.11 [3, 6]. Thus, in addition to the aggregated (**1**) and unaggregated (**2**) species that can exist in hydrocarbon solution, in polar solvents it is necessary to consider the intervention of free ions (**5**) and the contact (**3**) and solvent-separated (**4**) ion-paired carbanion species as propagating species as shown in Scheme 7.11.

In general, as the polarity (dielectric constant) and solvating ability of the medium increase, a transition to more ionic species (a shift in the Winstein spectrum from left to right) occurs. In weakly polar solvents such as dioxane ($\varepsilon = 2.21$), the kinetics of styrene propagation exhibits pseudo-first-order behavior as illustrated in Equation 7.17,

$$(RMt)_n \rightleftharpoons n\,RMt \rightleftharpoons R^-,Mt^+ \rightleftharpoons R^- // Mt^+ \rightleftharpoons R^- + Mt^+$$

$$\textbf{1} \qquad\qquad \textbf{2} \qquad\quad \textbf{3} \qquad\quad \textbf{4} \qquad\quad \textbf{5}$$

$$\downarrow k_1[M] \qquad \downarrow k_2[M] \qquad \downarrow k_3[M] \qquad \downarrow k_4[M] \qquad \downarrow k_5[M]$$

**Scheme 7.11** Possible reactive entities involved in propagation in polar solvents.

where $k_{obs}$ is the observed pseudo-first-order rate constant, $k_p$ is the propagation rate constant and $PS^-Mt^+$ represents the concentration of carbanionic chain ends that does not change for a living polymerization [48]. The values of $k_p$ can be obtained by
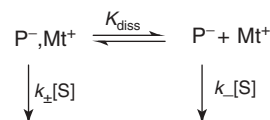
$$-\frac{d[S]}{dt} = k_{obs}[S] = k_p\left[PS^-Mt^+\right][S] \qquad (7.17)$$

plotting $k_{obs}$ versus $[PS^-Mt^+]$. The order of reactivity (rate constants in brackets are in units of l/(mol s)) of alkali metal counterions is $Li^+$ [0.9] $<Na^+$ [3.4–6.5] $<K^+$ [19–27] $Rb^+$ [21.5–34 $<Cs^+$ [15–24.5] [48]. The trend of increasing reactivity with increasing ionic radius, also observed in hydrocarbon solution, has been taken as evidence for contact ion pairs as the reactive propagating species. Similar behavior has been observed for isoprene polymerization in diethyl ether ($\varepsilon = 4.34$) [95].

In more polar solvents such as THF ($\varepsilon = 7.6$), a concentration dependence was observed for the plots of $k_{obs}$ versus $[PS^-Mt^+]$, that is, $k_p$ exhibits a linear dependence on $(1/[PS^-Mt^+]^{1/2})$ [48, 96–98]. This dependence has been interpreted in terms of the participation of both ion pairs and free ions as active propagating species as shown in Scheme 7.12, where $k_\pm$ is the propagation rate constant for the ion pair species, $k_-$ is the propagation rate constant for the free ion, and $K_{diss}$ is the equilibrium constant for dissociation of ion pairs ($P_\pm$) to free ions ($P_-$). The corresponding rate expression for this system is shown in Equation 7.18.

$$-\frac{d[S]}{dt} = [S]\left(k_\pm\left[P_\pm\right] + k_-\left[P_-\right]\right) \qquad (7.18)$$

Assuming that $K_{diss}$ is small, then the concentration of ion-paired species can be assumed to be approximately equal to $[PMt]_{total}$ and the concentration of free ions can

$$(PDLi)_4 \xrightarrow{\ K_d\ } 4\,PDLi$$

$$PDLi + D \xrightarrow{\ k_p\ } PD\text{-}DLi$$

$$= k_p K_d^{1/4}[PDLi]_o^{1/4}[D]$$
$$= k_{obs}[PDLi]_o^{1/4}[D]$$

**Scheme 7.10** Kinetics and mechanism for poly(dienyl)lithium propagation.

$$P^-,Mt^+ \xrightarrow{\ K_{diss}\ } P^- + Mt^+$$

$$\downarrow k_\pm[S] \qquad\qquad \downarrow k_-[S]$$

**Scheme 7.12** Participation of ion pairs and free ions for the mechanism of anionic propagation in polar solvents such as THF.

be calculated using the dissociation equilibrium constant as in Equation 7.19.

$$[P_-] = K_{diss}^{1/2}[PMt]_{total}^{1/2} \qquad (7.19)$$

Substituting this expression for the concentration of free ions into the rate equation generates the final rate expression as shown in Equation 7.20.

$$-\frac{d[S]}{dt} = [M]\left(k_{\pm}[PMt]_{total} + k_- K_{diss}^{1/2}[Mt]_{total}^{1/2}\right) \qquad (7.20)$$

The corresponding expression for $k_p$ is shown in Equation 7.21, recognizing that this $k_p$ is only an apparent propagation rate constant (Eq. 7.16).

$$k_p = \frac{k_{\pm} + k_- K_{diss}^{1/2}}{[PMt]_{total}^{1/2}} \qquad (7.21)$$

From plots of the apparent propagation rate constant versus $1/[P^-Mt^+]^{1/2}$, the slope corresponds to $k_- K_{diss}^{1/2}$ and the intercept is $k_{\pm}$; the results are shown in Table 7.1 [48, 97–99]. It is observed that the slopes of the lines decrease as the cation size increases from lithium to cesium. Since $k_-$ is independent of the cation, the variation of the slope with counterion reflects a decrease in $K_{diss}$ (Scheme 7.12) as the counterion size increases. It is also observed that $k_{\pm}$ also decreases with increasing cation size. Thus, the order of reactivity of alkali metal counterions in THF is $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$, the inverse of the order observed in the less polar solvent, dioxane, or in hydrocarbon solution. This order is in accord with expectations based on cation solvation energies, which decrease with increasing cation size. Values of the propagation rate constant for free styryl anions are relatively insensitive to solvent; the values for $k_-$ are $6.5 \times 10^4$ and $4.0 \times 10^4$ l/(mol s) at 25 °C in THF and in dimethoxyethane, respectively [48]. Even though free ions are present in small amounts (Table 7.1), their contribution to the overall rate of polymerization is significant because of their much higher reactivity.

**TABLE 7.1   Equilibrium Dissociation Constants of Organoalkali Metal Salts of Polystyryl Carbanions and the Propagation Rate Constants for the Corresponding Ion Pairs and Free Ions in THF at 25 °C [48, 97–99]**

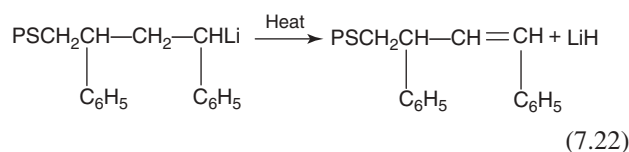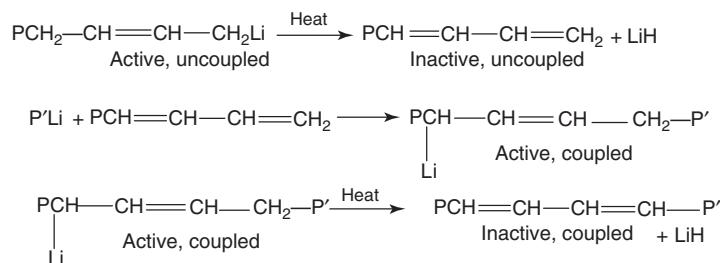| Countercation | $10^7 K_{diss}$ (mol/l) | $k_{\pm}$ (l/(mol s)) | $10^{-4}k_-$ (l/(mol s)) |
|---|---|---|---|
| $Li^+$ | 1.9–2.2 | 160 | — |
| $Na^+$ | 1.5 | 80 | 6.5 |
| $K^+$ | 0.7–0.77 | ≈60 | — |
| $Rb^+$ | 0.10 | ≈50 | — |
| $Cs^+$ | 0.02–0.047 | 22 | 6.3 |
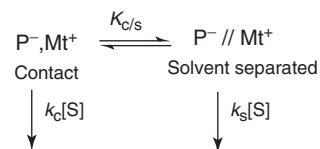


**Scheme 7.13**   Participation of both contact and solvent-separated ion pairs for the mechanism of anionic propagation in polar solvents such as THF.

Although normal Arrhenius behavior was observed for $k_-$, anomalous increases of $k_{\pm}$ with decreasing temperature were observed in polar solvents such as THF and dimethoxyethane (glyme) [97–99]. These results have been explained in terms of a temperature-dependent equilibrium between contact and solvent-separated ion pairs as shown in Scheme 7.13. This equilibrium shifts from the less reactive contact ion pairs ($k_c$) to the much more reactive solvent-separated ion pairs ($k_s$) as temperature is decreased because the contribution from the unfavorable (negative) entropy of dissociation ($T\Delta S_{c/s}$) decreases and the enthalpy of dissociation ($\Delta H_{c/s}$) is negative. The values of $k_c$ and $k_s$ are not very dependent upon solvent, but the equilibrium constants $K_{c/s}$ are very dependent on the polarity of the solvent (Table 7.2). It is noteworthy that the reactivity of the solvent-separated ion pairs approaches that of the free ions. These results also provide a rationalization for the effect of counterion on $k_{\pm}$. Smaller cations such as lithium interact more strongly with solvent and form significant amounts of more reactive, solvent-separated ion pairs.

**7.4.1.3   Termination Reactions**   The categorization of a given polymerization system as living is based on results obtained on the laboratory time scale, that is, the absence of chain termination or chain transfer reactions occurring within the normal time required to complete the polymerization and carry out any subsequent chemical reactions with the active carbanionic polymer chain ends [3, 1, 100]. In fact, the amount of spontaneous termination reactions in typical alkyllithium-initiated polymerizations of styrene and diene monomers depends on time, temperature, and whether polar additives are present [3, 101, 102].

Polymeric organolithium compounds exhibit good stability in hydrocarbon solutions at ambient temperatures and for short periods at elevated temperatures [101, 102]. The principal mode of decomposition is loss of lithium hydride to form a double bond at the chain end as illustrated in Equation 7.22 for poly(styryl)lithium.



$$(7.22)$$

**TABLE 7.2   Ion Pair Rate Constants for Anionic Polymerization of Poly(styryl)sodium in Ethereal Solvents and the Equilibrium Constant and Thermodynamic Parameters for Ion Pair Equilibrium [48]**

| Solvent | $k_c$ (l/(mol s)) | $10^{-4}k_s$ (l/(mol s)) | $K_{c/s}(25\,°C)$ | $\Delta H_{c/s}$ (kcal/mol) | $\Delta S_{c/s}$ (e.u.) |
|---|---|---|---|---|---|
| DME | 12.5 | 5.5 | 0.13 | −5.5 | −22.5 |
| THF | 34 | 2.4 | $2.25 \times 10^{-3}$ | −6.5 | −34 |
| 3-Me-THF | 20 | 12.4 | $5.8 \times 10^{-4}$ | −5.1 | −32 |
| THP | 10.7 | 5.3 | $1.3 \times 10^{-4}$ | −3.0 | −28 |
| Dioxane | 5.5 | — | $<10^{-5}$ | — | — |

*Abbreviations*: DME, 1,2-dimethoxyethane; 3-Me-THF, 3-methyltetrahydrofuran; THP, tetrahydropyran.

Poly(styryl)lithium exhibits good stability over the duration of the polymerizations and beyond, that is, days, at ambient temperatures in hydrocarbon media. However, at elevated temperatures, it is observed that the initial UV absorption intensity at 334 nm decreases and a new absorption is observed at 450 nm, which is assigned to a 1,3-diphenylallyllithium species as shown in Equation 7.23 [101].

The rate constant for spontaneous decomposition was reported to be $40 \times 10^{-6}$ s$^{-1}$ at 65 °C in cyclohexane [101, 103]. The rate of decomposition of PSLi in cyclohexane at 150 °C is 0.205 min$^{-1}$, corresponding to a 3.5-min half-life [104]. In the presence of 2 equivalents of *n,sec*-dibutylmagnesium at 100 °C, the rate of decomposition of PSLi is $1.9 \times 10^{-5}$ min$^{-1}$ while it is $6.4 \times 10^{-4}$ in the absence of additive, corresponding to half-lives of 102 and 3 h, respectively [105]. Similar decomposition reactions have been observed for poly(styryl)sodium [102]. The thermal stability of poly(α-methylstyryl)lithium is much lower than that of poly(styryl)lithium. The observed half-lives for spontaneous termination are 5 h and a few minutes at 25 and 60 °C, respectively [106]. The relative thermal stability of styryl carbanionic chain ends follows the order K ≫ Na > Li for the alkali metal counterions.



$$(7.23)$$

The carbanionic active centers based on 1,3-butadiene and isoprene with lithium as counterion generally possess good stability in hydrocarbon solvents at ambient temperatures. However, poly(dienyl)lithiums undergo complex decomposition reactions upon prolonged storage or heating at elevated temperatures. Poly(butadienyl)lithium in ethylbenzene exhibits an absorption maximum at 300 nm, which gradually decreases in intensity with the formation of absorption tails between 350 and 500 nm [101]. Approximately 20% of the active centers were destroyed in less than 3 h at 100 °C in ethylbenzene [42]. The apparent first-order rate constant for decomposition of poly(butadienyl)lithium in hexane was estimated to be $1.9 \times 10^{-5}$ s$^{-1}$ at 93 °C and a chain-end concentration of 2.2 milliequivalents of poly(butadienyl)lithium per 100 g of solution (25 wt% polymer) [103]. The corresponding first-order rate constant for chain-end decomposition of poly(isoprenyl)lithium at 93 °C was estimated to be $6.7 \times 10^{-5}$ s$^{-1}$ [103]. Although the differences are not large, the relative order of increasing stabilities of chain ends toward thermal degradation is poly(α-methylstyryl)lithium ≪ poly(styryl)lithium <poly(isoprenyl)lithium < poly(butadienyl)lithium as estimated by chain-end titration data.

Size-exclusion chromatography (SEC) analyses of the thermal decomposition products of poly(dienyl)lithiums in heptane at 80 °C have shown that the chain-end decomposition is accompanied by formation of species that have double and triple the molecular weight of the original living polymer [107]. After heating for 46 h at 80 °C in heptane, a 12 wt% yield of coupled products was observed for poly(isoprenyl)lithium; after heating for 27 h at 80 °C in heptane, a 19 wt% yield of coupled products was observed for poly(butadienyl)lithium. Scheme 7.14 illustrates the type of reactions proposed to explain the formation of dimeric products.

Evidence also suggests that athermal metalation of the backbone can occur as shown in Equation 7.24. It would be expected that this in-chain metalation



$$(7.24)$$

coupled with elimination of lithium hydride would lead to in-chain diene units which would have even more reactive allylic hydrogens for further metalation–elimination–coupling sequences that would promote thermal decomposition, branching, and ultimately gel formation.

PCH$_2$—CH$=$CH—CH$_2$Li $\xrightarrow{\text{Heat}}$ PCH$=$CH—CH$=$CH$_2$ + LiH
Active, uncoupled          Inactive, uncoupled

P'Li + PCH$=$CH—CH$=$CH$_2$ $\longrightarrow$ PCH—CH$=$CH—CH$_2$—P'
                                            |                Active, coupled
                                            Li

PCH—CH$=$CH—CH$_2$—P' $\xrightarrow{\text{Heat}}$ PCH$=$CH—CH$=$CH—P'
|          Active, coupled                    Inactive, coupled  + LiH
Li

**Scheme 7.14**  Proposed mechanism for thermal decomposition reactions for poly(butadienyl) lithium.

Polymeric organolithium compounds exhibit limited stability in ether solvents similar to alkyllithium compounds. Living carbanionic polymers react with ether solvents such as THF in a pseudo-first-order decay process and the rate decreases in the order Li > Na > K. For example, a $10^{-5}$ M solution of poly(styryl)lithium in THF at $25\,^\circ$C exhibited a rate of decay of a few percent per minute, but poly(styryl)cesium was found to be exceptionally stable [96]. Metalation and decomposition reactions can also occur in the presence of amines such as TMEDA.

### 7.4.1.4  *Chain Transfer Reactions*

Chain transfer reactions to polymeric organoalkali compounds can occur from solvents, monomers, and additives that have $pK_a$ values lower than or similar to those of the conjugate acid of the carbanionic chain end [3]. Relatively few monomers that undergo anionic polymerization exhibit chain transfer to monomer. Chain transfer has been well documented for the anionic polymerization of 1,3-cyclohexadiene. The chain transfer constant ($k_{tr}/k_p$) was calculated to be $2.9 \times 10^{-2}$ at $20\,^\circ$C and $9.5 \times 10^{-3}$ at $5\,^\circ$C in cyclohexane [29]. Although chain transfer would be expected for *p*-methylstyrene, controlled polymerizations can be effected when the temperature is maintained at room temperature or below. The observations of broad molecular weight distributions and a low molecular weight tail by SEC analysis have provided evidence for chain transfer during the anionic polymerization of *p*-isopropyl-$\alpha$-methylstyrene [108]. Significant chain transfer effects have also been reported for alkyllithium-initiated polymerizations using alkenes as solvents [3].

The kinetics of chain transfer to ammonia has been investigated for potassium amide-initiated polymerization of styrene in liquid ammonia at $-33.5\,^\circ$C. The calculated chain transfer constant ($k_{tr}/k_p$) was $2.34 \times 10^{-4}$ [109]. The chain transfer reaction of poly(styryl)lithium with toluene at $60\,^\circ$C was investigated during the polymerization of styrene using $^{14}$C-labeled toluene. The calculated chain transfer constant ($k_{tr}/k_p$) was $5 \times 10^{-6}$ [41]. A much larger chain transfer constant ($k_{tr}/k_p = 1.28 \times 10^{-4}$) was found for analogous transfer from toluene to poly(styryl)sodium. In general, alkyllithium-initiated anionic polymerizations of styrenes and dienes should not be carried out in toluene as

solvent because of the occurrence of chain transfer reactions [110]. Even after one day at $20\,^\circ$C, 13% of the PSLi undergoes chain transfer to toluene [110]. Ethylbenzene exhibits a chain transfer rate constant to PSLi of $2.2 \times 10^{-5}$ l/(mol s) [111].

Allenes and alkynes are regarded as impurities whose concentration cannot exceed certain minimum levels in monomer feed streams [112]. However, these same compounds, especially 1,2-butadiene, are also added as modifiers in alkyllithium-initiated diene polymerizations to prevent thermal branching at higher temperatures via chain termination and/or chain transfer reactions [3, 112–114]. Although these carbon acids can terminate chain growth, the ability of the resulting metalated chain transfer product to reinitiate chain growth has only been demonstrated for 1,2-butadiene [115].

Chain transfer reactions are promoted by Lewis bases. A chain transfer constant of 0.2 was reported for the telomerization of butadiene initiated by metallic sodium in a toluene/THF mixture at $40\,^\circ$C [116]. Such processes are used for the preparation of liquid rubbers (polybutadienes), with varying amounts of 1,2-microstructure depending on the type and amount of Lewis base, counterion, and temperature [117].

### 7.4.2  Polar Monomers

### 7.4.2.1  *Polar Vinyl Monomers*

The anionic polymerization of polar vinyl monomers is often complicated by side reactions of the monomer with both anionic initiators and growing carbanionic chain ends, as well as chain termination and chain transfer reactions. However, synthesis of polymers with well-defined structures can be effected under carefully controlled conditions. The anionic polymerizations of alkyl methacrylates and 2-vinylpyridine exhibit the characteristics of living polymerizations under carefully controlled reaction conditions and low polymerization temperatures to minimize or eliminate chain termination and transfer reactions [118, 119]. Proper choice of initiator for anionic polymerization of polar vinyl monomers is of critical importance to obtain polymers with predictable, well-defined structures. As an example of an initiator that is too reactive, the reaction of methyl methacrylate (MMA)

with $n$-butyllithium in toluene at $-78\,^{\circ}$C produces approximately 51% of lithium methoxide by attack at the carbonyl carbon [120].

### 7.4.2.2 Methyl Methacrylate

The most generally useful initiator for anionic polymerization of MMA and related compounds is 1,1-diphenylhexyllithium which is formed by the quantitative and facile addition of butyllithium with DPE (Eq. 7.13) [121]. Using this initiator in THF at $-78\,^{\circ}$C, it is possible to polymerize MMA to obtain homopolymers and block copolymers with predictable molecular weights and narrow molecular weight distributions. Controlled polymerizations are not effected in nonpolar solvents such as toluene, even at low temperatures [3, 118]. Other useful initiators for polymerization of MMA are oligomers of $\alpha$-methylstyryllithium whose steric requirements minimize attack at the ester carbonyl group in the monomer. These initiators are also useful for the polymerization of 2-vinylpyridine.

The principal termination reaction in the anionic polymerization of MMA is a unimolecular back-biting reaction with the penultimate ester group to form a six-membered ring, $\beta$-keto ester group at the chain end as shown in Equation 7.25. The rate of this back-biting reaction decreases with increasing size of the counterion [118].



$$(7.25)$$
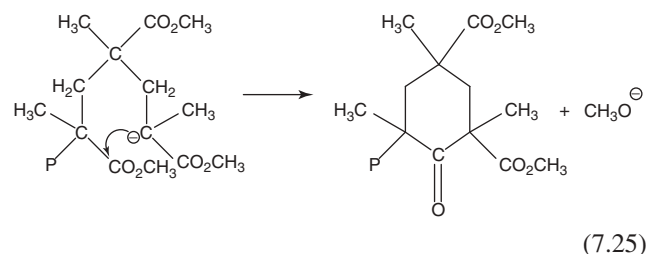
A dramatic development in the anionic polymerization of acrylate and methacrylate monomers was the discovery that by addition of lithium chloride it was possible to effect the controlled polymerization of $t$-butyl acrylate [122]. Thus, using oligomeric ($\alpha$-methylstyryl)lithium as initiator in THF at $-78\,^{\circ}$C, the molecular weight distribution ($M_w/M_n$) of the polymer was 3.61 in the absence of lithium chloride but 1.2 in the presence of lithium chloride ([LiCl]/[RLi] = 5). In the presence of 10 equivalents of LiCl, $t$-butyl acrylate was polymerized with 100% conversion and 95% initiator efficiency to provide a polymer with quite narrow molecular weight distribution ($M_w/M_n$ = 1.05). More controlled anionic polymerizations of alkyl methacrylates are also obtained in the presence of lithium chloride. Other additives that promote controlled polymerization of acrylates and methacrylates include lithium $t$-butoxide, lithium (2-methoxy)ethoxide, and crown ethers [79, 80]. The addition of lithium chloride also promotes the controlled anionic polymerization of 2-vinylpyridine [81].

The kinetics of anionic polymerization of MMA is complicated by chain-end association effects and the involvement of both free ions and ion pairs as propagating species. The propagating species, lithium ester enolates, are highly aggregated even in THF; association numbers range from 2.3 to 3.5 [123]. Because of chain-end association, a dependence of propagation rate constants on chain-end concentration has been observed for lithium and sodium counterions. The propagation rate constant for the free ions at $-75\,^{\circ}$C in THF is $4.8 \times 10^5$ l/(mol s) [124]. The propagation rate constant for ion pairs varies in the order Cs $\approx$ K $\approx$ Na $\gg$ Li. This is consistent with the conclusion that contact ion pairs are the predominant propagating species. The ion pair rate constants for lithium and potassium as counterions in THF at $-40\,^{\circ}$C are 100 and 750 l/(mol s), respectively [125].

The kinetic effects of lithium chloride on anionic polymerization of alkyl acrylates and methacrylates have been carefully examined [79, 80, 126, 127]. Added lithium chloride decreases the rate of propagation but has little effect on the rate of termination. In the absence of lithium chloride, free ions as well as associated and unassociated species can participate in the propagation event. By a common ion effect, the role of free ions is minimized by the addition of lithium chloride. In the absence of lithium chloride, the rate of interconversion between tetrameric aggregates, dimeric aggregates, and unassociated ion pairs is slow relative to the propagation, resulting in broader molecular weight distributions. Lithium chloride decreases the amount of aggregated species and forms cross-associated complexes with the lithium ester enolate ion pairs. Most importantly, the equilibration among these lithium chloride cross-aggregated species is fast relative to propagation so that narrow molecular weight distributions can be obtained.

### 7.4.2.3 Heterocyclic Monomers

A variety of heterocyclic monomers can be polymerized by anionic ring-opening polymerizations. The types of anionically polymerizable heterocyclic monomers include oxiranes (epoxides), thiacyclopropanes, thiacyclobutanes, lactones, lactides, lactams, anhydrides, carbonates, and silicones [128]. Among these heterocyclic monomers, the anionic polymerizations of epoxides have been examined most extensively.

*Ethylene Oxide*   The anionic polymerization of ethylene oxide is complicated by the association phenomenon and the participation of ion-pair and free ion intermediates in the propagation reactions [129, 130]. Simple lithium alkoxides are strongly associated into hexamers and tetramers even in polar media such as THF and pyridine [130]. As a consequence, lithium alkoxides are unreactive as initiators for the anionic polymerization of oxiranes. Association effects can be minimized by effecting polymerizations in alcohol media or in dipolar aprotic solvents.

KOH $+ n$ ⬡ $\longrightarrow$ HO—[CH$_2$CH$_3$O]—CH$_2$CH$_2$O$^{\ominus}$

HO—[CH$_2$CH$_3$O]—CH$_2$CH$_2$O$^{\ominus}$ + HOCH$_2$CH$_2$OCH$_2$CH$_2$OH $\rightleftharpoons$

HO—[CH$_2$CH$_3$O]—CH$_2$CH$_2$OH + HOCH$_2$CH$_2$OCH$_2$CH$_2$O$^{\ominus}$
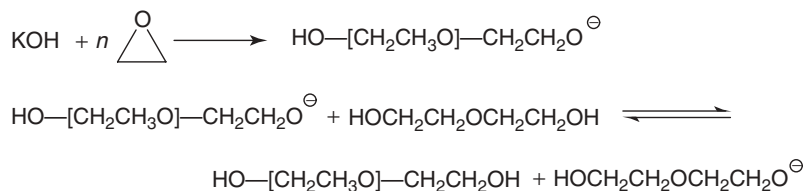
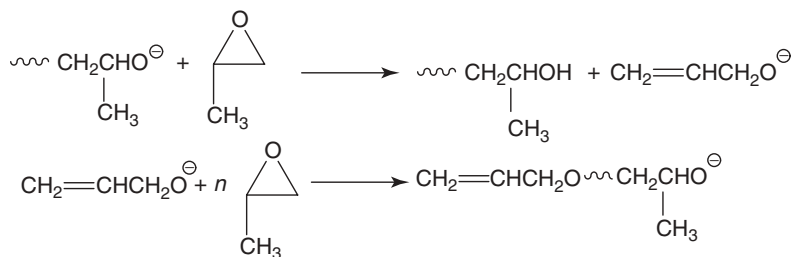**Scheme 7.15**    Reversible chain transfer in epoxide polymerizations.

The potassium hydroxide-initiated polymerization of ethylene oxide in alcoholic solvents such as diethylene glycol produces low molecular weight polyols (MW $\approx$ 600–700) with broad molecular weight distributions because of chain transfer reactions with alcohol that occur throughout the polymerization as shown in Scheme 7.15 [131]. "Living polymerizations with reversible chain transfer" [100] can be effected for alkoxide-initiated polymerizations of ethylene oxide in the presence of alcohol ([ROH]/[NaOR] $\approx$ 10) in solvents such as dioxane [132, 133]. Narrow molecular weight distributions are obtained because, although there is formally a chain transfer reaction between HO-ended polymers and alkoxide-ended polymers, the equilibrium between these two types of chain ends is rapid and reversible such that all chains participate uniformly in chain growth as described by Flory [13].

Association phenomena and the presence of both ion pairs and free ions as propagating species complicate the kinetics of sodium alkoxide-initiated polymerizations of ethylene oxide even in dipolar aprotic solvents such as HMPA ($\varepsilon = 26$). However, living polymerizations occur in dipolar aprotic solvents and in ethers such as THF, although the rates are much slower in ethers. The rates of propagation increase with increasing radius of the cation. The rates of propagation of ethylene oxide are also accelerated in the presence of cation complexing agents such as crown ethers and cryptands. Although the cryptated ion pairs are somewhat less reactive than the uncomplexed ion pairs, cryptands promote dissociation of the ion pairs to form free ions that are 70 times more reactive than the ion pairs [134]. Because of the concentrated charge on

oxygen, contact ion pairs predominate. The propagation rate constants in THF at 20 °C for the cesium ion pair and the free ion are 7.3 and 100 l/(mol s), respectively [134]. An optimized living polymerization procedure utilized $N$-carbazolylpotassium as initiator in THF at 20 °C in the presence of crown ether (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane); narrow molecular weight distribution polymers with controlled molecular weights as high as 266,000 g/mol could be obtained [135].

*Propylene Oxide*    The anionic ring-opening polymerization of propylene oxide is much slower than the analogous polymerization of ethylene oxide. The propagation rate constant at 40 °C in neat propylene oxide is $1.9 \times 10^{-4}$ l/(mol s) [136]. The anionic ring-opening polymerization of propylene oxide using hydroxide or alkoxide initiators is not a living polymerization. Chain transfer to monomer competes with propagation to limit the maximum molecular weight attainable and to broaden the molecular weight distribution as shown in Scheme 7.16. Thus, chains are formed that have the unsaturated allyloxy end groups.

The chain transfer constant $k_{tr}/k_p$ is approximately 0.01; thus, the molecular weight attainable is theoretically limited to approximately $6 \times 10^3$ g/mol [137]. However, molecular weights as high as 13,000 g/mol have been obtained for polymerization of neat propylene oxide with potassium as counterion in the presence of 18-crown-6 ether. Under these conditions, chain transfer constants as low as $0.08 \times 10^{-2}$ have been reported [138]. The addition of trialkylaluminum compounds to the alkali metal alkoxide/propylene oxide initiating system in hydrocarbon media accelerates the

CH$_2$CHO$^{\ominus}$ + ⬡ $\longrightarrow$ CH$_2$CHOH + CH$_2$=CHCH$_2$O$^{\ominus}$
|                                    |                |
CH$_3$          CH$_3$              CH$_3$

CH$_2$=CHCH$_2$O$^{\ominus}$ $+ n$ ⬡ $\longrightarrow$ CH$_2$=CHCH$_2$O∿CH$_2$CHO$^{\ominus}$
|                                                                    |
CH$_3$                                                    CH$_3$

**Scheme 7.16**    Chain transfer to monomer in propylene oxide polymerization.

polymerization rate and reduces the rate of chain transfer reactions, with attainment of molecular weights up to 20,000 g/mol [139]. This is due to the rapid equilibration between hydroxyl-ended chains and alkoxide-ended chains, which ensures uniform growth of all chains even after chain transfer as shown in Scheme 7.15 for the analogous polymerization of ethylene oxide.

However, chain transfer to monomer will still broaden the molecular weight distribution and prevent molecular weight control even when reversible chain transfer among growing species occurs. This rapid and reversible chain transfer is used to prepare branched polypropylene oxide polymers. Initiation of propylene oxide polymerization with an alkali metal alkoxide and a triol such as glycerol will produce the corresponding polypropylene oxide with an average functionality of 3.

The anionic polymerization of propylene oxide initiated by potassium alkoxide or hydroxide occurs predominantly (95%) by cleavage of the O–CH$_2$ bond. For bulk polymerization at 80 °C, approximately 4% head-to-head placements occur. However, there is no stereocontrol in this alkoxide-initiated ring opening and the resulting polymer is nontactic [140].

Chain transfer reactions to monomer occur with other homologs of propylene oxide. The reactivity of higher epoxides decreases as expected based on steric hindrance effects on nucleophilic attack at the oxirane carbons.

*Propylene Sulfide*   The anionic polymerization of propylene sulfide is a living polymerization that proceeds in the absence of termination and chain transfer [133]. The regiochemisry of addition corresponds to regular head-to-tail addition without detectable amounts of head-to-head or tail-to-tail additions. The polymer stereochemistry is nontactic. The kinetics of propagation of propylene sulfide initiated by carbazylsodium [p$K_a$ (DMSO) = 1.99] [2] in THF at chain-end concentrations <10$^{-3}$ M is not complicated by chain-end association effects. The reported propagation rate constants for contact ion pairs and free ions at −40 °C are 1 × 10$^{-3}$ and 1.7 l/(mol s), respectively [133]. The ion pair rate propagation constants increase rapidly with the size of the counterion and become higher than that of the free ion for all cryptated counterions. For example, the ion pair propagation rate constant for the corresponding [2.2.2]cryptate-solvated sodium thiolate (11.9 l/(mol s)) is more than 2 times larger than the corresponding free ion propagation rate constant (5.6 l/(mol s)) in THF at −39 °C [134]. A purportedly living anionic emulsion polymerization of propylene sulfide in water has been described [141]. Although quantitative chain-end functionalization was reported, the conversions reached limiting values and the observed $M_n$ values were much lower than the values expected from the feed ratio. The polydispersity ($M_w/M_n$)
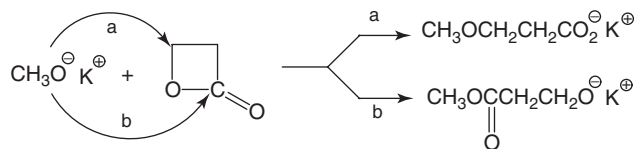


**Scheme 7.17**   Mechanism of initiation of β-propiolactone with methoxide anions.

values were 1.11–1.15. The initiating system consisted of 1,3-propanedithiol and equimolar diaza[5.4.0]bicycloundec-7-ene (DBU). A rather unusual initiation process, sulfur extrusion, has been reported for alkyllithium initiators; however, normal ring opening was reported for poly(styryl)lithium [142]. The low basicity but high nucleophilicity of thiolate chain ends promotes nucleophlic substitution reactions; however, dimerization readily occurs in the presence of oxygen.

*Lactones*
β-PROPIOLACTONE   The anionic polymerizations of the β-lactones and ε-lactones have been extensively investigated [143]. Living characteristics are observed for the polymerization of β-propiolactone using a dibenzo-18-crown-6 ether complex of sodium acetate as the initiator in dichloromethane [144]. Depending on the reactivity of the initiator, either acyl–oxygen cleavage or alkyl–oxygen cleavage can occur to form the corresponding alkoxide or carboxylate anions, respectively, as illustrated in Scheme 7.17 for initiation with potassium methoxide, which results in both modes of ring opening. Only alkyl–oxygen cleavage is observed for initiation with potassium acetate. Regardless of the initiator, all propagating species eventually become carboxylate anions because in subsequent propagation steps a fraction of the alkoxide anions are converted to carboxylate anions. Sterically hindered anions with high basicisity (e.g., $t$-butoxide) initiate with irreversible proton transfer from the ester enolate hydrogens of β-propiolactone [129, 145].

The kinetics of these polymerizations is complex. Both complexed ion pairs and free ions are involved in the propagation reactions and the free ion rate constants depend on monomer concentration. The relative reactivity of complexed ion pairs and free ions is temperature dependent. Above the inversion temperature of −35 °C, free ions are more reactive than ion pairs, but below this temperature the ion pairs are more reactive. At 30 °C in DMF, the observed (average) propagation rate constant is 0.13 l/(mol s) [146]. The anionic polymerization of α,α-dialkyl-β-propiolactones such as pivalolactone (α,α,-dimethyl-β-propiolactone) initiated with carboxylate anions exhibits the main characteristics of living polymerizations.

ε-CAPROLACTONE The anionic polymerization of ε-lactones, especially ε-caprolactone, is generally complicated by intramolecular cyclization reactions and redistribution reactions which prevent control of molecular weight and lead to broader molecular weight distributions [143]. Alkoxides, but not carboxylates, are active initiators for polymerization of ε-caprolactone, consistent with the identification of the alkoxide anion as the propagating species as shown in Equation 7.26. Chain-end association complicates the kinetics of



$$RO^{\ominus} + \quad \longrightarrow \quad ROC(CH_2)_4CH_2O^{\ominus} \qquad (7.26)$$
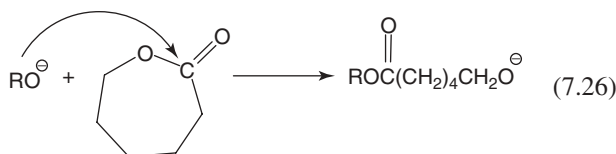
polymerization. Evidence for aggregation of lithium and sodium alkoxides, but not of potassium alkoxides, in THF has been found. The propagation rate constants in THF at $20\,^{\circ}C$ for the free ions and potassium ion pairs are $3.5 \times 10^2$ (mol s) and 4.8 l/(mol s), respectively [147]. The anionic polymerization of ε-caprolactone leads to the formation of a considerable amount of oligomers as by-products. In dilute solution (i.e., when the monomer unit concentration is <0.25 mol/l), no high polymer is formed [148]. In THF with potassium $t$-butoxide, the system consists of a living ring–chain equilibrium system; the monomer consumption is completed in minutes and entropy-controlled equilibrium is established quickly [148]. In bulk polymerization, more than one-third of the equilibrium distribution of products are oligomers which have been identified to be cyclic. Linear chains are formed initially and then cyclic oligomers are formed by a back-biting reaction of the active chain ends, see Equation 7.27 [143, 148]. This intermolecular transesterification leads to scrambling of the polymer molecular



$$(7.27)$$
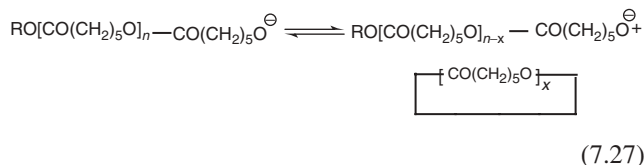
weight and a molecular weight distribution that broadens with time. Polymerizations with lithium as counterion in benzene minimize back-biting reactions at short reaction times (e.g., 3 min) [149].

*Cyclic Carbonates* Aliphatic cyclic carbonates such as 5,5-dimethyl-1,3-diox-2-one can be polymerized using alkyllithium compounds as initiators in hydrocarbon solution to high molecular weight polymers [150, 151]. Ring–chain equilibration is promoted at long reaction times and in THF as solvent. At $-10\,^{\circ}C$ in toluene,

*sec*-butyllithium-initiated polymerization of 5,5-dimethyl-1,3-diox-2-one proceeds via a lithium alkoxide propagating species to form high molecular weight polymer ($M_n \approx 100,000$ g/mol) with only small amounts of a cyclic oligomer fraction after 1 h as shown in Equation 7.28.



$$(7.28)$$
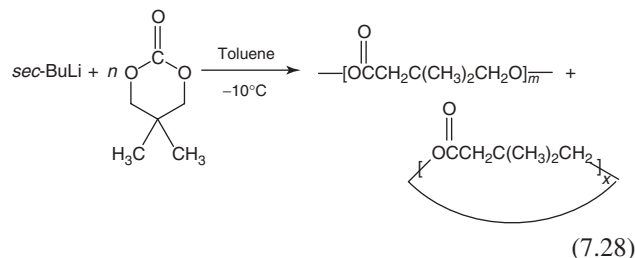
Efficient methods for the synthesis of cyclic bisphenol-A polycarbonates have provided a practical technology for the rapid synthesis of high molecular weight bisphenol-A polycarbonates by anionic ring-opening polymerization as shown in Equation 7.29 [150]. A mixture of cyclic oligomers ($M_w \approx 1300$) was polymerized with lithium stearate for 0.5 h at $300\,^{\circ}C$ to yield the corresponding linear polymer with $M_w = 300,000$ g/mol and $M_w/M_n = 2.4$ [152]. Rapid chain–chain equilibration occurs under these conditions. Other useful anionic polymerization initiators include lithium phenoxide, lithium phenylacetate, and sodium benzoate. Diphenylcarbonate can be used as a chain transfer agent to control the molecular weight.



$$(7.29)$$
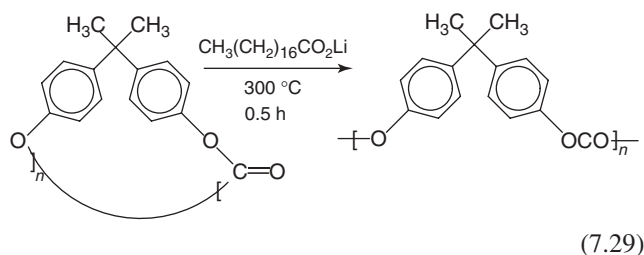
*Siloxanes* A variety of bases, for example, hydroxides, alkoxides, phenolates, and silanolates, are effective initiators for the anionic polymerization of hexamethyl cyclotrisiloxane ($D_3$) and octamethyl cyclotetrasiloxane ($D_4$) [153]. The heat of polymerization for the cyclic oligomers in the series from the tetramer ($D_4$) to the decamer ($D_{10}$) is approximately zero and the only driving force is a small positive entropy (circa 1.4 cal/mol (SiO groups) K) [153]. The trimer, $D_3$, is unique in having a slightly exothermic heat of polymerization (3.5 kcal/mol) [154]. The growing polymer for $D_4$ polymerization is in equilibrium with the monomer (2% at $140\,^{\circ}C$) as well as with various kinds of oligomers and cyclic polymers (10–15%); a Gaussian distribution of linear polymers is obtained. The concentrations of each of the various cyclics ($n > 15$) are in accord with the Jacobsen–Stockmayer cyclization theory
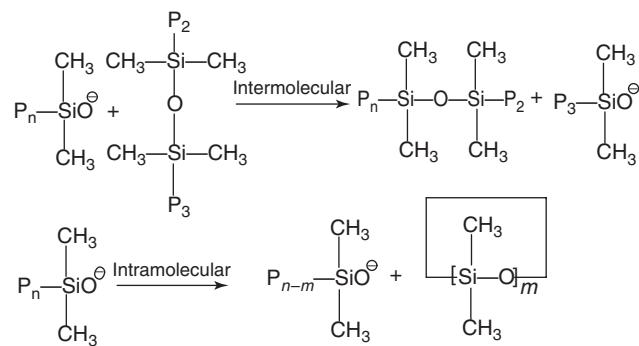
**Scheme 7.18**  Intermolecular and intramolecular exchange reactions in siloxane polymerizations.
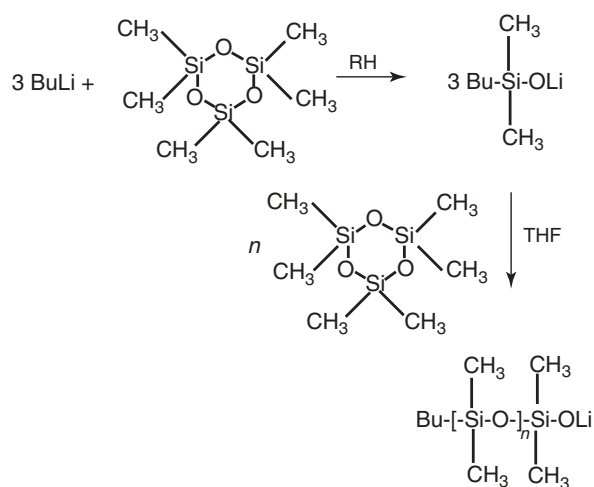


**Scheme 7.19**  Living polymerization of $D_3$.

[155]. The mechanism of polymerization can be described as an equilibration among these various components; in addition to reaction with the monomer, the growing silanolate chain ends react with all siloxane bonds via intramolecular cyclization and intermolecular chain transfer as shown in Scheme 7.18.

In contrast to the polymerization of $D_4$, the anionic polymerization of hexamethyl cyclotrisiloxane ($D_3$) with lithium as counterion is a living polymerization which produces polydimethylsiloxanes with well-defined structures. Useful initiators include lithium silanolates or the product from the reaction of 3 mol of butyllithium with $D_3$ in a hydrocarbon solvent as shown in Scheme 7.19. It is noteworthy that no polymerization occurs in the absence of a Lewis base promoter such as THF, glymes, DMSO, or HMPA.

The kinetics of polymerization of cyclosiloxanes is complicated by chain-end association. Complexation of counterions with cryptands disrupts the aggregates. For the lithium [2.1.1] cryptand complex in aromatic solvent at 20 °C, the propagation rate constants for $D_3$ and $D_4$ are 1.4 and $4 \times 10^{-3}$ l/(mol s), respectively [134].

## 7.5  STEREOCHEMISTRY

### 7.5.1  Polydienes

***7.5.1.1  Hydrocarbon Solvents***  One of the most important synthetic and commercial aspects of anionic polymerization is the ability to prepare polydienes [poly(1,3-dienes)] with high 1,4-microstructure using lithium as the counterion in hydrocarbon solutions [3, 156]. The key discovery was reported in 1956 by scientists at the Firestone Tire and Rubber Company that polyisoprene produced by lithium metal-initiated anionic polymerization had a high (>90%) *cis*-1,4-microstructure similar to natural rubber [47]. In general, conjugated 1,3-dienes [$CH_2$=$C(R)$–$CH$=$CH_2$] can polymerize to form four constitutional isomeric microstructures as shown below. The stereochemistry of the anionic polymerization of isoprene and
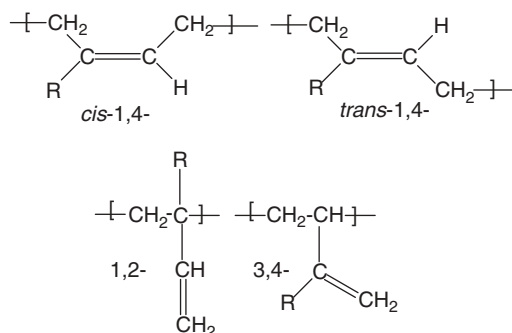


R = H (butadiene,1,2- = 3,4); R = CH_3 (isoprene)

butadiene depends on the counterion, monomer concentration, chain-end concentration, solvent, temperature, and the presence of Lewis base additives. The effect of counterion on polyisoprene stereochemistry is illustrated by the data in Table 7.3, which shows that lithium is unique among alkali metal counterions in producing polyisoprene with high 1,4 microstructure. Similar results have been reported for the stereochemistry of the anionic polymerization of butadiene except that the stereochemistry with lithium as the counterion in neat isoprene is 94% *cis*-1,4 and 6% 3,4 compared with 35% *cis*-1,4, 52% *trans*-1,4, and 13% 1,2 for analogous polymerization of butadiene. From the data in Table 7.4, it is possible to delineate the effects of monomer concentration, chain-end concentration, and solvent. The highest *cis*-1,4-microstructures are obtained in the absence of solvent, that is, with neat monomer, at low concentrations of initiator (circa $10^{-6}$ M). High *cis*-1,4 enchainment is also

**TABLE 7.3   Effect of Counterion on Polyisoprene Microstructure for Neat Polymerizations [157, 158]**

| Microstructure | Temperature (°C) | 1,4-*cis* | 1,4-*trans* | 1,2 | 3,4 |
|---|---|---|---|---|---|
| Lithium | 25 | 94 | — | — | 6 |
| Sodium | 25 | — | 45 | 7 | 48 |
| Potassium | 25 | — | 52 | 8 | 40 |
| Rubidium | 25 | 5 | 47 | 8 | 39 |
| Cesium | 25 | 4 | 51 | 8 | 37 |

**TABLE 7.4   Microstructure of Polydienes in Hydrocarbon Media using Organolithium Initiators [159–162]**

| Initiator Concentration (M) | Solvent | Temperature (°C) | 1,4-cis | 1,4-trans | 3,4 |
|---|---|---|---|---|---|
| *Polyisoprene* | | | | | |
| $6 \times 10^{-3}$ | Heptane | −10 | 74 | 18 | 8 |
| $1 \times 10^{-4}$ | Heptane | −10 | 84 | 11 | 5 |
| $8 \times 10^{-6}$ | Heptane | −10 | 97 | — | 3 |
| $5 \times 10^{-6}$ | Heptane | 25 | 95 | 2 | 3 |
| $9 \times 10^{-3}$ | Benzene | 20 | 69 | 25 | 6 |
| $5 \times 10^{-6}$ | Benzene | 25 | 72 | 20 | 8 |
| $1 \times 10^{-2}$ | Hexane | 20 | 70 | 25 | 5 |
| $1 \times 10^{-5}$ | Hexane | 20 | 86 | 11 | 3 |
| $3 \times 10^{-3}$ | None | 20 | 77 | 18 | 5 |
| $8 \times 10^{-6}$ | None | 20 | 96 | — | 4 |

| Initiator Concentration (M) | Solvent | Temperature (°C) | 1,4-cis | 1,4-trans | 1,2 |
|---|---|---|---|---|---|
| *Polybutadiene* | | | | | |
| $8 \times 10^{-6}$ | Benzene | 20 | 52 | 36 | 12 |
| $5 \times 10^{-1}$ | Cyclohexane | 20 | 53* | 53* | 47 |
| $1 \times 10^{-5}$ | Cyclohexane | 20 | 68 | 28 | 4 |
| $3 \times 10^{-2}$ | Hexane | 20 | 30 | 60 | 8 |
| $2 \times 10^{-5}$ | Hexane | 20 | 56 | 37 | 7 |
| $3 \times 10^{-3}$ | None | 20 | 39 | 52 | 9 |
| $5 \times 10^{-6}$ | None | 20 | 86 | 9 | 5 |

*Total 1,4-content (cis + trans).

favored by the use of aliphatic versus aromatic solvents at low concentrations of initiator; however, the total amount of 1,4-microstructure (cis +trans) is relatively insensitive to solvent and chain-end concentration. In general, temperature is not an important variable for polydienes prepared in hydrocarbon solutions with lithium as the counterion.

A comprehensive hypothesis has been proposed to explain the effects of the concentrations of active chain ends and monomer on polydiene microstructure [163]. Based on studies with model compounds and the known dependence of polydiene microstructure on diene monomer (D) and chain-end concentrations as shown in Table 7.4,
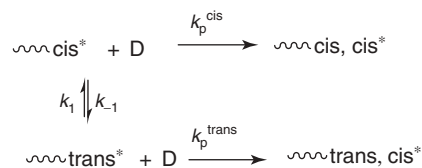


**Scheme 7.20**  Proposed mechanism for diene microstructure control.

the mechanistic hypothesis shown in Scheme 7.20 was advanced.

It was proposed that isomerization of the initially formed cis form of the active chain end occurs competitively with monomer addition at each step of the reaction [163, 159]. Thus, when the concentration of monomer is high relative to the chain-end concentration, the first-order isomerization of the cis form does not compete effectively with monomer addition. However, at low concentrations of monomer relative to chain ends, the isomerization does compete and significant amounts of the trans form will be in equilibrium with the cis form.

The kinetic order dependence on the active chain-end concentration is approximately 0.25 for diene propagation, while the kinetic order dependence on the active chain end concentration is approximately 1.0 for cis–trans isomerization of the chains ends [3, 56]. Thus, while the unassociated chain ends add monomer, isomerization of the chain ends occurs in the aggregated state. Since aggregation is favored by increasing chain-end concentrations, high 1,2-microstructure is observed (47% for butadiene) for high chain-end concentrations ([PBDLi] = circa 0.1 M) and high *cis*-1,4 microstructure (86% for butadiene) is obtained at low chain-end concentrations (circa $10^{-6}$M; Table 7.4).

The microstructure of anionic polymerization of other poly(1,3-diene)s with lithium as counterion in hydrocarbon media is also predominantly 1,4 microstructure [3]. However, higher amounts of *cis*-1,4-microstructures are obtained with more sterically hindered diene monomers. Thus, using conditions that provide polyisoprene with 70% *cis*-1,4, 22% *trans*-1,4, and 7% 3,4 microstructure, 2-*i*-propyl-1,3-butadiene and 2-*n*-propyl-1,3-butadiene provide 86% and 91% *cis*-1,4 enchainment, respectively. Both 2-phenyl-1,3-butadiene (92% *cis*-1,4) and 2-(triethylsilyl)-1,3-butadiene (100% *cis*-1,4) also exhibit high *cis*-1,4-enchainment.

***7.5.1.2  Polar Solvents and Polar Additives***  In polar media, the unique high 1,4-stereospecificity with lithium as counterion that is observed in hydrocarbon media is lost and large amounts of 1,2-polybutadiene and 3,4-polyisoprene enchainments are obtained [3, 156]. There is a tendency toward higher 1,4-content with increasing size of the counterion in polar media. The highest 1,2-content

in polybutadiene and the highest amounts of 1,2 and 3,4 enchainments in polyisoprene are obtained with lithium and sodium [156]. In THF at $0\,^\circ$C, 88% 1,2-enchainment is reported with lithium as counterion [156, 164]. The highest 1,4-enchainments are observed for cesium as counterion in polar media. Higher 1,4-contents are also obtained in less polar solvents such as dioxane. For example, with cesium as counterion, 60% 1,4-content is obtained in dioxane [156]. The use of polar solvents is generally not practical because of the instability of the polymeric carbanions in these media and because of the lack of control of diene microstructure.

It is more common to add polar modifiers as additives in anionic polymerizations.

Small amounts of Lewis base additives in hydrocarbon media can exert dramatic effects on polydiene microstructure as shown by the data in Table 7.5 [165–167]. Lewis bases that interact most strongly with lithium produce the highest amount of 1,2-microstructure. For example, there is a correlation between the enthalpies of interaction of Lewis bases with polymeric organolithium compounds and the ability of these bases to promote 1,2-enchainment [168]. The highest vinyl contents for polybutadiene are obtained with the most strongly coordinating ligands such as the bidentate bases, TMEDA and bispiperidinoethane (DIPIP). To obtain significant amounts of vinyl microstructure with weak donor-type bases such as diethyl ether and triethylamine, they must be present in large amounts relative to lithium. In contrast, the strongly coordinating bases produce high vinyl polybutadiene microstructure at low base to lithium atom ratios (R = [base]/[Li] = 1 − 2).

**TABLE 7.5   Effects of Temperature and Concentration of Lewis Base on Vinyl Content of Polybutadiene in Hexane [171–173]**

| Base | [Base]/[Li] | \% 1,2 Microstructure | | | |
|---|---|---|---|---|---|
| | | $5\,^\circ$C | $30\,^\circ$C | $50\,^\circ$C | $70\,^\circ$C |
| Triethylamine | 30 | — | 21 | 18 | 14 |
| | 270 | — | 37 | 33 | 25 |
| Diethyl ether | 12 | — | 22 | 16 | 14 |
| | 180 | — | 38 | 29 | 27 |
| Tetrahydrofuran | 5 | — | 44 | 25 | 20 |
| | 85 | — | 73 | 49 | 46 |
| Diglyme | 0.1 | — | 51 | 24 | 14 |
| | 0.8 | — | 78 | 64 | 40 |
| TMEDA* | 0.6 | — | 73 | 47 | 30 |
| | 0.4 | 78 | — | — | — |
| | 6.7 | 85 | — | — | — |
| | 1.14 | — | 76 | 61 | 46 |
| DIPIP† | 0.5 | 91 | 50 | 44 | 21 |
| | 1 | 99.99 | 99 | 68 | 31 |

*$N,N,N',N'$-Tetramethylethylenediamine
†Bispiperidinoethane

An important feature of the effect of Lewis base additives on diene microstructure is the fact that the amount of vinyl microstructure generally decreases with increasing temperature as shown in Table 7.5 [3, 165, 169]. A simple explanation for the temperature dependence of vinyl microstructure, compared to the lack of dependence of microstructure in hydrocarbon media with lithium as counterion, is that high vinyl microstructure is associated with the addition of monomer to a base-coordinated chain end ($\alpha$-carbon) and this base coordination is reversed (less favorable) at higher temperatures. The sensitivity of the microstructure to polymerization temperature depends on the Lewis base and the $R$ value ([base]/[Li]) as shown in Table 7.5. Although the strongly chelating bidentate bases promote 1,2-polybutadiene microstructure at low temperatures, they generally exhibit a dramatic decrease in their ability to promote vinyl microstructure at elevated temperatures as shown in Table 7.5. This temperature dependence presents a particular problem in high temperature processes, for example, commercial batch or continuous processes, in which medium vinyl polybutadienes are desired [3].

The ability to prepare polydienes with variable microstructures is an important aspect of alkyllithium-initiated anionic polymerization. The main consequence of the change in microstructure is that the glass transition temperatures of the corresponding polymers are higher for polymers with more side-chain vinyl microstructure. For example, the glass transition temperature of polybutadiene is an almost linear function of the percent 1,2 configuration in the chain [170]. Thus, while cis-1,4-polybutadiene has a glass transition temperature of $-113\,^\circ$C, 1,2-polybutadiene has a glass transition temperature of $-5\,^\circ$C [171]. This has practical consequences because polybutadienes with medium vinyl contents (e.g., 50%) have glass transition temperatures (ca. $-60\,^\circ$C) and properties that are analogous to those of SBR (styrene-butadiene rubber). Analogously, the glass transition temperature of cis-1,4-polyisoprene is circa $-71\,^\circ$C, while a polyisoprene with 49% 3,4-enchainment exhibited a $T_g$ of $-36\,^\circ$C [172].

### 7.5.2   Methacrylate Stereochemistry

Like the anionic polymerization of dienes, the anionic polymerization of alkyl methacrylates, especially MMA, is dependent on the counterion, solvent, and, to a certain extent, temperature [156, 173, 121]. In general, the stereochemistry of the anionic polymerization of alkyl methacrylates in toluene solution with lithium as the counterion is highly isotactic (68–99% mm) and the isotacticity increases with the steric requirements of the alkyl ester. For example 90% mm triads are obtained for $t$-butyl methacrylate at $-70\,^\circ$C in toluene [174], while 68% mm triads are observed for MMA [120]. Isospecificity for polymerizations in toluene

is also observed for alkyl sodium initiators (67% mm) [175] but not for potassium or cesium alkyls in toluene [176]. Sterically hindered Grignard reagents, in particular *t*-butylmagnesium bromide or isobutylmagnesium bromide prepared in ether, provide controlled living polymerizations and highly isotactic polymers (96.7% and 92.5% mm, respectively), provided that excess magnesium bromide is present to shift the Schlenk equilibrium, Equation 7.30, in favor of RMgBr [177]. In contrast, using

$$R_2Mg + MgX_2 \rightleftharpoons 2RMgX \qquad (7.30)$$
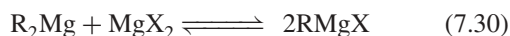
di-*t*-butylmagnesium, prepared in ether, poly(methyl methacrylate) (PMMA) was obtained with predominantly syndiotactacity (79% rr) [177]. Highly isotactic PMMA is obtained for ether-free dibenzylmagnesium-initiated polymerization in toluene [178]. Ate-type complexes of *t*-butyllithium with trialkylaluminums ([Al]/[Li] $\geq$ 3) effect living and highly syndiotactic ($\geq$90% rr) polymerization of MMA in toluene [179]. Analogous complexes of *t*-butyllithium with (2,6-di-*t*-butyl-4-methylphenoxy)-diisobutylaluminum ([Al]/[Li] $\geq$ 1) at 0 °C in toluene generate PMMA with predominantly syndiotactic placements (71–75% rr) [180]. In contrast, the ate complex of *t*-butyllithium with bis(2,6-*di*-*t*-butylphenoxy) methylaluminum forms predominantly heterotactic PMMA (67.8% mr) and poly(ethyl methacrylate) (87.2% mr at −78 °C; 91.6% mr at −95 °C) [181].

In polar media, highly syndiotactic PMMA is formed for free ions and with lithium and sodium as counterions; for sodium, syndiospecificity is observed only in more polar solvents such as dimethyoxyethane or in the presence of strongly solvating ligands such as cryptands [182–186]. Lithium is the smallest alkali metal cation and the most strongly solvated; the equilibrium constants for formation of free ions and solvent-separated ion pairs are largest for lithium and smallest for cesium. Since cesium and potassium have a tendency to form 52% heterotactic placements [187, 188], it is proposed that contact ion pairs result in predominantly heterotactic placements whereas solvent-separated ion pairs and free ions form predominantly syndiotactic placements in polar media. These results are general for a variety of alkyl methacrylates; even diphenylmethyl methacrylate gives 87% syndiotactic triads in THF with lithium as counterion at −78 °C [173]. However, the exception is trityl methacrylate, which forms 94% isotactic triads under the same conditions and also 96% isotactic triads in toluene.

A variety of stereoregulating mechanisms have been invoked to explain the stereochemistry of anionic polymerization of alkyl methacrylates. As discussed by Pino and Suter [189], although syndiotactic diads are thermodynamically slightly more favored over isotactic diads, the free energy differences are so small that the formation of stereoregular

chains must be kinetically controlled. Since only limited tools are available to predict or understand the physical and chemical basis of such factors as solvation, particularly those associated with small energy differences of this order of magnitude, it is prudent to limit phenomenological interpretations of these stereochemical effects. Thus, any explanation of the predominantly syndiotactic polymerization stereochemistry in THF with lithium as the counterion (84% rr at −85 °C ) is tempered by the fact that the stereochemistry for the free-radical polymerization of MMA is also highly syndiotactic (78.5% at −55 °C) [121]. Many factors such as polar monomer coordination and interaction of the counterion with the chain end with the penultimate groups have been invoked to explain the formation of isotactic polymers in nonpolar media. The coordination of the penultimate ester group with the lithium ester enolate group at the chain end would dictate a meso placement. This simple picture, however, does not take into account the fact that these lithium ester enolates are highly associated in hydrocarbon solutions and in polar media such as THF [118, 119, 123].

The control of PMMA stereochemistry is important because the glass transition temperature of PMMA strongly depends on the microstructure [121]. The measured $T_g$ for 99% mm PMMA is reported to be 50 °C, and that for PMMA with 96–98% r diads is 135 °C. To obtain PMMA with higher upper use temperature, polymers with the highest syndiotactic microstructure are desired; hence the interest in developing anionic systems for MMA at higher temperatures [118, 119, 190].

### 7.5.3 Styrene

The stereoregularity of polystyrenes prepared by anionic polymerization is predominantly syndiotactic (racemic diad fraction ($P_r = 0.53$–0.74) and the stereoregularity is surprisingly independent of the nature of the cation, the solvent, and the temperature, in contrast to the sensitivity of diene stereochemistry to these variables [3, 156]. The homogeneous alkyllithium-initiated polymerization of styrene in hydrocarbon media produces polystyrene with an almost random (i.e., *atactic*) microstructure; for example, $P_r$ was 0.53 for the butyllithium/toluene system [3, 191, 192]. A report on the effect of added alkali metal alkoxides showed that polystyrene stereochemistry can be varied from 64% *syndiotactic* triads with lithium *t*-butoxide to 58% *isotactic* triads with potassium *t*-butoxide [193].

When small amounts of water were deliberately added to butyllithium in hydrocarbon solutions, it was possible to prepare polystyrene with as much as 85% polymer that was insoluble in methyl ethyl ketone under reflux and identified as *isotactic* polystyrene by X-ray crystallography [194, 195]. Isotactic polystyrene (10–22% crystalline) can be prepared when lithium *t*-butoxide is

added to *n*-BuLi initiator and the polymerization in hexane (styrene/hexane = 1) is effected at −30 °C [196]. This polymerization becomes heterogeneous and is quite slow (after 2–5 days, 50% monomer conversion; 20–30% conversion to isotactic polymer).

### 7.5.4 Vinylpyridines

The stereochemistry of anionic polymerization of 2-vinylpyridine is predominantly isotactic for most polymerization conditions [197]. The coordination of the penultimate pyridyl nitrogen with the magnesium pyridylamide at the chain end has been invoked to explain the high meso triad content for initiation by Grignard-type reagents in hydrocarbon solution. The absence of this interaction for 4-vinylpyridine results in almost *atactic* polymer stereochemistry.

### 7.6 COPOLYMERIZATION OF STYRENES AND DIENES

Relatively few comonomer pairs undergo anionic copolymerization to incorporate significant amounts of both monomers into the polymer chains [3, 45]. In general, the comonomer that is most reactive (lowest $pK_a$ value for the conjugate acid of the propagating anion) [2] will be incorporated to the practical exclusion of the other comonomer. Comonomer pairs that can be effectively copolymerized include styrenes with dienes and methacrylates with acrylates, that is, comonomer pairs with similar reactivity.

Anionic copolymerizations have been investigated by applying the classical Mayo–Lewis treatment which was originally developed for free-radical chain reaction polymerization [198]. The copolymerization of two monomers ($M_1$ and $M_2$) can be uniquely defined by the following the four elementary kinetic steps in Scheme 7.21, assuming that the reactivity of the chain end ($M_1^-$ or $M_2^-$) depends only on the last unit added to the chain end, that is, there are no penultimate effects.

From these four basic kinetic equations, the Mayo–Lewis instantaneous copolymerization equation can be derived, Equation 7.31 (see also Chapter 6):

$$\frac{d\,[M_1]}{d\,[M_2]} = \frac{[M_1]\,(r_1\,[m_1] + [m_2])}{[M_2]\,(r_2\,[m_2] + [m_1])} \quad (7.31)$$

where $r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{21}$, and $d[M_1]/d[M_2]$ represents the instantaneous copolymer composition. The monomer reactivity ratios $r_1$ and $r_2$ represent the relative reactivity of each growing chain end for addition of the same monomer compared to crossover to the other monomer. Representative monomer reactivity ratios for anionic copolymerizations are listed in Table 7.6. The applicability of standard copolymerization theory to anionic

**TABLE 7.6  Anionic Copolymerization Parameters in Hydrocarbon Solution with Alkyllithium Initiators [45, 56, 199–205]**

| $M_1$ | $M_2$ | Solvent | °C | $r_1$ | $r_2$ |
|---|---|---|---|---|---|
| Butadiene | Styrene | None | 25 | 11.2 | 0.04 |
| | | Benzene | 25 | 10.8 | 0.04 |
| | | Cyclohexane | 25 | 15.5 | 0.04 |
| | | Hexane | 0 | 13.3 | 0.03 |
| | | | 50 | 11.8 | 0.04 |
| | | THF | −78 | 0.04 | 11.0 |
| | | | 25 | 0.3 | 4.0 |
| | | Diethylether | 25 | 1.7 | 0.4 |
| | | Triethylamine | 25 | 3.5 | 0.5 |
| | | Anisole | 25 | 3.4 | 0.3 |
| | Isoprene | Hexane | 20 | 2.72 | 0.42 |
| | | THF | 0 | 0.13 | ∼0 |
| Isoprene | Styrene | Benzene | 30 | 7.7 | 0.13 |
| | | Toluene | 27 | 9.5 | 0.25 |
| | | Cyclohexane | 40 | 16.6 | 0.046 |
| | | THF | 27 | 0.1 | 9 |
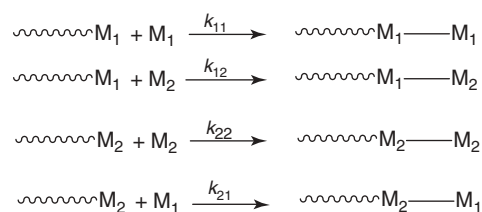


**Scheme 7.21**

polymerization has been considered in detail. The four equations in Scheme 7.21 represent an oversimplification since the chain ends are aggregated in hydrocarbon solution and there is a spectrum of ion pairs and free ions in polar media, see Equation 7.2.

In most copolymerizations, $r_1 \neq r_2$ and one monomer is preferentially incorporated into the initially growing polymer. This leads to a depletion of the preferentially incorporated monomer in the feed and the composition of the copolymer formed changes with conversion. For systems undergoing continuous initiation, propagation, and termination, the resulting compositional heterogeneity is intermolecular, that is, the copolymer formed initially has a different composition from the copolymer formed at the end of the reaction. However, in living anionic copolymerization, all of the compositional heterogeneity arising from the disparity in monomer reactivity ratios is incorporated into each growing polymer chain.

### 7.6.1 Tapered Block Copolymers

The alkyllithium-initiated copolymerizations of styrene with dienes, especially isoprene and butadiene, have been

extensively investigated, and illustrate the important aspects of anionic copolymerization. As shown in Table 7.6, monomer reactivity ratios for dienes copolymerizing with styrene in hydrocarbon solution range from approximately 9 to 15, while the corresponding monomer reactivity ratios for styrene vary from 0.04 to 0.25. Thus, butadiene and isoprene are preferentially incorporated into the copolymer initially. This type of copolymer composition is described as either a *tapered block copolymer* or a *graded block copolymer*. The monomer sequence distribution can be described by the structures below:

$$-[D]_n-[D/S]-[S]_m-   \qquad   -[D]_n-[D \rightarrow S]-[S]_m-$$

First, there is a diene-rich block; a middle block follows which is initially richer in butadiene with a gradual change in composition until eventually it becomes richer in styrene; a final block of styrene completes the structure.

For a typical copolymerization of styrene and butadiene (25/75, wt/wt), the solution is initially almost colorless, corresponding to the dienyllithium chain ends, and the rate of polymerization is slower than the hompolymerization rate of styrene. The homopolymerization rate constants for styrene, isoprene, and butadiene are $1.6 \times 10^{-2}$(l/mol)$^{1/2}$/s, $1.0 \times 10^{-3}$(l/mol)$^{1/4}$/s, and $2.3 \times 10^{-4}$(l/mol)$^{1/4}$/s, respectively [56]. After approximately 70–80% conversion, the solution changes to orange-yellow, which is characteristic of styryllithium chain ends. At the same time, the overall rate of polymerization increases (inflection point). Although the percent conversion at which the inflection point is observed does not appear to depend on the solvent, the time to reach this percent conversion is quite solvent dependent. Analysis of the copolymer composition indicates that the total percentage of styrene in the copolymer is less than 5% up to approximately 75% conversion [55]; these incorporated styrene units exist predominantly as isolated sequences [206]. When these samples are analyzed by oxidative degradation by ozonolysis, polystyrene segments (corresponding to polystyrene blocks in the copolymer) are recovered only after the inflection point is reached [206]. For a 75/25 (wt/wt) feed mixture of butadiene/styrene, 72% of the styrene is incorporated into the tapered block copolymer as block styrene [207, 208].

The kinetics of copolymerization provides a partial explanation for the copolymerization behavior of styrenes with dienes. One useful aspect of living anionic copolymerizations is that stable carbanionic chain ends can be generated and the rates of their crossover reactions with other monomers measured independently of the copolymerization reaction. Two of the four rate constants involved in copolymerization correspond at least superficially to the two homopolymerization reactions of butadiene and styrene, for example, $k_{BB}$ and $k_{SS}$, respectively. The other

two rate constants can be measured independently as shown in Equations 7.32 and 7.33.

$$\text{PSLi} + \text{butadiene} \xrightarrow{k_{SB}} \text{PS–BDLi} \qquad (7.32)$$

$$\text{PBDLi} + \text{styrene} \xrightarrow{k_{BS}} \text{PBD–SLi} \qquad (7.33)$$
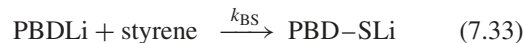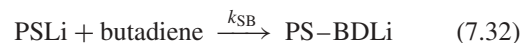
Results of a number of independent kinetic studies can be summarized as follows for styrene-butadiene copolymerization [56, 209]:

$$k_{SB} > k_{SS} > k_{BB} > k_{BS}$$
$$\left(1.1 \times 10^{2}\text{l}/\left(\text{mol s}\right)\right) >> \left(4.5 \times 10^{-1}\text{l}/\left(\text{mol s}\right)\right)$$
$$> \left(8.4 \times 10^{-2}\text{l}/\left(\text{mol s}\right)\right) > \left(6.6 \times 10^{-3}\text{l}/\left(\text{mol s}\right)\right)$$

The surprising result is that the fastest rate constant is associated with the crossover reaction of the poly(styryl)lithium chain ends with butadiene monomer ($k_{SB}$); conversely, the slowest reaction rate is associated with the crossover reaction of the poly(butadienyl)lithium chain ends with styrene monomer ($k_{BS}$). Similar kinetic results have been obtained for styrene-isoprene copolymerization [204].

In polar media, the preference for preferential diene incorporation is reduced as shown by the monomer reactivity ratios in Table 7.6. In THF, the order of monomer reactivity ratios is reversed compared to hydrocarbon media. The monomer reactivity ratios for styrene are much larger than the monomer reactivity ratio for dienes.

The counterion also has a dramatic effect on copolymerization behavior for styrene and dienes [61]. It is particularly noteworthy that the monomer reactivity ratios for styrene ($r_S = 0.42$) and butadiene ($r_B = 0.30$) are almost equal for copolymerization in toluene at $20\,^{\circ}$C using a hydrocarbon-soluble organosodium initiator 2-ethylhexylsodium [210, 211]. Thus, an alternating-type copolymer structure ($r_S r_B = 0.126$) would be formed for this system; however, butadiene is incorporated predominantly as vinyl units (60% 1,2). In contrast, initial preferential styrene incorporation ($r_S = 3.3$; $r_B = 0.12$) is observed for an analogous organopotassium initiator, the DPE adduct of 2-ethylhexylpotassium [61].

Tapered butadiene-styrene copolymers are important commercial materials because of their outstanding extrusion characteristics, low water absorption, good abrasion resistance, and good electrical properties. Tapered block copolymers are used for wire insulation and shoe soles (after vulcanization) as well as for asphalt modification [3].

### 7.6.2 Random Styrene-Diene Copolymers (SBR)

Random copolymers of butadiene (SBR) or isoprene (SIR) with styrene can be prepared by addition of small

amounts of ethers, amines, or alkali metal alkoxides with alkyllithium initiators in hydrocarbon solution. Random copolymers are characterized as having only small amounts of block styrene content. The amount of block styrene can be determined by ozonolysis [206] or more simply by integration of the $^1$H NMR region corresponding to block polystyrene segments ($\delta = 6.50$–$6.94$ ppm) [212]. Monomer reactivity ratios of $r_B = 0.86$ and $r_B = 0.91$ have been reported for copolymerization of butadiene and styrene in the presence of 1 equivalent of TMEDA, [TMEDA]/[RLi] = 1) [212]. However, the random SBR produced in the presence of TMEDA will incorporate the butadiene predominantly as 1,2-units. At 66 °C using 1 equivalent of TMEDA, an SBR copolymer will be obtained with 50% 1,2-polybutadiene microstructure [165]. In the presence of Lewis bases, the amount of 1,2-polybutadiene enchainment decreases with increasing temperature. The use of methyl $t$-butyl ether (MTBE) as a randomizer for styrene-butadiene copolymerizations has been reported. Using a [MTBE]/[BuLi] molar ratio of 15 at 50 °C in cyclohexane, the monomer reactivity ratios were reported to be $r_S = 0.7$ and $r_B = 1.84$ and the vinyl microstructure amounted to 21% [213].

In general, random SBR with a low amount of block styrene and low amounts of 1,2-butadiene enchainment (<20%) can be prepared in the presence of small amounts of added potassium or sodium metal alkoxides [214, 215]. For example, at 50 °C in the presence of as little as 0.067 equivalents of potassium $t$-butoxide in cyclohexane, the amount of bound styrene was relatively independent of conversion, in contrast to the heterogeneity observed in the absence of randomizer, that is, tapered block copolymer formation [214]. The polybutadiene microstructure obtained under these conditions corresponds to about 15% 1,2- microstructure [215]. Using 0.2 of hydrocarbon-soluble sodium 2,3-dimethyl-2-pentoxide in cyclohexane at 50 °C, the monomer reactivity ratios for alkyllithium-initiated SBR were found to be of $r_B = 1.1$ and $r_S = 0.1$ [216]. The resulting copolymer had only 5% block styrene and 18% 1,2-vinyl microstructure. It was found that there is a very narrow compositional window ([RONa]/[RLi]) at which a minimum amount of styrene blockiness was obtained [217]. At both lower and higher ratios, significant and unacceptably high levels of block styrene content were formed in the copolymer. It is expected that sodium alkoxide may change the aggregation degree of the organolithium chain ends, may form cross-associated species, and may even exchange counterions with the propagating chain ends. Equilibrium among these active species obviously affects styrene incorporation and diene microstructure [217]. Recent studies have indicated the participation of multicomponent active species (complex cross-aggregates and equilibria between metal–metal exchanged species) depending on the stoichiometry of the mixed initiator [218, 219].

The effects of dibutylmagnesium and triisobutylaluminum "retarders" on the copolymerization of neat styrene and butadiene have been investigated at 25 °C [220]. Although the monomer reactivity ratio for styrene was relatively constant ($r_S = 0.03$ and 0.04 at [R$_2$Mg]/[RLi] = $r$ = 1 and 4, respectively), the butadiene monomer reactivity ratio was sensitive to the [Mg]/[Li] ratio ($r_B = 9.1$ and 1.9 at [R$_2$Mg]/[RLi] = 1 and 4, respectively). The percentage of 1,2-units in the copolymer increased with increasing molar ratio of [Mg]/[Li] from circa 12% at $r = 1$ to circa 33% at $r = 4$. These results were at 25 °C, however. It would be expected that the amount of vinyl microstructure would decrease at higher temperatures [169]. For triisobutylaluminum, the monomer reactivity ratios reported were $r_S = 0.6$ and $r_B = 1.1$ and for [$i$ - Bu$_3$Al]/[RLi] = 0.85. Thus, whereas tapered structures would be formed for the magnesium system, a random copolymer structure would be expected for the aluminum system. In addition, the presence of triisobutylaluminum did not significantly affect the polybutadiene microstructure (13% 1,2-microstructure for [$i$ - Bu$_3$Al]/[RLi]=0.9).

Commercial random SBR polymers (solution SBR) prepared by alkyllithium-initiated polymerization typically have 32% $cis$-1,4-, 41% $trans$-1,4-, and 27% vinyl-microstructure compared to 8% $cis$-1,4-, 74% $trans$-1,4-, and 18% vinyl-microstructure for emulsion SBR with the same comonomer composition [3, 221]. Solution SBRs typically have branched architectures to eliminate cold flow [17, 49]. Compared to emulsion SBR, solution random SBRs require less accelerator and give higher compounded Mooney, lower heat buildup, increased resilience, and better retread abrasion index [3]. Terpolymers of styrene, isoprene, and butadiene (SIBR) have been prepared using a chain of single-stirred reactors whereby the steady-state concentration of each monomer and Lewis base modifier at any degree of conversion could be controlled along the reactor chain [3, 222–224].

## 7.7 SYNTHETIC APPLICATIONS OF LIVING ANIONIC POLYMERIZATION

### 7.7.1 Block Copolymers.

One of the unique and important synthetic applications of living polymerizations is the synthesis of block copolymers by sequential monomer addition [225–228, 192]. The ability to prepare block copolymers is a direct consequence of the stability of the carbanionic chain ends on the laboratory time scale when all of the monomer has been consumed. Since a living polymerization and the ability to prepare well-defined block copolymers require the absence (or reduction to a negligible level) of chain termination and chain transfer reactions, monomer purity, and the absence of side reactions with the monomer are necessary

requirements [229, 37, 230]. An important consideration for successful synthesis of block copolymers is the order of monomer addition. In general, a carbanionic chain end from one monomer will crossover to form the chain end of another monomer and initiate polymerization of this monomer provided that the resulting carbanion is either of comparable stability or more stable than the original carbanion [3]. The $pK_a$ values of the conjugate acids of carbanions provide a valuable guide to the relative stabilities of carbanions [2]. With this limitation in mind, living anionic polymerization provides a powerful synthetic method for preparing block copolymers with well-defined structures, including copolymer composition, block molecular weights, block molecular weight distributions, block sequence, and low degrees of compositional heterogeneity [226–228, 192, 229, 37, 230–232]. Organolithium initiators have been particularly useful in this regard, since they are soluble in a variety of solvents [44] and since they can initiate the polymerization of a variety of monomers, such as styrene and its homologs, the 1,3-dienes, alkyl methacrylates, vinylpyridines, cyclic oxides and sulfides, lactones, lactides, and cyclic siloxanes [3]. Utilizing these monomers, various block copolymers have been synthesized, some commercially, but the outstanding development in this area has been in the case of the ABA type of triblock copolymers, particularly polystyrene-*b*-polydiene-*b*-polystyrene (S-D-S) [233–236]. There are three general methods for anionic synthesis of triblock copolymers: (i) three-step sequential monomer addition; (ii) two-step sequential addition followed by coupling reactions; and (iii) difunctional initiation and two-step sequential monomer addition [3, 229]. Each of these methods has certain advantages and limitations.

### 7.7.1.1  Block Copolymer Synthesis by Three-Step Sequential Monomer Addition

The preparation of block copolymers by sequential addition of monomers using living anionic polymerization and a monofunctional initiator is the most direct method for preparing well-defined block copolymers. Detailed laboratory procedures for anionic synthesis of block copolymers are available [37, 230]. Several important aspects of these syntheses can be illustrated by considering the preparation of an important class of block copolymers (Scheme 7.22), the polystyrene-*b*-polydiene-*b*-polystyrene triblock copolymers.

The molecular weight of each block segment is uniquely determined by the stoichiometry, that is, the ratio of the grams of monomer to the moles of initiator. In order to obtain a narrow molecular weight distribution polystyrene block in hydrocarbon solution ($k_i \geq k_p$) [3, 100], the use of a reactive initiator such as *sec*-butyllithium (tetrameric degree of aggregation) [44] is preferred; however, the less reactive but the cheaper and more thermally stable initiator *n*-butyllithium (hexameric degree of aggregation)

[44] can be used if activated by small amounts of polar modifier that will not compromise the generally desired high 1,4-polydiene microstructure (low $T_g$) in the elastomeric second block. The "crossover" reaction of poly(styryl)lithium with the diene is known to be very rapid, ensuring a fast initiation of the center polydiene block ($k_i > k_p$) [56, 204, 209]; this ensures that the molecular weight distribution of the polydiene block will be narrow. However, to overcome the well-known slow crossover reaction rate of poly(dienyl) lithium to styrene relative to styrene propagation [56, 204, 209] with the final styrene charge in nonpolar media, it is necessary to add a small amount of a Lewis base, for example, THF [45, 237, 238]. The limitations of this method are [3, 229] (i) the requisite addition of polar additives for the final crossover reaction to styrene; (ii) the increasing viscosity of the solution as the polymerization proceeds (poly(styryl)lithium and poly(dienyl)lithium chain ends are associated predominantly into dimers and tetramers, respectively) [83, 85, 86, 89–94]; (iii) the high monomer purity required to prevent chain termination when two subsequent monomers are added sequentially; and (iv) the undesirability of potentially contaminating the recycle solvent stream with polar materials, which affects the polydiene microstructure in commercial plants.

### 7.7.1.2  Block Copolymer Synthesis by Two-Step Sequential Monomer Addition and Coupling

In order to avoid the problems associated with the three-step sequential monomer addition process, a two-step sequential monomer addition process followed by addition of a difunctional
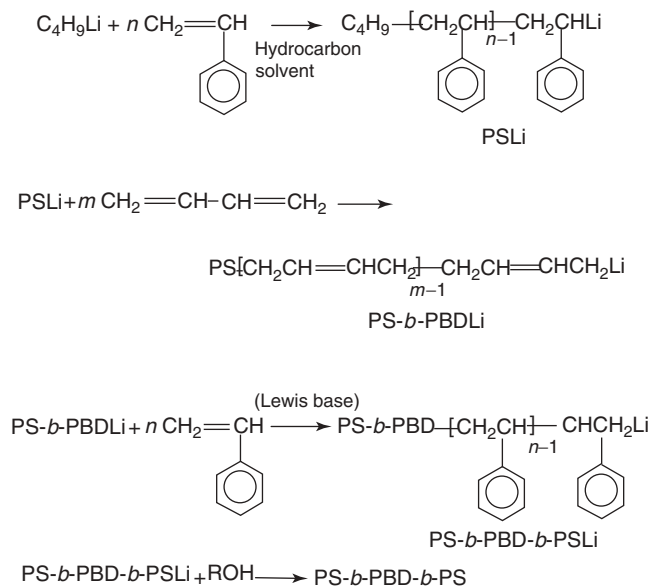


**Scheme 7.22**  Triblock copolymer synthesis by three-step sequential monomer addition.
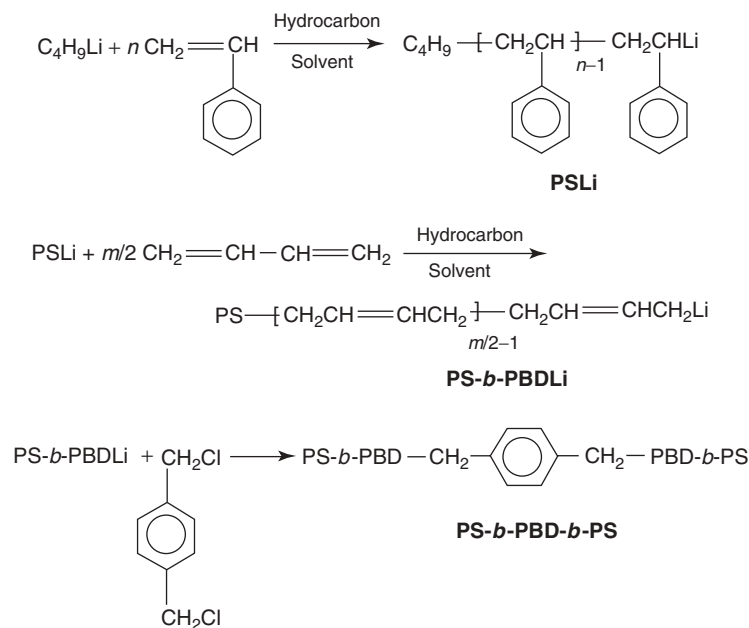
**Scheme 7.23**   Triblock copolymer synthesis by two-step sequential monomer addition and coupling.

coupling agent was developed as shown in Scheme 7.23 [3, 229]. This process also uses a monofunctional organolithium initiator, but the polymerization is carried only to the diblock (S-D) stage. The triblock copolymers are then formed by using a coupling agent, for example, a dihalide or an ester, to join the lithium chain ends of the diblock [3, 235, 239]. This has the advantage of involving only two monomer additions, thus reducing the possibility of introduction of impurities. However, the efficiency of the coupling reaction is dependent on the ratio of the linking agent to the chain-end concentration; any deviation from exact stoichiometry leads to the formation of free diblock impurity. The latter have been found to have a dramatic effect on the strength of the material (free chain ends in the network) [240, 241]. It is interesting to note, in this connection, that a certain amount of free polystyrene (terminated monoblock) can be easily tolerated since it is apparently incorporated into the polystyrene domains. One of the main advantages of this method is the fact that the slow crossover reaction from dienyllithium to styrene monomer is avoided, along with the necessity of adding a Lewis base to promote this crossover reaction. From a practical point of view, the polymerization time is reduced to one-half of that required for the three-step synthesis of a triblock copolymer with the same molecular weight and composition.

### 7.7.1.3   Block Copolymers by Difunctional Initiation and Two-Step Sequential Monomer Addition   This process requires a dilithium initiator, so that the center block (D) is

formed first, by a dianionic polymerization, followed by the addition of styrene to form the two end blocks as shown in Scheme 7.24. It, too, has the advantage of requiring only two monomer additions. However, it has several serious limitations. In the first place, it is difficult to obtain a useful dilithium initiator that is soluble in hydrocarbon media, as required for polymerization of dienes, because of the association of the chain ends to form insoluble network-like structures [3, 44, 70, 168]; however, some success in preparing hydrocarbon-soluble dilithium initiators has been reported [45, 73, 71, 242, 243]. Furthermore, any loss of difunctionality, either in the initiator or after the addition of the diene, leads to the formation of undesirable diblocks. However, this method can be especially useful in the case of "unidirectional" block copolymerization, that is, where monomer A can initiate monomer B but not vice versa, for example, for polar B monomers. The dilithium initiator formed by the dimerization of DPE with lithium in cyclohexane in the presence of anisole has been utilized for the synthesis of an poly(α-methylstyrene-b-isoprene-b-α-methylstyrene triblock copolymer [243]. The dilithium initiator formed by the addition of 2 mol of sec-butyllithium with 1,3-bis(1-phenylethenyl)benzene forms a hydrocarbon-soluble dilithium initiator which has been used in the presence of lithium alkoxide to form well-defined polystyrene-b-polybutadiene-b-polystyrene [73, 242] and poly(methyl methacrylate)-b-polyisoprene-b-poly(methyl methacrylate) triblock copolymers [244].
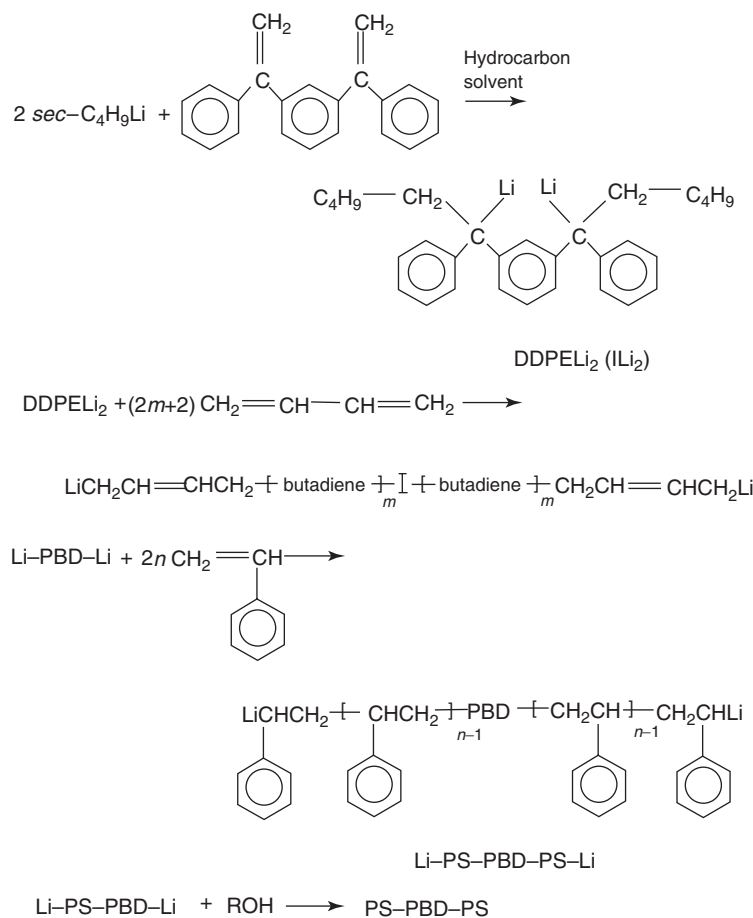
**Scheme 7.24**  Triblock copolymers by difunctional initiation and two-step sequential monomer addition.

## 7.7.2  Star-Branched Polymers

Molecular architecture, and particularly long-chain branching, can have a profound effect on the processing and properties of polymers. The methodology of living anionic polymerization provides a variety of procedures for the synthesis of both compositionally homogeneous and compositionally heterogeneous branched polymers [3, 226, 231, 245–250]. A star-branched polymer is a particularly important type of anionically prepared branched polymer that consists of several linear chains linked together at one end of each chain by a single branch or junction point. Thus, after anionic polymerization of a given monomer is completed, the resulting living polymer with a reactive carbanionic chain end can be reacted with a variety of linking reagents to generate the corresponding star-branched polymer with uniform arm lengths. After analogous sequential polymerization of two or more monomers, linking reactions with the resulting living diblock, or multiblock, copolymers will generate star-branched block copolymers with uniform block arm length [227, 231]. It is noteworthy that, in principle, each

arm is of uniform block copolymer composition with precise block molecular weights and narrow molecular weight distributions, that is, with low degrees of compositional heterogeneity. Although various types of linking agents have been used to prepare star-branched copolymers, two of the most useful and important types of linking agents are the multifunctional silyl chlorides and DVB [251, 252].

### 7.7.2.1  Linking Reactions with Silyl Halides    The most general methods for the preparation of regular star polymers are based on linking reactions of polymeric organolithium compounds with multifunctional electrophilic species such as silicon tetrachloride as shown in Equation 7.34 [3, 231, 239, 251]. Analogous linking reactions with multifunctional halogenated hydrocarbons are complicated by side reactions such as lithium–halogen exchange, Wurtz coupling, and elimination reactions [3, 44, 252]. In contrast, the reactions with chlorosilane compounds are very efficient and uncomplicated by similar side reactions. However, the extents and efficiencies of these linking reactions

are sensitive to the steric requirements of the carbanionic chain end [246].

$$4PLi + SiCl_4 \rightarrow P_4Li + 4LiCl \qquad (7.34)$$
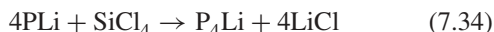
In general, for a given multifunctional silicon halide, the efficiency of the linking reaction decreases in the order poly(butadienyl)lithium > poly(isoprenyl)lithium > poly(styryl)lithium. In pioneering work by Morton, Helminiak, Gadkary, and Bueche [253] in 1962, the reaction of poly(styryl)lithium ($M_n = 60.6 \times 10^3$ g/mol; $M_w/M_n = 1.06$) with a less than stoichiometric amount of silicon tetrachloride in benzene at 50 °C for 48 h produced a polymer product with $M_w = 1.93 \times 10^5$ g/mol. After fractionation of this product, a four-armed star polymer ($M_w = 2.57 \times 10^5$ g/mol; $M_w/M_n = 1.09$) and a three-armed star polymer ($M_w = 1.70 \times 10^5$ g/mol; $M_w/M_n = 1.0$) were isolated in weight fraction amounts corresponding to 0.252 and 0.349, respectively. In contrast to the results of inefficient linking for poly(styryl)lithiums, the linking reactions of poly(butadienyl)lithiums with methyltrichlorosilane and silicon tetrachloride in cyclohexane at 50 °C for 3 h were reported to proceed efficiently to form the corresponding three-arm and four-arm stars, respectively [254]. However, the linking efficiency of poly(isoprenyl)lithium with silicon tetrachloride is not high, as in the case of poly(styryl)lithium. The stoichiometric reaction of poly(isoprenyl)lithium with silicon tetrachloride is reported to form predominantly the three-armed star product [255]. However, high linking efficiency to form the three-armed star is obtained with methyltrichlorosilane [255].

There have been two general approaches that have been used to increase the efficiency of linking reactions of polymeric organolithium compounds with multifunctional silyl halides. The first procedure is to add a few units of butadiene to either the poly(styryl)lithium or poly(isoprenyl)lithium chain ends to effectively convert them to the corresponding less sterically hindered poly(butadienyl)lithium chain ends. For example, after crossover to butadienyllithium chain ends, the yield of four-armed star polyisoprene with silicon tetrachloride was essentially quantitative in cyclohexane [255]. The second method is to utilize a polychlorosilane compound in which the silyl halide units are more separated to reduce the steric repulsions in the linked product.

The efficiency of the linking reactions of polychlorosilanes with poly(dienyl)lithium compounds has been documented by synthesis of well-defined, narrow molecular weight distribution, 18-armed star-branched polyisoprenes, polybutadienes, and butadiene end-capped polystyrenes by linking reactions with a decaoctachlorosilane [(SiCl)$_{18}$] [256, 257]. The linking reactions of poly(butadienyl)lithium ($M_n = 5.3–89.6 \times 10^3$ g/mol) with carbosilane dendrimers with up to 128 Si–Cl bonds have been reported to proceed

smoothly at room temperature but requiring periods of up to 3 weeks [258].

From a practical point of view, the effective molecular weight distribution of an anionically prepared polymer can be broadened by reaction with less than a stoichiometric amount of a linking agent such as silicon tetrachloride [239]. This results in a product mixture composed of unlinked arm, coupled product, three-arm, and four-arm star-branched polymers. Heteroarm star-branched polymers can be formed by coupling of a mixture of polymeric organolithium chains that have different compositions and molecular weights. This mixture can be produced by the sequential addition of initiator as well as monomers [3, 259, 260].

### 7.7.2.2 Divinylbenzene Linking Reactions

The linking reactions of polymeric organolithium compounds with DVB provide a very versatile, technologically important, but less precise method of preparing star-branched polymers [251]. The linking reactions with DVB can be conceptually divided into three consecutive and/or concurrent reactions: (i) crossover to DVB; (ii) block polymerization of DVB; and (iii) linking reactions of carbanionic chain ends with pendant vinyl groups in the DVB block [poly(4-vinylstyrene)] [3, 252, 261, 262]. These reactions are illustrated in Scheme 7.25. The uniformity of the lengths of the DVB blocks depends on the relative rate of the crossover reaction (i) compared to the block polymerization of DVB (ii) and the linking reactions (iii). This block copolymerization-linking process has been described as due to the formation of a DVB microgel nodule which serves as the branch point for the star-shaped polymer [252]. In principle, $j$ molecules of DVB could link together ($j + 1$) polymer chains [252]. Although the number of arms in the star depends on the ratio of DVB to polymeric organolithium compound, the degree of linking obtained for this reaction is a complex function of reaction variables [252, 261–263]. It should be noted that these linking reactions are effected with various technical grades of DVB which have been reported to consist of (i) 33% DVB (11% p-DVB, 22% m-DVB), and 66% o-, m- and p-ethylvinylbenzene (EVB) [252]; (ii) 78% DVB (meta/para = 2.6), 22% EVB isomers [262]; (iii) 56% DVB, 44% EVB isomers [263]; and (iv) 18 mol% p-DVB, 39 mol% m-DVB, 10 mol% p-EVB, and 33 mol% m-EVB [252, 264]. The purity and composition of DVB are critical since the course of the linking reaction depends on the [DVB]/[PLi] ratio; impurities can terminate the active chain ends, thus changing the effective molar ratio of DVB to active chain-end concentration.

For poly(styryl)lithium chains, the rate of crossover to DVB is comparable to the rate of DVB homopolymerization and both of these rates are faster than the rate of the linking reaction of poly(styryl)lithium with the pendant double bonds in the poly(vinylstyrene) block formed from DVB.
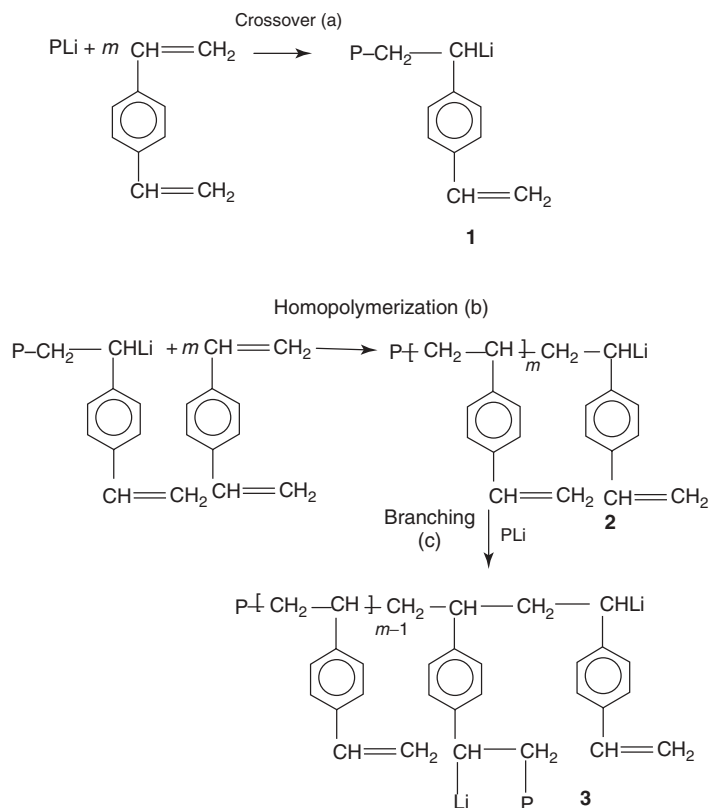
**Scheme 7.25**  Branching chemistry of polymeric organolithium compounds with divinylbenzenes.

Therefore, it would be expected that the DVB block formed by crossover from poly(styryl)lithium would be relatively uniform and that the linking reaction would generally occur after the formation of the DVB block. In general, the linking efficiency of poly(styryl)lithiums by DVB is quite high except for very low ratios of DVB/PSLi [3].

For poly(dienyl)lithium chain ends, the rate of crossover to DVB is much slower than the rate of DVB homopolymerization. Therefore, it would be expected that the DVB block length would be longer for poly(dienyl)lithiums compared to poly(styryl)lithium. As a consequence, although one obtains a higher degree of branching, the linking efficiency is lower for polydiene versus polystyrene stars. However, it is possible to obtain good linking efficiencies for dienyllithium chains using ratios of DVB/PLi $\geq$ 3 [3]. When small amounts of DVB are added as a comonomer during polymerization of styrenes and dienes, it is incorporated into the chain in a statistical distribution dictated by the comonomer reactivity ratios and the feed composition. Subsequent to DVB incorporation, growing chains can add to the pendant vinylstyrene units followed by further monomer addition to generate long-chain branching sites [3]. Although the resulting branch structure is not well defined, it is very effective in modifying the low and high shear viscosity characteristics of the resulting polymers.

### 7.7.3  Synthesis of Chain-End-Functionalized Polymers

***7.7.3.1  Chain-End Functionalization by Termination with Electrophilic Reagents***  Another unique attribute of living anionic polymerization is the ability to tailor-make well-defined polymers with low degrees of compositional heterogeneity and with functional chain-end groups [3, 265–267]. The products of living anionic polymerization are polymer chains with stable carbanionic chain ends. In principle, these reactive anionic end groups can be readily converted into a diverse array of $\omega$-chain-end functional end groups by reaction with a variety of electrophilic species as shown in Equation 7.35, where PLi is a polymeric organolithium chain, E is an electrophilic reagent, and X represents a chain-end functional group. Unfortunately, many of these functionalization reactions have not been well characterized [3, 268]. Thus, it is generally necessary to carefully develop, analyze, and optimize new procedures for each different functional group introduced by a specific post-polymerization functionalization reaction. Two representative chain-end functionalization reactions will be described, followed by progress in the area of development of general functionalization methods.

$$PLi + E \rightarrow P\text{--}X + \ LiY \qquad (7.35)$$

### 7.7.3.2 Specific Functionalization Reactions

*Carbonation*   Although the carbonation of polymeric car-banions using carbon dioxide is one of the most use-ful and widely used functionalization reactions, there are special problems associated with the simple reaction of polymeric organolithium compounds with carbon diox-ide. Even when carbonations with high purity, gaseous carbon dioxide are carried out in benzene solution at room temperature using standard high vacuum techniques, the carboxylated polymers are obtained in only 27–66% yields for poly(styryl)lithium, poly(isoprenyl)lithium, and poly(styrene-*b*-isoprenyl)lithium [269–271]. The function-alized polymer is contaminated with dimeric ketone (23–27%) and trimeric alcohol (7–50%) as shown in Equation 7.36, where P represents a polymer chain. It was proposed that the formation of these side-products is favored relative to the desired carboxylated polymer by ag-gregation of the chain ends in hydrocarbon

$$PLi \xrightarrow[\substack{Hydrocarbon \\ solvent}]{CO_2} \xrightarrow{H_3O^+} PCO_2H + P_2CO + P_3COH$$

(7.36)
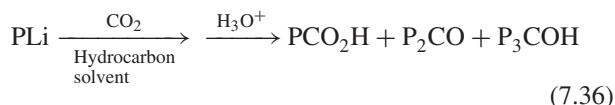
solution [270]. Furthermore, it has been reported that the addition of sufficient quantities of Lewis bases such as THF and TMEDA can reduce or even eliminate the association of polymeric organolithium chain ends [85, 168, 272]. In accord with these considerations, it was found that addition of large amounts of either THF (25 vol%) or TMEDA ([TMEDA]/[PLi] = 1–46) was effective in favoring the carbonation reaction to the extent that the carboxylated polymer was obtained in yields >99% for poly(styryl)lithium, poly(isoprenyl)lithium, and poly(butadienyl)lithium [269–271].

*Hydroxylation*   The preparation of hydroxyl-terminated polymers from polymeric organolithium compounds by reaction with ethylene oxide is one of the few simple and efficient functionalization reactions. The reaction of poly(styryl)lithium with excess ethylene oxide in benzene solution produces the corresponding hydroxyethylated poly-mer in quantitative yield without formation of detectable amounts of oligomeric ethylene oxide blocks, Equation 7.37 [273]. For example, $^{13}C$-NMR analysis of a hydroxyethy-lated polystyrene ($M_n = 1.3 \times 10^3$ g/mol; $M_w/M_n = 1.08$) showed no evidence for the formation of any ether link-ages expected for oligomerization of ethylene oxide, even using $^{13}C$-labeled ethylene oxide [274]. No evidence for oligomerization was found by matrix-assisted laser desorp-tion/ionization time-of-flight (MALDI-ToF) mass spectral analysis using the standard conditions of 4 equivalents of
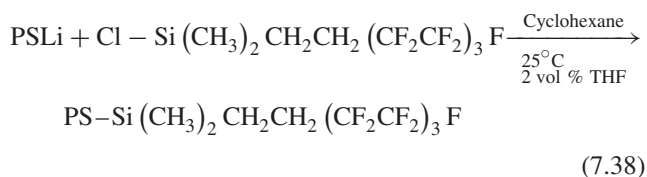
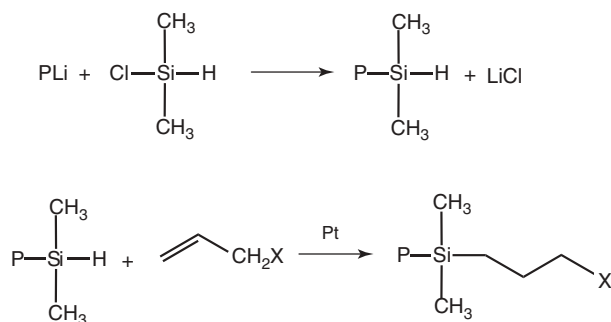ethylene oxide after 12 h in benzene [275]. This result is surprising in view

$$PSLi \; + \; \triangle \xrightarrow[\substack{Hydrocarbon \\ solvent}]{} \xrightarrow{H_3O^+} PSCH_2CH_2OH$$

(7.37)
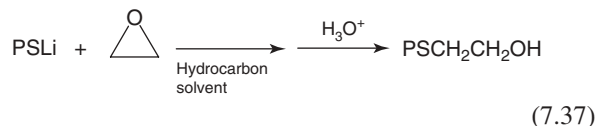
of the steric strain and intrinsic reactivity of ethylene oxide toward nucleophiles. Apparently, the high degree of aggre-gation of lithium alkoxides and the strength of this associ-ation even in polar solvents renders them unreactive [276]. MALDI-ToF mass spectral evidence for oligomerization de-tected for poly(styryl)lithium functionalization was effected with 10 equivalents of ethylene oxide for longer reaction times [275]. Quite surprisingly, oligomerization is observed for functionalization of poly(butadienyl)lithium under the standard functionalization conditions [277]. Specific func-tionalizations using a variety of different epoxides have been reviewed [278]. α-Chain-end, hydroxyl-functionalized polymers have also been prepared using protected alkyl-lithium initiators [77, 76].

### 7.7.3.3 General Functionalization Reactions   General functionalization reactions are reactions of organolithium compounds that proceed efficiently to introduce a variety of different functional groups [3]. The most useful reactions can be utilized at elevated temperatures in hydrocarbon solution so that the unique characteristics of organolithium-initiated polymerizations can be preserved.

*Functionalizaton Reactions with Silyl Halides*   The re-action of polymeric organolithium compounds with silyl halides is a very efficient reaction that is not complicated by competing side reactions [251, 252]. Therefore, these reactions provide a general functionalization methodology that can be used to prepare a variety of end-functionalized polymers by reactions with silyl halides containing either functional groups or protected functional groups [279, 280]. For example, the reaction of poly(styryl)lithium with tridecafluoro-1,1,2,2-tetrahydrooctyl)-1-dimethyl-chlorosilane has been used to prepare perfluoroalkyl-terminated polystyrenes ($M_n$ = 1000–40,000 g/mol) as shown in Equation 7.38 [279]. This methodology was also used to prepare the analogous functionalized polybutadienes and polyisoprenes.

$$PSLi + Cl - Si\,(CH_3)_2\,CH_2CH_2\,(CF_2CF_2)_3\,F \xrightarrow[\substack{25^\circ C \\ 2\,vol\,\%\,THF}]{Cyclohexane}$$

$$PS - Si\,(CH_3)_2\,CH_2CH_2\,(CF_2CF_2)_3\,F$$

(7.38)

$$PLi + Cl-Si(CH_3)_2-H \longrightarrow P-Si(CH_3)_2-H + LiCl$$

$$P-Si(CH_3)_2-H + CH_2=CH-CH_2X \xrightarrow{Pt} P-Si(CH_3)_2-CH_2CH_2CH_2-X$$

**Scheme 7.26** General anionic functionalization using chlorosilanes and hydrosilation chemistry.

*Functionalizations via Silyl Hydride Functionalization and Hydrosilation* A new general functionalization method based on the combination of living anionic polymerization and hydrosilation chemistry has been developed as illustrated in Scheme 7.26 [281]. First, a living polymeric organolithium compound is quantitatively terminated with chlorodimethylsilane to prepare the corresponding ω-silyl hydride-functionalized polymer. The resulting ω-silyl hydride-functionalized polymer can then react with a variety of readily available substituted alkenes to obtain the desired chain-end functionalized polymers via efficient regioselective transition-metal-catalyzed hydrosilation reactions [282–284].

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