

CHAPTER 5

IONIC CHAIN POLYMERIZATION

5-1 COMPARISON OF RADICAL AND IONIC POLYMERIZATIONS

Almost all monomers containing the carbon–carbon double bond undergo radical polymerization, while ionic polymerizations are highly selective (Table 3-1). Cationic polymerization is essentially limited to those monomers with electron-releasing substituents such as alkoxy, phenyl, vinyl, and 1,1-dialkyl. Anionic polymerization takes place with monomers possessing electron-withdrawing groups such as nitrile, carbonyl, phenyl, and vinyl. The selectivity of ionic polymerization is due to the very strict requirements for stabilization of anionic and cationic propagating species (Sec. 3-1b-2). The commercial utilization of cationic and anionic polymerizations is rather limited because of this high selectivity of ionic polymerizations compared to radical polymerization (and the greater importance of coordination polymerization compared to ionic polymerization).

Ionic polymerizations, especially cationic polymerizations, are not as well understood as radical polymerizations because of experimental difficulties involved in their study. The nature of the reaction media in ionic polymerizations is often not clear since heterogeneous inorganic initiators are often involved. Further, it is extremely difficult in most instances to obtain reproducible kinetic data because ionic polymerizations proceed at very rapid rates and are extremely sensitive to the presence of small concentrations of impurities and other adventitious materials. The rates of ionic polymerizations are usually greater than those of radical polymerizations. These comments generally apply more to cationic than anionic polymerizations. Anionic systems are more reproducible because the reaction components are better defined and more easily purified.

Cationic and anionic polymerizations have many similar characteristics. Both depend on the formation and propagation of ionic species, a positive one in one case and a negative one in the other. The formation of ions with sufficiently long lifetimes for propagation to yield high-molecular-weight products generally requires stabilization of the propagating centers by solvation. Relatively low or moderate temperatures are also needed to suppress termination, transfer, and other chain-breaking reactions which destroy propagating centers.

Although solvents of high polarity are desirable to solvate the ions, they cannot be employed for several reasons. The highly polar hydroxylic solvents (water, alcohols) react with and destroy most ionic initiators. Other polar solvents such as ketones prevent initiation of polymerization by forming highly stable complexes with the initiators. Ionic polymerizations are, therefore, usually carried out in solvents of low or moderate polarity such as tetrahydrofuran, ethylene dichloride, and pentane, although moderately high polarity solvents such as nitrobenzene are also used. In such solvents one usually does not have only a single type of propagating species. For any propagating species such as $\sim\sim\sim\text{BA}$ in cationic polymerization, one can visualize the range of behaviors from one extreme of a completely *covalent* species (**I**) to the other of a completely *free* (and highly solvated) *ion* (**IV**)



The intermediate species include the *tight* or *contact ion pair* (**II**) (also referred to as the *intimate ion pair*) and the *solvent-separated* or *loose ion pair* (**III**). The intimate ion pair has a *counter-* or *gegenion* of opposite charge close to the propagating center (unseparated by solvent). The solvent-separated ion pair involves ions that are partially separated by solvent molecules. The propagating cationic chain end has a negative counterion. For an anionic polymerization the charges in species **II-IV** are reversed; that is, B carries the negative charge and A the positive charge. There is a propagating anionic chain end with a positive counterion. Alternate terms used for free ion and ion pair are *unpaired ion* and *paired ion*, respectively.

Most ionic polymerizations involve two types of propagating species, an ion pair and a free ion **IV**, coexisting in equilibrium with each other. The identity of the ion pair (i.e., whether the ion pair is best described as species **II** or **III**) depends on the particular reaction conditions, especially the solvent employed. Increased solvent polarity favors the loose ion pair while the tight ion pair predominates in solvents of low polarity. The ion pairs in cationic polymerization tend to be loose ion pairs even in solvent of low or moderate polarity since the counterions (e.g., bisulfate, SbCl_6^- , perchlorate) are typically large ions. The lower charge density of a large counterion results in smaller electrostatic attractive forces between the propagating center and counterion. The nature of the ion pairs is much more solvent-dependent

in anionic polymerizations where the typical counterion (e.g., Li^+ , Na^+) is small. The covalent species **I** is generally ignored since it is usually unreactive (or much lower in reactivity) compared to the other species. Free-ion concentrations are generally much smaller than ion-pair concentrations but the relative concentrations are greatly affected by the reaction conditions. Increased solvent polarity results in a shift from ion pairs to free ions. The nature of the solvent has a large effect in ionic polymerization since the different types of propagating species have different reactivities. Loose ion pairs are more reactive than tight ion pairs. Free ions are orders of magnitude higher in reactivity than ion pairs in anionic polymerization. Ion pairs are generally no more than an order of magnitude lower in reactivity compared to free ions in cationic polymerization.

Ionic polymerizations are characterized by a wide variety of modes of initiation and termination. Unlike radical polymerization, termination in ionic polymerization never involves the bimolecular reaction between two propagating polymer chains of like charge. Termination of a propagating chain occurs by its reaction with the counterion, solvent, or other species present in the reaction system.

5-3 ANIONIC POLYMERIZATION OF THE CARBON-CARBON DOUBLE BOND

Anionic chain polymerizations show many of the same characteristics as cationic polymerizations, although there are some distinct differences. The propagating species are anionic ion pairs and free ions with relative concentrations that depend on the reaction media as in cationic polymerization. Unlike cationic polymerization, there is a large difference between the reactivities of ion pairs and free ions in anionic polymerization. Although anionic polymerizations generally proceed rapidly at low temperatures, they are seldom as temperature-sensitive as cationic polymerizations. Further, most anionic polymerizations possess positive E_R values and proceed well at and somewhat above ambient temperatures. Many anionic polymerizations are easier to understand, since the identities of the initiating species and counterions are much better established. The range of solvents useful for anionic polymerization is limited to aliphatic and aromatic hydrocarbons and ethers. Halogenated solvents, suitable for cationic polymerization, cannot be used for anionic polymerization because of their facile nucleophilic substitution reactions with carbanions. Other polar solvents such as esters and ketones are also excluded as a result of reaction with carbanions.

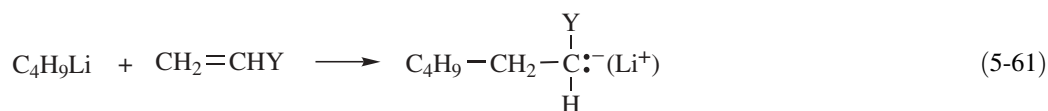
Termination occurs by transfer of a positive fragment, usually a proton, from the solvent or some transfer agent (often deliberately added), although other modes of termination are also known. Many anionic polymerizations are living polymerizations when the reaction components are appropriately chosen.

5-3a Initiation

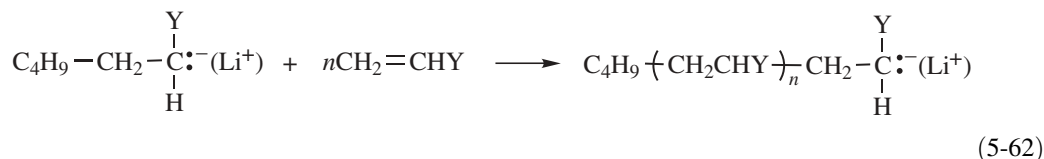
5-3a-1 Nucleophilic Initiators

A variety of basic (nucleophilic) initiators have been used to initiate anionic polymerization [Bywater, 1975, 1976, 1985; Fontanille, 1989; Hsieh and Quirk, 1996; Morton, 1983; Morton and Fetters, 1977; Quirk, 1995, 1998, 2002; Richards, 1979; Szwarc, 1983; Young et al., 1984]. These include covalent or ionic metal amides such as NaNH_2 and $\text{LiN}(\text{C}_2\text{H}_5)_2$, alkoxides, hydroxides, cyanides, phosphines, amines, and organometallic compounds such as $n\text{-C}_4\text{H}_9\text{Li}$ and ϕMgBr . Initiation involves the addition to monomer of a nucleophile (base), either a neutral ($\text{B}:$) or negative (B^-) species.

Alkyl lithium compounds are probably the most useful of these initiators, employed commercially in the polymerizations of 1,3-butadiene and isoprene. Initiation proceeds by addition of the metal alkyl to monomer



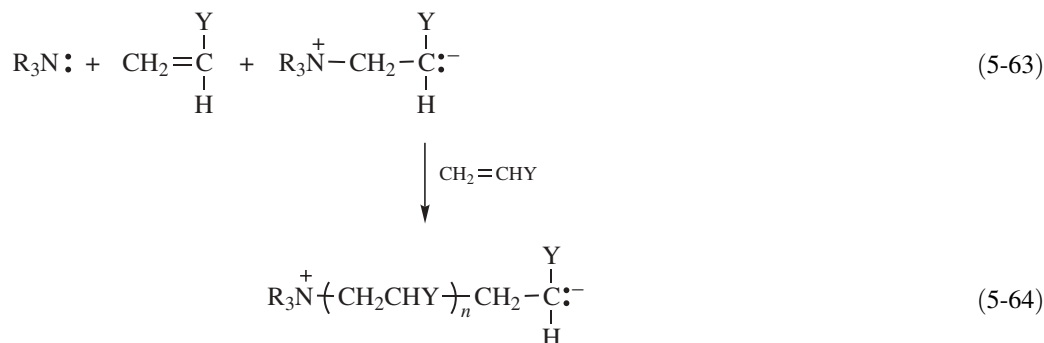
followed by propagation:



The extensive use of alkyllithium initiators is due to their solubility in hydrocarbon solvents. Alkyls or aryls of the heavier alkali metals are poorly soluble in hydrocarbons, a consequence of their more ionic nature. The heavier alkali metal compounds, as well as alkyllithiums, are soluble in more polar solvents such as ethers. The use of most of the alkali metal compounds, especially, the more ionic ones, in ether solvents is somewhat limited by their reactivity toward ethers. The problem is overcome by working below ambient temperatures and/or using less reactive (i.e., resonance-stabilized) anions as in benzylpotassium, cumylcesium and diphenylmethylithium.

Alkyl derivatives of the alkaline-earth metals have also been used to initiate anionic polymerization. Organomagnesium compounds are considerably less active than organolithiums, as a result of the much less polarized metal-carbon bond. They can only initiate polymerization of monomers more reactive than styrene and 1,3-dienes, such as 2- and 4-vinylpyridines, and acrylic and methacrylic esters. Organostrontium and organobarium compounds, possessing more polar metal-carbon bonds, are able to polymerize styrene and 1,3-dienes as well as the more reactive monomers.

In the relatively few anionic polymerizations initiated by neutral nucleophiles such as tertiary amines or phosphines the proposed propagating species is a zwitterion [Cronin



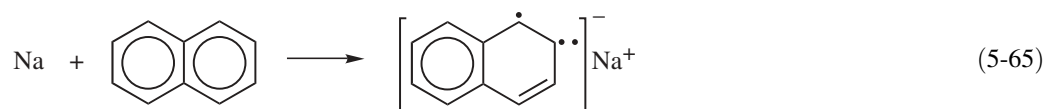
and Pepper, 1988; Eromosele et al., 1989; Klemarczyk, 2001; Pepper and Ryan, 1983]. Primary and secondary amines are much less effective than tertiary amines. The zwitterion propagating species has the glaring deficiency of requiring increasing charge separation as propagation proceeds. Stabilization of zwitterion species may involve the positive end of one zwitterion propagating chain acting as the counterion of the carbanion end of another zwitterion propagating chain. The need for a zwitterion propagating species is avoided if initiation is proposed as occurring via hydroxide ion formed by the reaction of amine with adventitious water [Donnelly et al., 1977; Ogawa and Romero, 1977].

The initiator required to polymerize a monomer depends on the reactivity of the monomer toward nucleophilic attack. Monomer reactivity increases with increasing ability to stabilize the carbanion charge. Very strong nucleophiles such as amide ion or alkyl carbanion are needed to polymerize monomers, such as styrene and 1,3-butadiene, with relatively weak electron-withdrawing substituents. Weaker nucleophiles, such as alkoxide and hydroxide

ions, can polymerize monomers with strongly electron-withdrawing substituents, such as acrylonitrile, methyl methacrylate, and methyl vinyl ketone, although the efficiency is lower than that of the stronger nucleophiles. A monomer, such as methyl- α -cyanoacrylate, with two electron-withdrawing substituents can be polymerized with very mild nucleophiles such as Br^- , CN^- , tertiary amines, and phosphines. This monomer, used in many so-called superglues, polymerizes on contact with many surfaces. Polymerization probably involves initiation by adventitious water (or OH^- from water) [Donnelly et al., 1977].

5-3a-2 Electron Transfer

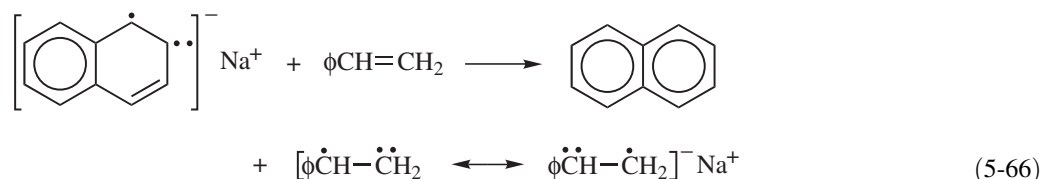
Szwarc and coworker have studied the interesting and useful polymerizations initiated by aromatic radical-anions such as sodium naphthalene [Szwarc, 1968, 1974, 1983]. Initiation proceeds by the prior formation of the active initiator, the naphthalene radical-anion (**XVIII**)



XVIII

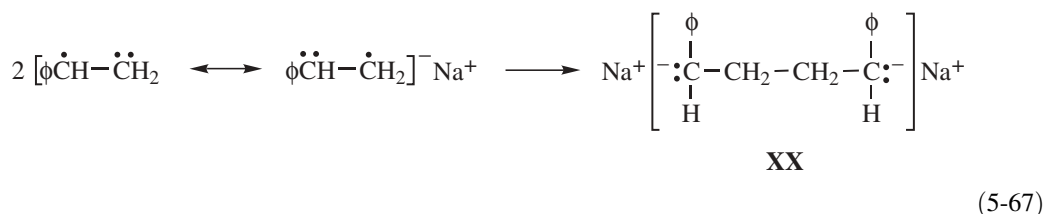
The reaction involves the transfer of an electron from the alkali metal to naphthalene. The radical nature of the anion-radical has been established from electron spin resonance spectroscopy and the carbanion nature by their reaction with carbon dioxide to form the carboxylic acid derivative. The equilibrium in Eq. 5-65 depends on the electron affinity of the hydrocarbon and the donor properties of the solvent. Biphenyl is less useful than naphthalene since its equilibrium is far less toward the anion-radical than for naphthalene. Anthracene is also less useful even though it easily forms the anion-radical. The anthracene anion-radical is too stable to initiate polymerization. Polar solvents are needed to stabilize the anion-radical, primarily via solvation of the cation. Sodium naphthalene is formed quantitatively in tetrahydrofuran (THF), but dilution with hydrocarbons results in precipitation of sodium and regeneration of naphthalene. For the less electropositive alkaline-earth metals, an even more polar solvent than THF [e.g., hexamethylphosphoramide (HMPA)] is needed.

The naphthalene anion-radical (which is colored greenish-blue) transfers an electron to a monomer such as styrene to form the styryl radical-anion (**XIX**)



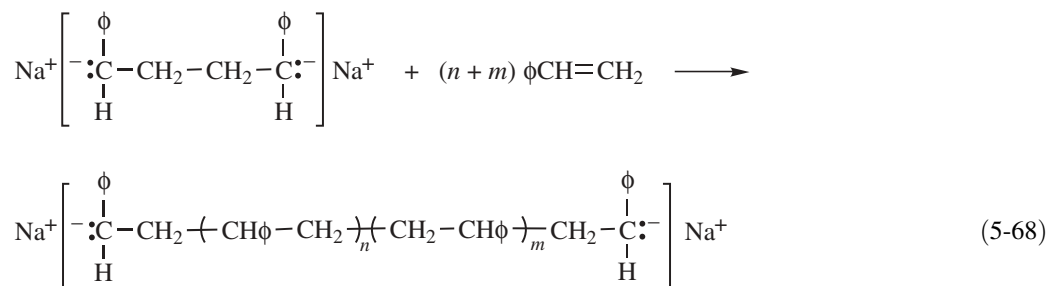
XIX

The styryl radical-anion is shown as a resonance hybrid of the forms wherein the anion and radical centers are alternately on the α - and β -carbon atoms. The styryl radical-anion dimerizes to form the dicarbanion (**XX**)



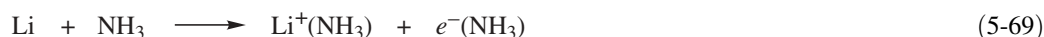
XX

That this reaction occurs is shown by electron spin resonance measurements, which indicate the complete disappearance of radicals in the system immediately after the addition of monomer. The dimerization occurs to form the styryl dicarbanion instead of $^-\text{:CH}_2\text{CH}\phi\text{CH}\phi\text{CH}_2\text{:}^-$, since the former is much more stable. The styryl dianions so-formed are colored red (the same as styryl monocarbanions formed via initiators such as *n*-butyllithium). Anionic propagation occurs at both carbanion ends of the styryl dianion



Although the suggestion that the styryl anion-radical adds a few monomer molecules prior to dimerization has not been discounted, the reaction kinetics clearly show that better than 99% of the propagation occurs through the dianion. Dimerization of radical centers is highly favored by their high concentrations, typical 10^{-3} – 10^{-2} *M* (much higher than in a radical polymerization) and the larger rate constants (10^6 – 10^8 $\text{L mol}^{-1} \text{ s}^{-1}$) for radical coupling [Wang et al., 1978, 1979].

Electron-transfer initiation from other radical-anions, such as those formed by reaction of sodium with nonenolizable ketones, azomethines, nitriles, azo and azoxy compounds, has also been studied. In addition to radical-anions, initiation by electron transfer has been observed when one uses certain alkali metals in liquid ammonia. Polymerizations initiated by alkali metals in liquid ammonia proceed by two different mechanisms. In some systems, such as the polymerizations of styrene and methacrylonitrile by potassium, the initiation is due to amide ion formed in the system [Overberger et al., 1960]. Such polymerizations are analogous to those initiated by alkali amides. Polymerization in other systems cannot be due to amide ion. Thus, polymerization of methacrylonitrile by lithium in liquid ammonia proceeds at a much faster rate than that initiated by lithium amide in liquid ammonia [Overberger et al., 1959]. The mechanism of polymerization is considered to involve the formation of a *solvated electron*:



Such ammonia solutions are noted by their characteristic deep blue color. The solvated electron is then transferred to the monomer to form a radical-anion,



The radical-anion proceeds to propagate in the same manner as discussed above for initiation by sodium naphthalene. (Polymerizations in liquid ammonia are very different from those in organic solvents in that free ions probably constitute the major portion of propagating species.)

Electron-transfer initiation also occurs in heterogeneous polymerizations involving dispersions of an alkali metal in monomer. Initiation involves electron transfer from the metal to monomer followed by dimerization of the monomer radical-anion to form the propagating

dianion [Fontanille, 1989; Gaylord and Dixit, 1974; Morton and Fetters, 1977]. The rate of initiation is dependent on the surface area of the metal since the reaction is heterogeneous. Increased surface area of metal is achieved by condensing metal vapors directly into a reaction mixture or as a thin coating (mirror) of the metal on the inside walls of the reaction vessel or simply using small particle size of the metal.

Initiation by ionizing radiation occurs by electron transfer. Some component of the reaction system, either the solvent or monomer, undergoes radiolysis to yield a cation–radical and



solvated electron [Stannett et al., 1989]. If a monomer with an electron-withdrawing substituent is present, polymerization occurs by addition of the electron to monomer followed by dimerization to the dicarbanion and propagation (Sec. 5-2a-6).

Electroinitiated polymerization proceeds by direct electron addition to monomer to generate the monomer anion–radical, although initiation in some systems may involve the formation of an anionic species by electrolytic reaction of some component of the reaction system (often the electrolyte) [Olaj, 1987].

5-3b Termination

5-3b-1 Polymerizations without Termination

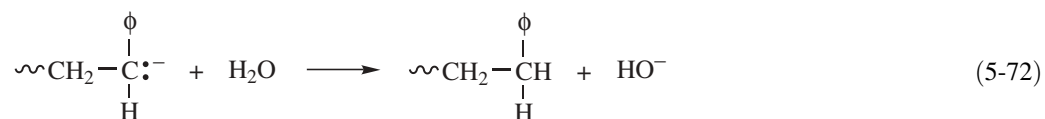
Termination of a propagating carbanion by combination with the counterion occurs in only a few instances, such as in electroinitiated polymerization when the contents of the anode and cathode chambers are mixed and in initiation by ionizing radiation. Termination by combination of the anion with a metal counterion does not take place. Many anionic polymerizations, especially of nonpolar monomers such as styrene and 1,3-butadiene, take place under conditions in which there are no effective termination reactions. Propagation occurs with complete consumption of monomer to form living polymers. The propagating anionic centers remain intact because transfer of proton or other positive species from the solvent does not occur. Living polymers are produced as long as one employs solvents, such as benzene, tetrahydrofuran, and 1,2-dimethoxyethane, which are relatively inactive in chain transfer with carbanions. The polymerization of styrene by amide ion in liquid ammonia, one of the first anionic systems to be studied in detail, is one of the few anionic polymerizations where chain transfer to solvent is extensive [Higginson and Wooding, 1952].

The nonterminating character of living anionic polymerization (LAP) is apparent in several different ways. Many of the propagating carbanions are colored. If a reaction system is highly purified so that impurities are absent, the color of the carbanions is observed to persist throughout the polymerization and does not disappear or change at 100% conversion. Further, after 100% conversion is reached, additional polymerization can be effected by adding more monomer, either the same monomer or a different monomer. The added monomer is also polymerized quantitatively and the molecular weight of the living polymer is increased.

5-3b-2 Termination by Impurities and Deliberately Added Transfer Agents

Most anionic (as well as cationic) polymerizations are carried out in an inert atmosphere with rigorously cleaned reagents and glassware since trace impurities lead to termination [Hadji-christidis et al., 2000]. Moisture absorbed on the surface of glassware is usually removed by

flaming under vacuum or washing with a living polymer solution. Oxygen and carbon dioxide from the atmosphere add to propagating carbanions to form peroxy and carboxyl anions. These are normally not reactive enough to continue propagation. (The peroxy and carboxyl anions usually are finally obtained as HO and HOOC groups when a proton donor is subsequently added to the polymerization system.) Any moisture present terminates propagating carbanions by proton transfer:



The hydroxide ion is usually not sufficiently nucleophilic to reinitiate polymerization and the kinetic chain is broken. Water has an especially negative effect on polymerization, since it is an active chain-transfer agent. For example, $C_{tr,s}$ is approximately 10 in the polymerization of styrene at 25°C with sodium naphthalene [Szwarc, 1960], and the presence of even small concentrations of water can greatly limit the polymer molecular weight and polymerization rate. The adventitious presence of other proton donors may not be as much of a problem. Ethanol has a transfer constant of about 10^{-3} . Its presence in small amounts would not prevent the formation of high polymer because transfer would be slow, although the polymer would not be living.

Living polymers are terminated by the deliberate addition of chain-transfer agent such as water or alcohol to the reaction system after all of the monomer has reacted.