INITIATORS, ANIONIC

1. Introduction

Chain-reaction polymerization generally comprises the kinetic steps of initiation, propagation, and termination. Chain-reaction polymerizations can be effected using a variety of initiating species broadly classified as free-radical, cationic, anionic, or coordination (organometallic) initiators, depending on their electrochemical nature. The initiation step generates reactive intermediates (eg, free-radical, anion, cation, or organometallic species), which can add monomer (M) repetitively in a chain reaction as shown in equations 1 and 2, where I is an initiator that generates the initiating species I* in the first step of initiation.

$$\mathrm{I} \longrightarrow \mathrm{I}^* \tag{1}$$

$$\mathrm{I}^* + \mathrm{M} \longrightarrow \mathrm{IM}^* \tag{2}$$

In anionic polymerization, the reactive propagating intermediate generated by the initiation reaction is an anion, ie, a species that carries a formal negative charge, with a corresponding positively charged counterion. In living anionic polymerization, the kinetic steps of chain termination and chain transfer are absent (1–4). This unique aspect of many anionic polymerizations provides a methodology for preparing polymers with control of the significant variables affecting polymer properties including molecular weight, molecular weight distribution, block copolymer composition, copolymer sequence distribution, and microstructure, as well as molecular architecture (linear, branched, and cyclic macromolecules), especially using alkyllithium initiators (1,2,4,5).

An important consideration for preparation of polymers with well-defined structures and low degrees of compositional heterogeneity is the choice of a suitable initiator. In general, an appropriate initiator is a species that has approximately the same structure and reactivity as the propagating anionic species, ie, the pK_a of the conjugate acid of the propagating anion should correspond closely to the pK_a of the conjugate acid of the initiating species. If the initiator is too reactive, side reactions between the initiator and monomer can occur; if the initiator is not reactive enough, then the initiation reaction may be slow or inefficient. The efficiency of an initiator can be calculated by taking the ratio of the stoichiometry-determined, calculated number average molecular weight (M_n) over the observed M_n. When the rate of initiation is slow relative to the rate of propagation, a broader molecular weight distribution ($M_\mathrm{w}/M_\mathrm{n}$) is obtained (2–4).

The general relationship between monomer structural type, pK_a, and appropriate initiating species is shown in Table 1. Those monomers that form the least stable propagating anions, ie, which have the largest values of pK_a for the corresponding conjugate acids, are the least reactive monomers in anionic polymerization; in turn, these less reactive monomers require the use of the most reactive initiators as shown in Table 1. Thus, although the anionic polymerization of many heterocyclic monomers can be initiated with relatively weak bases such as alkoxides, hydroxides, and tertiary amines, in general the polymerization of vinyl monomers requires the use of alkali metals, aromatic radical anions, or organoalkali compounds.

2. Alkali Metals

The use of alkali metals for anionic polymerization of diene monomers is primarily of historical interest. A patent disclosure issued in 1910 (16) detailed the use of metallic sodium to polymerize isoprene and other dienes. Independently and simultaneously, the use of sodium metal to polymerize butadiene , isoprene, and 2,3-dimethyl-1,3-butadiene was described (17). Interest in alkali metal initiated polymerization of 1,3-dienes culminated in the discovery (18) at Firestone Tire and Rubber Co. that polymerization of neat isoprene with lithium dispersion produced high *cis*-1,4-polyisoprene, similar in structure and properties to Hevea natural rubber (see Polyisoprene; rubber, natural).

The mechanism of the anionic polymerization of styrenes and 1,3-dienes initiated by alkali metals has been described in detail (3,19) as shown in equations 3–5 where Mt represents an alkali metal and M is a monomer molecule. Initiation is a heterogeneous process occurring on the metal surface. The first step is an electron-transfer reaction from the metal to the lowest unoccupied molecular orbital of an adsorbed monomer molecule to form radical anion intermediates that rapidly dimerize to form dianions (20–22). Monomer addition to these dianions forms adsorbed oligomers that eventually desorb and

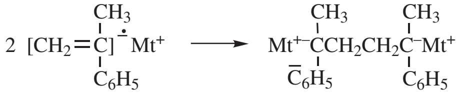
$$\mathrm{Mt} + \mathrm{M} \longrightarrow \mathrm{Mt}^{+}, \mathrm{M}^{\overset{\bullet}{-}} \tag{3}$$

$$2\mathrm{Mt}^{+}, \mathrm{M}^{\overset{\bullet}{-}} \longrightarrow \mathrm{Mt}^{+}, {}^{-}\mathrm{M}\text{—}\mathrm{M}^{-}, \mathrm{Mt}^{+} \tag{4}$$

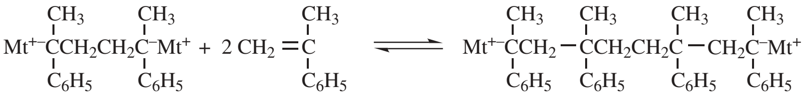
$$\mathrm{Mt}^{+}, {}^{-}\mathrm{M}\text{—}\mathrm{M}^{-}, \mathrm{Mt}^{+} + n\mathrm{M} \longrightarrow \mathrm{Mt}^{+}, {}^{-}\mathrm{M}\text{—}[M]_{n}\text{—}\mathrm{M}^{-}, \mathrm{Mt}^{+} \tag{5}$$

continue 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 ($M_{\mathrm{w}}/M_{\mathrm{n}} = 3–10$) have been reported for the soluble polymer obtained in bulk polymerizations (23). A polybutadiene polymer produced using sodium metal as initiator exhibits a high degree of branching and gel content (45%) combined with inhomogeneity in composition and molecular weight distribution (23,24).

These reactions are useful for the preparation of homogeneous difunctional initiators from α-methylstyrene in polar solvents such as tetrahydrofuran (THF). Because of the low ceiling temperature of α-methylstyrene ($T_{\mathrm{c}} = 61^{\circ}\mathrm{C}$) (25), dimers or tetramers can be formed depending on the alkali metal system, temperature, and concentration. Thus the reduction of α-methylstyrene by sodium–potassium alloy produces the dimeric dianionic initiator in THF (26), while the reduction with sodium metal forms the tetrameric dianion as the main product (27). The structure of the dimer corresponds to initial tail-to-tail addition to form the most stable dianion as shown in equation 6 (27). Monomer addition to this dianion then forms the tetramer (equation 7).



$$2\ [CH_2{=}\overset{\overset{CH_3}{|}}{\underset{\underset{C_6H_5}{|}}{C}}]^{\dot{-}}Mt^{+} \longrightarrow Mt^{+-}\overset{\overset{CH_3}{|}}{\underset{\underset{\overline{C}_6H_5}{|}}{C}}CH_2CH_2\overset{\overset{CH_3}{|}}{\underset{\underset{C_6H_5}{|}}{C}}{}^{-}Mt^{+} \qquad (6)$$

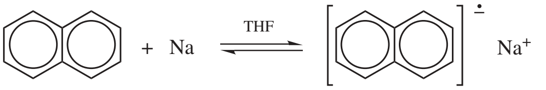


$$Mt^{+-}\overset{\overset{CH_3}{|}}{\underset{\underset{C_6H_5}{|}}{C}}CH_2CH_2\overset{\overset{CH_3}{|}}{\underset{\underset{C_6H_5}{|}}{C}}{}^{-}Mt^{+} + 2\,CH_2{=}\overset{\overset{CH_3}{|}}{\underset{\underset{C_6H_5}{|}}{C}} \rightleftharpoons Mt^{+-}\overset{\overset{CH_3}{|}}{\underset{\underset{C_6H_5}{|}}{C}}CH_2-\overset{\overset{CH_3}{|}}{\underset{\underset{C_6H_5}{|}}{C}}CH_2CH_2\overset{\overset{CH_3}{|}}{\underset{\underset{C_6H_5}{|}}{C}}-CH_2\overset{\overset{CH_3}{|}}{\underset{\underset{C_6H_5}{|}}{C}}{}^{-}Mt^{+} \qquad (7)$$

2.1. Aromatic Radical Anions. Many aromatic hydrocarbons react with alkali metals in polar aprotic solvents to form stable solutions of the corresponding radical anions as shown in equation 8 (3,19) . These solutions can be analyzed by uv–visible spectroscopy and stored for further use. The unpaired electron is added to the lowest unoccupied molecular orbital of the aromatic hydrocarbon and a

$$Mt + Ar \rightleftharpoons Ar^{\bullet}Mt^{+}Mt = Li, Na, K, Rb, Cs \qquad (8)$$

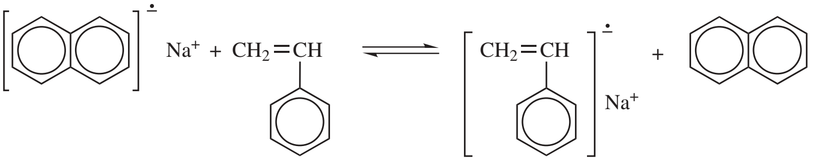
delocalized radical anion is formed as illustrated for sodium naphthalene in equation 9 (28–30). This oxidation–reduction reaction of the aromatic hydrocarbon with the metal is reversible; thus sodium metal and naphthalene are



(9)

re-formed when THF is removed. These radical anions can only be formed efficiently in polar aprotic solvents such as THF and glycol methyl ethers (glymes). For example, although sodium naphthalene formation is 95% complete in THF, this radical anion is formed in <1% yield in diethyl ether (19). For biphenyl, which has a lower electron affinity compared to naphthalene, only 20% of the corresponding radical anions are formed by sodium reduction in THF (19).

Sodium naphthalene [25398-08-7] and other aromatic radical anions react with monomers such as styrene by reversible electron transfer to form the corresponding monomer radical anions. Although the equilibrium (eq. 10)



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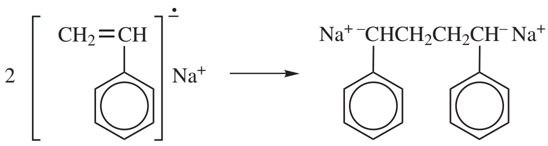
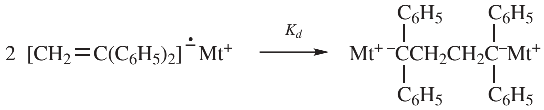

(11)

between the monomer radical anion and the aromatic radical anion lies far to the left because of the low electron affinity of the monomer (3), this is an efficient initiation process because the resulting monomer radical anions dimerize rapidly (eq. 11) with rate constants that approach the limits of diffusion control (19). For example, the rate constants for dimerization of the radical anions of 1,1-diphenylethylene (eq. 12) are 1.2×10^8, 3.5×10^8, 1×10^9, and $3 \times 10^9\,\mathrm{L/(mol \cdot s)}$ for the Li^+, Na^+, K^+, and Cs^+ salts, respectively (19). Based on these kinetic results, it has been concluded that the addition of monomer to the monomer radical anion is of little importance in the electron-transfer initiation process (19).



$$2\ [CH_2{=}C(C_6H_5)_2]^{\dot{-}}Mt^+ \xrightarrow{K_d} Mt^{+\,-}\underset{C_6H_5}{\overset{C_6H_5}{C}}CH_2CH_2\underset{C_6H_5}{\overset{C_6H_5}{C}}{}^{-}Mt^+ \qquad (12)$$

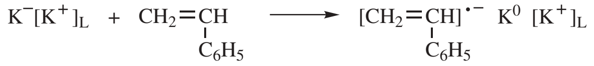
Monomers that can be polymerized with aromatic radical anions include styrenes, dienes, epoxides, and cyclosiloxanes. Aromatic radical anions that are too stable do not efficiently initiate polymerization of less reactive monomers; thus the anthracene radical anion cannot initiate styrene polymerization (19). In general, these aromatic radical anion initiators are formed and used in dipolar aprotic solvents; however, the addition of lithium naphthalene in THF to a benzene solution produces a finely divided suspension of lithium that reacts with styrene monomer to generate difunctional, narrow molecular weight distribution polymers (31). One of the consequences of the necessity to use polar solvents for aromatic radical anion initiators is that polydiene microstructure is high in 1,2- and 3,4-addition structures, ie, the high 1,4-stereospecificity observed with lithium in hydrocarbon solvent is lost in polar solvents such as tetrahydrofuran (1,2,32–36).

Alkali metals (Mt) can dissolve in solvating media such as ethers and amines to form blue solutions of solvated electrons (3). In the presence of strongly complexing ligands such as crown ethers or cryptands (L), electrides (complexed alkali cation and electron) or nuclides (complexed alkali metal cation and alkali metal anion) can be formed as shown in equations 13 and 14 (37).

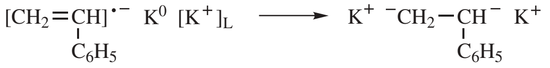
$$Mt \rightleftharpoons [Mt+]_L e^- \quad \text{(electride)} \qquad (13)$$

$$2\,Mt \rightleftharpoons [Mt+]_L Mt^- \quad \text{(nuclide)} \qquad (14)$$

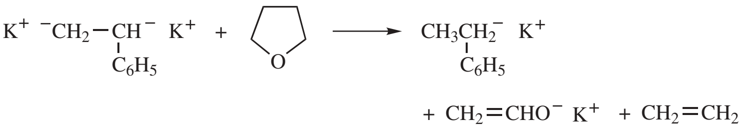
Nuclides have been shown to react with monomers such as styrene (38), isoprene (39) and methyl methacrylate (40) to form intermediate dianions that are rapidly protonated by the solvent THF at room temperature to form the monoanion initiating species as shown in equations 15–17 (40).



$$K^-[K^+]_L + CH_2{=}\underset{C_6H_5}{CH} \longrightarrow [CH_2{=}\underset{C_6H_5}{CH}]^{\bullet -}\ K^0\ [K^+]_L \tag{15}$$



$$[CH_2{=}\underset{C_6H_5}{CH}]^{\bullet -}\ K^0\ [K^+]_L \longrightarrow K^+\ {}^-CH_2{-}\underset{C_6H_5}{CH^-}\ K^+ \tag{16}$$



(17)

For the nuclide-initiated polymerization of methyl methacrylate and isoprene, although there was good agreement between calculated and observed molecular weights, the molecular weight distributions were broad ($M_w/M_n = 1.2{-}2.1$). These novel initiators have also been used to polymerize alkyl dihalides, dichlorosilanes and heterocyclic monomers such as lactones and oxiranes (41).

3. Alkyllithium Compounds

Anionic polymerization of vinyl monomers can be effected with a variety of organometallic compounds; alkyllithium compounds are the most useful class (1,2,32–35). A variety of simple alkyllithium compounds are available commercially. Most simple alkyllithium compounds are soluble in hydrocarbon solvents such as hexane and cyclohexane and they can be prepared by reaction of the corresponding alkyl chlorides with lithium metal (42,43). Methyllithium [917-54-4] and phenyllithium [591-51-5] are available in diethyl ether and cyclohexane–ether solutions, respectively, because they are not soluble in hydrocarbon solvents; vinyllithium [917-57-7] and allyllithium [3052-45-7] are also insoluble in hydrocarbon solutions and can only be prepared in ether solutions (42,43). Hydrocarbon-soluble alkyllithium initiators are used directly to initiate polymerization of styrene and diene monomers quantitatively; one unique aspect of lithium-based initiators in hydrocarbon solution is that elastomeric polydienes with high 1,4-microstructure are obtained (1,2,23,32–36). Certain alkyllithium compounds can be purified by recrystallization (ethyllithium), sublimation (ethyllithium, *tert*-butyllithium [594-19-4], isopropyllithium [2417-93-8] or distillation (*sec*-butyllithium) (44,45). Unfortunately, *n*-butyllithium is noncrystalline and too high boiling to be purified by distillation (42). Since methyllithium and phenyllithium are crystalline solids that are insoluble in hydrocarbon solution, they can be precipitated into these solutions and then redissolved in appropriate polar solvents (46,47).

Simple alkyllithium compounds are aggregated in solution, in the solid state, and even in the gas phase (42,48–50). The important differences between the various alkyllithium compounds are their degrees of aggregation in solution (Table 2) and their relative reactivity as initiators for anionic polymerization of styrene and diene monomers. Alkyllithium compounds are generally associated into dimers, tetramers, or hexamers in hydrocarbon solution (53). The degree of association is related to the steric requirements of the alkyl group, ie, the degree of association decreases as the steric requirements of the alkyl group increase. Models for the structures of the aggregated species have been deduced from analogous crystal structures determined in the solid state and are shown in Figure 1 (54,55). The tetramer can be described as interpenetrating tetrahedra of alkyl groups and lithium atoms or in terms of alkyl groups located above each of the triangular Li_3 faces of the tetrahedron formed by Li_4. In the hexameric aggregate, the lithium atoms occupy the apices of a distorted octahedron with six alkyl groups positioned above six of the eight octahedral Li_3 faces. Empty orbitals on lithium in the aggregates are available for interaction with Lewis bases.

The kinetics of initiation reactions of alkyllithium compounds often exhibit fractional kinetic order dependence on the total concentration of initiator as shown in Table 2. For example, the kinetics of the initiation reaction of *n*-butyllithium with styrene monomer in benzene exhibit a first-order dependence on styrene concentration and a one-sixth order dependence on *n*-butyllithium concentration as shown in equation 18, where k_i is the rate constant for

$$R_i = k_i K_d^{1/6}[\mathrm{C_4H_9Li}]^{1/6}[M] \tag{18}$$

the initiation step and K_d is the dissociation equilibrium constant for the hexamer-unassociated RLi equilibrium (eq. 19). Since *n*-butyllithium is aggregated predominantly into hexamers in hydrocarbon solution, the fractional kinetic-order dependency of the initiation process on total concentration of initiator is explained by assuming that the species which reacts with styrene monomer must be the unassociated form of the initiator and that this unassociated species may be formed by equilibrium dissociation processes. The kinetic order for *sec*-butyllithium-initiated polymerization of styrene is close to 0.25 in benzene solution. This result is consistent with the reaction of the unassociated form of the alkyllithium, since *sec*-butyllithium is associated predominantly into tetramers in benzene solution (see Table 2). However, this interpretation has been challenged based on consideration of the energetics of dissociation (32,56).

$$(\mathrm{RLi})_6 \overset{K_d}{\rightleftharpoons} 6\mathrm{RLi} \tag{19}$$

The use of aliphatic solvents causes profound changes in the observed kinetic behavior for the alkyllithium initiation reactions with styrene , butadiene, and isoprene, ie, the inverse correspondence between the reaction-order dependence for alkyllithium and degree of organolithium aggregation is generally not observed (32,45,51). Also, initial rates of initiation in aliphatic solvents are several orders of magnitude less than those observed, under equivalent conditions, in aromatic solvents (47). Furthermore, pronounced induction periods are observed in aliphatic hydrocarbon solvents (45,51). It has been proposed that the initiation process in aliphatic hydrocarbons involves the direct reaction of monomer with aggregated organolithiums, which then forms cross-associated species as shown in equation 20 (32,45,51). The induction periods are ascribed to the enhanced reactivity of the mixed (ie, cross-associated) aggregated species (51).

$$(\mathrm{RLi})_n + \mathrm{M} \longrightarrow [(\mathrm{RLi})_{n-1}(\mathrm{RMLi})] \qquad (20)$$

The relative reactivities of alkyllithiums as polymerization initiators are intimately linked to their degree of association. In the following, the average degree of association in hydrocarbon solution, where known, is indicated in brackets after the alkyllithium (57). For styrene polymerization, the relative reactivity of alkyllithium initiators is menthyllithium [2]>*sec*-C_4H_9Li [4]>*i*-C_3H_7Li [4–6]>*i*-C_4H_9Li >*n*-C_4H_9Li [6]>*t*-C_4H_9Li [4]. For diene polymerization, menthyllithium [2]>sec-C_4H_9Li [4]>*i*-C_3H_7Li[4–6]>*t*-C_4H_9Li [4]>*i*-C_4H_9Li>*n*-C_4H_9Li [6]. In general, the less associated alkyllithiums are more reactive as initiators than the more highly associated species. Aromatic solvents tend to decrease the average degree of association and promote dissociation of aggregates that leads to initiation rates that are two to three orders of magnitude faster than in aliphatic solvents. Addition of Lewis bases such as ethers and amines tends to decrease the degree of aggregation of alkyllithium compounds and accelerate rates of initiation (33).

Alkyllithium compounds are primarily used as initiators for polymerizations of styrenes and dienes in hydrocarbon solutions (58). These initiators are too reactive for alkyl methacrylates and vinylpyridines. *n*-Butyllithium [109-72-8] in hydrocarbon solutions [pentane, *n*-hexane, heptane, cyclohexane (or their mixtures) and toluene] is used commercially to initiate anionic homopolymerization and copolymerization of butadiene, isoprene, and styrene with linear and branched structures. Because of the high degree of association (hexameric), *n*-butyllithium-initiated polymerizations are often effected at elevated temperatures (>50°C) to increase the rate of initiation relative to propagation and thus to obtain polymers with narrower molecular weight distributions (59). Hydrocarbon solutions of this initiator are quite stable at room temperature for extended periods of time; the rate of decomposition per month is 0.06% at 20°C (43).

sec-Butyllithium [598-30-1] is the second most important organolithium initiator. It 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 (60). Hydrocarbon solutions of *sec*-butyllithium are thermally less stable than *n*-butyllithium solutions; the rate of decomposition is 1.4% per month at 20°C (43).

3.1. Quantitative Analysis of Alkyllithium Initiator Solutions. Solutions of alkyllithium compounds frequently show turbidity associated with the formation of lithium alkoxides by oxidation reactions or lithium hydroxide by reaction with moisture. Although these species contribute to the total basicity of the solution as determined by simple acid titration, they do not react with allylic and benzylic chlorides or ethylene dibromide rapidly in ether solvents. This difference is the basis for the double titration method of determining the amount of active carbon-bound lithium reagent in a given sample (61,62).

Thus the amount of carbon-bound lithium is calculated from the difference between the total amount of base determined by acid titration and the amount of base remaining after the solution reacts with either benzyl chloride, allyl chloride, or ethylene dibromide.

3.2. Copolymerization Initiators and Effects of Alkali Metal Alkoxides. The copolymerization of styrene and dienes in hydrocarbon solution with alkyllithium initiators produces a tapered block copolymer structure because of the large differences in monomer reactivity ratios for styrene ($r_s < 0.1$) and dienes ($r_d > 10$) (1,2,32,33). In order to obtain "random" (ie, nonblocky styrene distribution) copolymers of styrene and dienes, it is necessary to either add small amounts of a Lewis base such as THF or an alkali metal alkoxide (MtOR, where Mt = Na, K, Rb, or Cs). In contrast to Lewis bases that promote formation of undesirable vinyl microstructure in diene polymerizations (63), the addition of small amounts of an alkali metal alkoxide such as potassium amyloxide ($[\mathrm{ROK}]/[\mathrm{Li}] = 0.08$) is sufficient to promote random copolymerization of styrene and diene without producing significant increases in the amount of vinyl microstructure (64,65). The use of sodium 2,3-dimethyl-3-pentoxide ($[\mathrm{RONa}]/[\mathrm{RLi}] = 0.2$) as randomizer for alkyllithium-initiated styrene–butadiene copolymerization provides a copolymer with less block styrene content ($[\mathrm{S}]_n$) compared to the potassium alkoxide randomizer because of the lower monomer reactivity ratios for NaOR/BuLi system ($r_S = 0.04$; $r_B = 1.14$) (66,67). It is noteworthy that butyllithium-initiated polymerization of styrene in the presence of stoichiometric amounts of either lithium *tert*-butoxide or lithium hydroxide forms highly isotactic polystyrene in hexane solution at -30°C (68,69); nontactic polystyrene is obtained in the absence of these salts (2).

3.3. Difunctional and Trifunctional Initiators. These initiators are of considerable interest for the preparation of triblock copolymers, telechelic polymers, and macrocyclic polymers. Although triblock copolymers can be prepared with monofunctional initiators using a three-step, sequential monomer addition process, with difunctional initiators they can be formed in a more efficient two-step process (1,2,33,70,71). Difunctional initiators also provide a methodology to prepare new triblock copolymers that cannot be prepared by the three-step, sequential monomer addition route because the chain ends formed from the first monomer are too stable to initiate the polymerization of the second monomer; eg, a difunctional initiator can be used for the direct synthesis of poly(ethylene oxide)-*block*-polystyrene-*block*-poly(ethylene oxide) (71) or poly(methyl methacrylate)-*block*-polybutadiene-*block*-poly(methyl methacrylate) (72). Difunctional initiators provide direct, efficient methods for the formation of α,ω-difunctional polymers, ie, telechelic polymers (73) , by termination reactions of the polymeric α,ω-dianions with electrophilic functionalization agents. Analogously, termination of the α-dianions with a difunctional, electrophilic coupling agent under high dilution conditions promotes intramolecular cyclization reactions to form macrocyclic polymers (74).

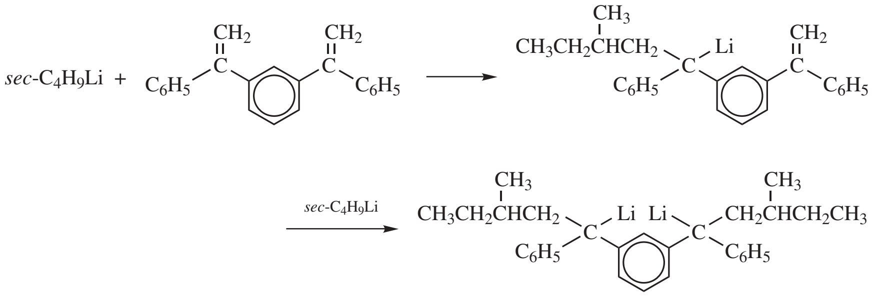
Aromatic radical anions, such as lithium naphthalene or sodium naphthalene, are efficient difunctional initiators (eqs. 10,11) (3,19,75). However, the necessity of using polar solvents for their formation and use limits their utility for diene polymerization, since the unique ability of lithium to provide high 1,4-polydiene microstructure is lost in polar media (1,2,32,33,63,75). Consequently, a significant research challenge has been to discover hydrocarbon-soluble dilithium initiators, which can initiate the polymerization of styrene and diene monomers to form monomodal α,ω-dianionic polymers at rates which are faster or comparable to the rates of polymerization, ie, to form narrow molecular weight distribution polymers (71,76,77).

The methodology for preparation of hydrocarbon-soluble, dilithium initiators is generally based on the reaction of an aromatic divinyl precursor with 2 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 (see Table 2) (32,42,48,78), attempts to prepare dilithium initiators in hydrocarbon media have generally resulted in the formation of insoluble, three-dimensionally associated species (33,77,79–83). These precipitates are not effective initiators because of their heterogeneous initiation reactions with monomers that tend to result in broader molecular weight distributions ($M_w/M_n > 1.1$) (79,81,83). Soluble analogues of these difunctional initiators have been prepared either by addition of small amounts of weakly basic additives such as triethylamine (84) or anisole (85), which have relatively minor effects on diene microstructure (36). Another method to solubilize these initiators is to use a seeding technique, whereby small amounts of diene monomer are added to form a hydrocarbon-soluble, oligomeric dilithium-initiating species (80,86).

The stoichiometric reaction of *m*-diisopropenylbenzene [3748-13-8] with 2 mol of *sec*-butyllithium in the presence of triethylamine has been reported to produce a useful, hydrocarbon-soluble dilithium initiator because of the low ceiling temperature of the monomer (87,88), which is analogous in structure to α-methylstyrene; however, other studies suggest that oligomerization occurs to form initiators with functionalities higher than two (89,90). A well-defined, hydrocarbon-soluble dilithium initiator was reportedly formed from the addition reaction of the more sterically hindered *tert*-butyllithium with *m*-diisopropenylbenzene in cyclohexane at −20°C in the presence of 1 equiv of triethylamine (91). However, it was necessary to add additional Lewis base (THF or diethyl ether) to obtain useful S-B-S triblock copolymers.

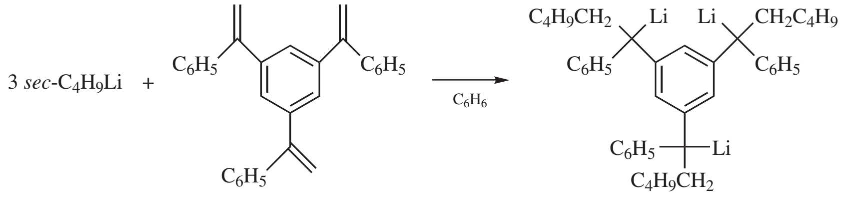
Analogously, the use of *m*-divinylbenzene [108-57-6] has been reported (87). However, oligomerization occurs on treatment of divinylbenzene with butyllithium resulting in initiators with functionalities >2 (79). From a commercial perspective this oligomerization and lack of precise functionality control is not necessarily a problem and useful multifunctional initiators have been prepared from the reaction of butyllithium with varying amounts of divinylbenzene (commercial divinylbenzene contains 22% meta, 11% para, and 66% *o*-, *m*-, and *p*-ethylvinylbenzene) (92) often in the presence of styrene or diene monomer to provide solubility (seeding technique). The reaction of high purity *sec*-butyllithium with pure *m*-divinylbenzene at −79°C in the presence of 10 mol% triethylamine was reported to result in an initiator with overall functionality of 1.98 and no traces of tri- and tetrafunctional impurities (93). A similar reaction with pure *p*-divinylbenzene at 0°C was reported to form a similar dilithium initiator with 96% difunctionality and 4% monofunctionality (94).

Although a plethora of divinyl aromatic compounds have been investigated as precursors for hydrocarbon-soluble dilithium initiators (79), the best system that has been demonstrated to produce a hydrocarbon-soluble dilithium initiator is based on 1,3-bis(1-phenylethenyl)benzene (70,95–101). This initiator is based on the fact that reactions of 1,1-diphenylethylene (DPE) with organolithium compounds are simple, quantitative, monoaddition reactions because DPE is a nonhomopolymerizable monomer (101). The addition reaction of *sec*-butyllithium with 1,3-bis(1-phenylethenyl)benzene [34241-86-6] (eq. 21) proceeds rapidly and efficiently to produce the corresponding dilithium species in toluene (102) or in cyclohexane (96). This dilithium initiator is not only soluble in hydrocarbon media such as cyclohexane, benzene, and toluene (even at −20°C) (98), but also functions as an efficient difunctional initiator for the preparation of homopolymers and triblock copolymers with relatively narrow molecular weight distributions (70,95–97) . However, it is necessary to add a small amount of Lewis base or 2 equiv of lithium *sec*-butoxide to produce narrow, monomodal molecular weight distributions. Lithium *sec*-butoxide is the preferred additive, since high 1,4-polybutadienes are obtained (70).



(21)

An analogous hydrocarbon-soluble, trilithium initiator has been prepared based on the addition of 3 mol of *sec*-butyllithium with 1,3,5-tris(1-phenylethenyl)benzene (eq. 22) (103).



(22)

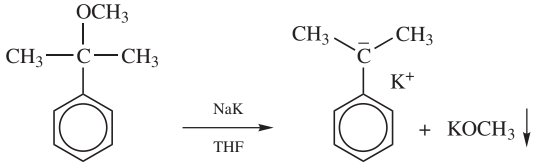
Using this initiator it is possible to directly synthesize star-branched polystyrenes, polydienes and their block copolymers with well-defined structures and functional end groups (103,104). It is necessary to add either a Lewis base or preferably a lithium alkoxide to obtain monomodal, narrow molecular weight distribution polymers.

3.4. Functionalized Initiators. The use of alkyllithium initiators that contain functional groups provides a versatile method for the preparation of end functionalized polymers and macromonomers (105). For a living anionic polymerization, each functionalized initiator molecule produces one macromolecule with the functional group from the initiator residue at one chain end and the active carbanionic propagating species at the other chain end. Thus, in contrast to most functionalization procedures that involve post-polymerization termination reactions with electrophilic reagents (106), the use of a functionalized initiator retains the anionic chain end and the ability to prepare block and star-branched polymers with the functional group at the initiating end (105). For example, dimethylaminopropyllithium can be prepared in hydrocarbon solution and has been used to prepare polystyrenes and polydienes with tertiary amine end group functionality (107,108). 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 (2). Therefore, it is necessary to convert these functional groups into suitable derivatives, ie, protected groups, which must be stable to the carbanionic chain ends and which can be removed readily after polymerization is completed (109,110). Examples of these types of protected functional initiators include the hydroxyl-protected initiators, 6-lithiohexyl acetaldehyde acetal (111) and 3-(*tert*-butyldimethylsiloxy)-1-propyllithium (112), the primary amine-protected initiator, 4-bis(trimethylsily)aminophenyllithium (113) and the tertiary amine-functionalized initiator, *N*-benzyl-*N*-methylamino)-1-propyllithium (114). The later initiator can generate secondary amine-functionalized polymers by hydrogenolysis of the N-benzyl moiety (114). Functionalized initiators offer an additional alternative for the preparation of chain-end functionalized polymers that have been proven to offer superior performance in the formulation of tire tread compounds with lower fuel consumption characteristics (115). Analogous improvements in properties of compounded elastomers, eg, reduced hysteresis, have been achieved using the initiator, tributyltin lithium, which results in tributyltin groups at each initiating chain end (116,117).

4. Other Initiators

4.1. Organosodium and Organopotassium Compounds. Normal alkyl derivatives of sodium and potassium, such as the butyl and pentyl derivatives, are colorless, nonvolatile ionic solids that are insoluble in hydrocarbon media (118). These materials are more reactive than the corresponding alkyllithium compounds, ie, they react with ethers and aromatic compounds much more rapidly. This has been attributed to the partially covalent nature of the carbon–lithium bond (2). However, higher homologous alkyl sodium derivatives, such as 2-ethylhexylsodium, are soluble in hydrocarbon solvents such as heptane and isooctane (119). 2-Ethylhexylsodium quantitatively initiated 1,3-butadiene and isoprene polymerization in heptane at 30°C to form the corresponding polydienes with somewhat broad molecular weight distributions ($M_w/M_n = 1.2–1.5$), which was attributed to chain transfer to polymer (120). The corresponding polybutadiene microstructure corresponded to 60–65% 1,2-, 20–25% *trans*-1,4- and 15% *cis*-1,4-enchainment. For polyisoprene, the microstructure consisted of 55–60% 4,3-, 33–36% trans-1,4- and 6–8% cis-1,4-units. The chain-transfer constant (k_{tr}/k_p) to toluene at 30°C was ≤ 0.000001 and 0.037 for lithium versus sodium as counterion, respectively (120). Styrene–butadiene copolymerization in heptane at 30°C using 2-ethylhexylsodium as initiator gave an alternating copolymerization ($r_S = 0.42$; $r_B = 0.3$) and a copolymer with 55–60% 1,2-microstructure (121). 2-Ethylhexylpotassium is also soluble in saturated hydrocarbon solvents; however, it is unstable and quickly decomposes at room temperature (122). A stable organopotassium initiator was prepared by the reaction of 2-ethylhexylpotassium with 1,1-diphenylethylene to form the corresponding 1,1-diphenylalkylpotassium derivative that was insoluble in heptane, but partially soluble in benzene (122). Using this organopotassium initiator, styrene–butadiene copolymerization in cyclohexane at 25°C gave a somewhat alternating copolymerization ($r_S = 0.12$; $r_B = 3.3$) and a copolymer with 55–60% 1,2-microstructure (122).

Cumyl potassium [3003-91-6] ($pK_a > 43$ based on toluene) (6) is another 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 23 (123). It is necessary to remove the potassium methoxide salt that precipitates from the solution; cooling to low temperature prior to filtration is recommended. The concentration of active initiating species can be determined by titration with standardized acid or by using this initiator with a known amount of styrene monomer and measuring the number average molecular weight of the polymer assuming that one initiator moiety produces one polystyrene macromolecule. This initiator is generally used at low temperatures in a polar solvent such as THF, which limits the microstructure of polydienes to low 1,4-contents.



(23)

4.2. Organomagnesium Compounds and Mixed Organometallic Compounds.

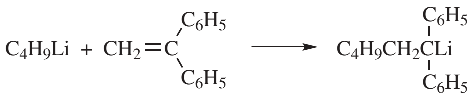
The isospecific, living polymerization of methyl methacrylate can be effected in toluene at −78°C using the complex of *tert*-butylmagnesium bromide with at least 1 equiv of magnesium bromide and long reaction times (>24 h) (124,125). The resulting poly(methyl methacrylate) is highly isotactic (>96% mm triads). Syndiospecific, living polymerization of methyl methacrylate was realized using a combination of *tert*-butyllithium with trialkylaluminum compounds such as triethylaluminum ($[Al]/[Li] \geq 3$) in toluene at −78°C for 24 h (125–127). The polymer was highly syndiotactic (>90% rr triads). Narrow molecular weight distributions ($M_w/M_n \leq 1.1$) and controlled molecular weights [$M_{n(calc)} \approx M_{n(obs)}$] were obtained for both of these stereospecific polymerizations.

The addition of *sec*-dibutylmagnesium to *sec*-butyllithium as coinitiator for styrene polymerization greatly reduces the rate of polymerization of styrene in cyclohexane such that controlled, quantitative polymerizations can be effected at elevated temperatures (eg, 100°C) and high monomer concentrations (128,129). Increased retardation effects are observed for [Mg]/[Li] up to 4. Molecular weights correspond to predictions based on the participation of *sec*-butyllithium and only the *sec*-butyl groups from *sec*-dibutylmagnesium as initiating groups. Studies with phenoxy-substituted magnesium compounds confirmed the retarding effect of magnesium compounds as well as the improved chain end stability even at 150°C (129).

4.3. Organobarium Compounds. Several organobarium anionic initiators were recently reported to polymerize styrene and 1, 3-butadiene (130). Initiation kinetics studies were performed for 1,4-barium-1,1,4,4-tetraphenylbutane, bis(triphenylmethyl)barium and bis(1,1,3-triphenylpropyl)barium using THF, benzene or their mixtures. Following the reasoning given in the introduction of this chapter, ie, "the pK_a of the conjugate acid of the propagating anion should correspond closely to the pK_a of the conjugate acid of the initiating species", it was expected that these 1,1-diphenylalkyl and much less basic triphenylmethyl carbanions would not efficiently initiate the polymerization of styrene and 1, 3-butadiene for which the corresponding propagating anions have conjugate acids with pK_a values that are 10 units higher than those of these initiators (see Table 1). However, by taking into account the exothermicity of the addition of the first monomer molecule, ie, conversion of a pi bond into a sigma bond, one can explain this apparent contradiction (2,101). It was reported that the efficiency of these initiators is very low in THF ($\sim 0.3-0.5$) but was quantitative in benzene. Quantitative styrene polymerization was also reported for the initiator, 1,4-barium-1,1,4,4-tetraphenylbutane, in cyclohexane although the molecular weight distribution was broad ($M_\mathrm{w}/M_\mathrm{n} = 1.20$) (131). Previous extensive studies on the use of organobarium initiators for styrene polymerization were carried out in THF (132,133).

Polybutadienes with high *cis*-1,4-microstructure (65–80%) and low 1,2-microstructure (10%) were obtained with barium as counterion in benzene solution (134). Using organolithium initiators in combination with barium salts in toluene solution, polybutadienes and poly(styrene-*co*-butadiene)s with high *trans*-1,4-polybutadiene microstructure (79%) and low 1,2-polybutadiene content (7%) have been prepared (135,136).

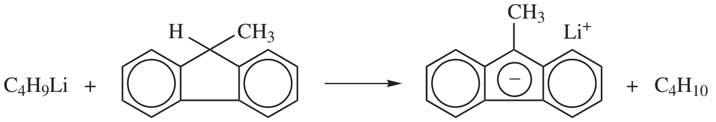
4.4. 1,1-Diphenylmethylcarbanions. The carbanions based on diphenylmethane (p$K_\mathrm{a} = 32$) (6) are useful initiators for vinyl and heterocyclic monomers, especially alkyl methacrylates at low temperatures (101,137,138). Addition of lithium salts such as lithium chloride, lithium *tert*-butoxide or lithium 2-(2-methoxyethoxy)ethoxide with these initiators has been shown to narrow the molecular weight distribution and improve the stability of active centers for anionic polymerization of both alkyl methacrylates and *tert*-butyl acrylate (101,139–141). Surprisingly, these more stable carbanions can also efficiently initiate the polymerization of styrene and diene monomers as discussed above for the analogous organobarium compounds (101,142). Diphenylmethyllithium [881-42-5] can be prepared by the metalation reaction of butyllithium with diphenylmethane; in addition, the adduct of butyllithium and 1,1-diphenylethylene, 1,1-diphenylhexyllithium, is conveniently prepared in either hydrocarbon or polar solvents such as THF as shown in equation 24 (101).



$$C_4H_9Li + CH_2{=}C(C_6H_5)_2 \longrightarrow C_4H_9CH_2C(C_6H_5)_2Li \qquad (24)$$

This reaction can also be utilized to prepare functionalized initiators by reaction of butyllithium with a substituted 1,1-diphenylethylene derivative (101,142). For example, polymers end functionalized with primary amine, tertiary amine, phenol, bis(phenol), and fluorescent groups have been prepared in essentially quantitative yield by using the reaction of butyllithium with the corresponding substituted (or protected) 1,1-diphenylethylene or aromatic analog (101,106).

4.5. Fluorenyl Carbanions. Salts of fluorene ($pK_a = 22.6$) (6) are more hindered and less reactive than many other organometallic initiators. These carbanions can be readily formed by reaction with alkali metal derivatives as shown in equation 25 for 9-methylfluorene (143). Carbanion salts of 9-methylfluorene are preferable to fluorene, since the latter generate chain ends that retain reactive, acidic fluorenyl hydrogens that can participate in chain-transfer reactions (144,145). Fluorenyl salts are useful initiators for the polymerization of alkyl methacrylates, epoxide, and thiirane monomers.



(25)

4.6. Enolate Initiators. In principle, ester enolate anions should represent the ideal initiators for anionic polymerization of alkyl methacrylates. Although general procedures have been developed for the preparation of a variety of alkali metal enolate salts, many of these compounds are unstable except at low temperatures (78,146,147). Useful initiating systems for acrylate polymerization have been prepared from complexes of ester enolates with alkali metal alkoxides (141,148,149).

4.7. Metal-Free Initiators. Metal-free initiators for acrylate and methacrylate ester polymerizations are anions of low nucleophilicity (eg, thiolates, malonates, phenylacetates , fluorenide, carbazolides, 2-nitropropanate) formed from thiols or CH-acidic organic compounds with tetrabutylammonium (TBA^+) counterions (150–153). They are generally prepared by deprotonation of the carbon acid followed by azeotropic water distillation as shown in equation 26 (153).

$$R{-}H + HO^- \ (Bu)_4N^+ \longrightarrow R^- \ (Bu)_4N^+ + H_2O\uparrow \qquad (26)$$

With these initiators, (meth)acrylate esters can be quantitatively polymerized at room temperature to form polymers with molecular weights from 1500–25,000 ($M_{n(obsd)} < M_{n(calc)}$ for acrylates; $M_{n(obsd)} > M_{n(calc)}$ for methacrylates) and with somewhat broad molecular weight distributions ($M_w/M_n = 1.1–3.6$). The lack of control for metal-free intiators has been attributed to incomplete and often slow, reversible initiation (methacrylates), Hofmann elimination to form tributylamine, and the normal backbiting termination reaction of the terminal ester enolate anion with the penultimate ester unit (153,154).

Tetraphenylphosphonium salts of triphenylmethanide (trityl carbanion) effect the rapid, controlled, quantitative polymerization of methyl methacrylate

(MMA) at room temperature to form PMMA with narrow molecular weight distribution ($M_w/M_n \leq 1.1$); however, the initiator efficiency was only 32–68% (155).

It has been proposed that group-transfer polymerization (acrylate monomer polymerization by a repeated silyl Michael addition) catalyzed by strong nucleophiles proceeds by a reversible generation of free ester enolate anions (156). Thus, this process is analogous to acrylate polymerizations using metal-free initiators.

4.8. Alkoxides and Related Initiators. Using the guide that an appropriate initiator should have approximately the same structure and reactivity as the propagating anionic species (see Table Table 1), alkoxide, thioalkoxide, carboxylate, and silanolate salts would be expected to be useful initiators for the anionic polymerization of aldehydes, epoxides, thiiranes, lactones, and siloxanes, respectively (157–160). Thus low molecular weight poly(ethylene oxide) can be prepared using catalytic amounts of potassium hydroxide in the presence of water, alcohol, or glycol (161) (see ETHYLENE OXIDE POLYMERS). The presence of hydroxylic groups is not a problem because of the fast proton-transfer equilibria between active chain ends as shown in equation 27 (161). In order to prepare

$$\mathrm{H{-}(OCH_2CH_2)_{\mathit{n}}{-}O^{-}K^{+}} + \mathrm{H{-}(OCH_2CH_2)_{\mathit{m}}{-}OH} \rightleftharpoons \mathrm{H{-}(OCH_2CH_2)_{\mathit{n}}{-}OH} + \mathrm{H{-}(OCH_2CH_2)_{\mathit{m}}{-}O^{-}K^{+}} \tag{27}$$

higher molecular weight poly(ethylene oxide) (10^5–10^6 g/mol), catalysts such as strontium carbonate (0.1–0.4% H_2O), calcium amide, or calcium amide alkoxide are required (161). Thiiranes are more reactive than epoxides and their polymerization can even be initiated with amines and phosphines (162). For β-propiolactone, the propagating anion is a carboxylate, while for ϵ-caprolactone it is an alkoxide (157,162). Thus, although carboxylates can be used to initiate polymerization of β-propiolactone , alkoxides are necessary for polymerization of less reactive ϵ-caprolactone. Hydroxides, alkoxides, and silanolates (R_3SiO^-) are effective initiators for the polymerization of cyclosiloxanes (159). In general, the larger counterions give rise to more active catalysts ($Li^+ < Na^+ < K^+ < Rb^+ < Cs^+ \approx R_4N^+$) (159).

The pK_a data in Table 1 suggest that alkoxides should be useful initiators for the anionic polymerization of methacrylate monomers. In the presence of either external complexing ligands or coordinating ligands in the monomer, alkoxides can initiate polymerization of alkyl methacrylates. Thus, potassium alkoxides can initiate polymerization of 2-(diethylamino)ethyl methacrylate and also methyl methacrylate in the presence of cryptand [222] (163,164).

5. Health and Safety Factors

The hazards associated with organolithium compounds and other reactive organometallic compounds such as cumyl potassium are corrosivity, flammability and pyrophoricity (165). The corrosive nature of organolitium compounds can cause both chemical and thermal burns. Organolithium compounds are flammable and they are typically supplied in flammable hydrocarbon solutions. *n*-Butyllithium, *sec*-butyllithium, and *tert*-butyllithium are pyrophoric, ie, they spontaneously ignite on exposure to air, oxygen or moisture. The pyrophoricity increases in the order *n*-butyllithium < *sec*-butyllithium < *tert*-butyllithium (165). Users of these reactive organometallic compounds are advised to strictly follow the handling instructions recommended by their suppliers. Because hydrocarbon solutions of alkyllithium compounds are air and moisture sensitive, they should be either handled in an inert atmosphere or by using syringes using recommended procedures for handling air-sensitive compounds (166). Alkyllithium reagents react with acidic compounds that contain reactive hydrogens such as water, alcohols, phenols, acids, and even primary and secondary amines (42,43). The reaction of butyllithium with water produces butane and lithium hydroxide, which can lead to spontaneous ignition in the presence of oxygen (43). Carbon dioxide fire extinguishers must not be used because carbon dioxide reacts exothermically with alkyllithium compounds. It is prudent to have an all-purpose fire extinguisher available when working with these organometallic compounds. Suitable fire-extinguishing chemicals include powdered limestone and powders containing sodium chloride and sodium bicarbonate (43).

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Table 1. **Relationships Between Monomer Reactivity, Carbanion Stability, and Suitable Initiators**

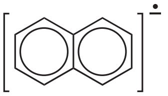
	pK_a[a]		
Monomer type	In DMSO[b]	In H_2O[c]	Initiators[d]
ethylene	56		RLi
dienes and	44		NH_2^-, RLi, RMt
styrenes	43		aromatic radical anions,[e] cumyl K, Mt, RMgX
acrylonitrile	32		
alkyl methacrylates, alkyl acrylates	30–31 (7)	27–28 (7)	fluorenyl$^-$, $Ar_2C^\bullet$, ketyl radical anions[f]
vinyl ketones	26	19 (8)	
oxiranes	29–32	16–18 (9)	RO^-
thiiranes	17	12–13 (10)	
nitroalkenes	17	10–14 (11)	
siloxanes		10–14 (12,13)	RO^-, OH^-
β-lactones	12	4–5 (14)	$RCOO^-$
alkyl cyanoacrylates	12.8 (15)		HCO_3^-, H_2O
vinylidene cyanide	11	11 (15)	

[a] The pK_a of the conjugate acid of the anionic propagating intermediate.

[b] The pK_a values in dimethyl sulfoxide (DMSO) are from Ref. 6 unless noted in parentheses after the number.

[c] Numbers in parentheses are references.

[d] Mt refers generally to alkali metals (Li, Na, K, Rb, Cs).

[e] For example, naphthalene radical anion  with counterion (Li^+, Na^+, K^+).

[f] Ar2CO●

Table 2. **Association Numbers and Fractional Kinetic Orders for Alkyllithium Initiators**

RLi	Solvent	N^a	Monomer	Reaction order[b]
n-C_4H_9Li	benzene	6	styrene	0.16
			butadiene	0.5–1.0
	cyclohexane	6.2	styrene	0.5–1.0
			butadiene	0.5–1.0
s-C_4H_9Li	benzene	4	styrene	0.25
			butadiene	0.9
			isoprene	0.25
	cyclohexane	4	styrene	1.0
			butadiene	1.0
			isoprene	0.66–1.09
t-C_4H_9Li				
	cyclohexane		butadiene	1.0
			isoprene	0.2–0.7

[a] Degree of association of RLi; Refs. (42,50,53).

[b] Kinetic order in [RLi] for initiation; Refs. (32,35,45,51,52).

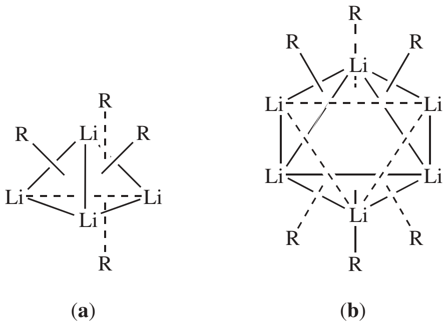


Fig. 1. Structures of alkyllithium tetramers and hexamers: (**a**) tetrahedron of lithium alkyl groups; (**b**) arrangement of alkyl groups around octahedron of lithium atoms in hexamer.