

PRINCIPLES OF POLYMERIZATION

Fourth Edition

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Fourth Edition

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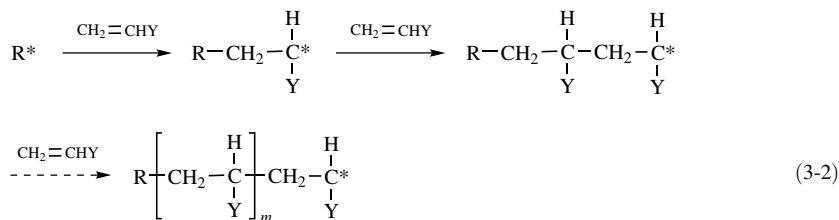
CHAPTER 3

RADICAL CHAIN POLYMERIZATION

In the previous chapter, the synthesis of polymers by step polymerization was considered. Polymerization of unsaturated monomers by chain polymerization will be discussed in this and several of the subsequent chapters. Chain polymerization is initiated by a reactive species R^* produced from some compound I termed an *initiator*:



The reactive species, which may be a free radical, cation, or anion, adds to a monomer molecule by opening the π -bond to form a new radical, cation, or anion center, as the case may be. The process is repeated as many more monomer molecules are successively added to continuously propagate the reactive center:



Polymer growth is terminated at some point by destruction of the reactive center by an appropriate reaction depending on the type of reactive center and the particular reaction conditions.

3-1 NATURE OF RADICAL CHAIN POLYMERIZATION

3-1a Comparison of Chain and Step Polymerizations

Chain polymerization proceeds by a distinctly different mechanism from step polymerization. The most significant difference is that high-molecular-weight polymer is formed immediately in a chain polymerization. A radical, anionic, or cationic reactive center, once produced, adds many monomer units in a chain reaction and grows rapidly to a large size. The monomer concentration decreases throughout the course of the reaction as the number of high-polymer molecules increases. At any instant the reaction mixture contains only monomer, high polymer, and the growing chains. The molecular weight of the polymer is relatively unchanged during the polymerization, although the overall percent conversion of monomer to polymer increases with reaction time.

The situation is quite different for a step polymerization. Whereas only monomer and the propagating species can react with each other in chain polymerization, any two molecular species present can react in step polymerization. Monomer disappears much faster in step polymerization as one proceeds to dimer, trimer, tetramer, and so on. The molecular weight increases throughout the course of the reaction, and high-molecular-weight polymer is not obtained until the end of the polymerization. Long reaction times are necessary for both high percent conversion and high molecular weights.

3-1b Radical versus Ionic Chain Polymerizations

3-1b-1 General Considerations of Polymerizability

Whether a particular monomer can be converted to polymer depends on both thermodynamic and kinetic considerations. The polymerization will be impossible under any and all reaction conditions if it does not pass the test of thermodynamic feasibility. Polymerization is possible only if the free-energy difference ΔG between monomer and polymer is negative (Sec. 3-9b). A negative ΔG does not, however, mean that polymerization will be observed under a particular set of reaction conditions (type of initiation, temperature, etc.). The ability to carry out a thermodynamically feasible polymerization depends on its kinetic feasibility—on whether the process proceeds at a reasonable rate under a proposed set of reaction conditions. Thus, whereas the polymerization of a wide variety of unsaturated monomers is thermodynamically feasible, very specific reaction conditions are often required to achieve kinetic feasibility in order to accomplish a particular polymerization.

Although radical, cationic, and anionic initiators are used in chain polymerizations, they cannot be used indiscriminately, since all three types of initiation do not work for all monomers. Monomers show varying degrees of selectivity with regard to the type of reactive center that will cause their polymerization. Most monomers will undergo polymerization with a radical initiator, although at varying rates. However, monomers show high selectivity toward ionic initiators. Some monomers may not polymerize with cationic initiators, while others may not polymerize with anionic initiators. The variety of behaviors can be seen in Table 3-1. The types of initiation that bring about the polymerization of various monomers to high-molecular-weight polymer are indicated. Thus, although the polymerization of all the monomers in Table 3-1 is thermodynamically feasible, kinetic feasibility is achieved in many cases only with a specific type of initiation.

The carbon-carbon double bond in vinyl monomers and the carbon-oxygen double bond in aldehydes and ketones are the two main types of linkages that undergo chain

TABLE 3-1 Types of Chain Polymerization Undergone by Various Unsaturated Monomers

Monomers	Type of Initiation		
	Radical	Cationic	Anionic ^a
Ethylene	+	—	+
1-Alkyl alkenes (α -olefins)	—	—	+
1,1-Dialkyl alkenes	—	+	—
1,3-Dienes	+	+	+
Styrene, α -methyl styrene	+	+	+
Halogenated alkenes	+	—	—
Vinyl esters ($\text{CH}_2=\text{CHOCOR}$)	+	—	—
Acrylates, methacrylates	+	—	+
Acrylonitrile, methacrylonitrile	+	—	+
Acrylamide, methacrylamide	+	—	+
Vinyl ethers	—	+	—
<i>N</i> -Vinyl carbazole	+	+	—
<i>N</i> -Vinyl pyrrolidone	+	+	—
Aldehydes, ketones	—	+	+

^aIncludes anionic coordination initiation (Chap. 8).

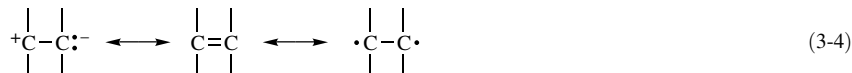
polymerization. The polymerization of the carbon–carbon double bond is by far the most important of the two types of monomers. The carbonyl group is not prone to polymerization by radical initiators because of its polarized nature:



Aldehydes and ketones are polymerized by both anionic and cationic initiators (Chap. 5).

3-1b-2 Effects of Substituents

Unlike the carbonyl linkage, the carbon–carbon double bond undergoes polymerization by both radical and ionic initiators. The difference arises because the π -bond of a vinyl monomer can respond appropriately to the initiator species by either homolytic or heterolytic bond breakage:



A wide range of carbon–carbon double bonds undergo chain polymerization. Table 3-1 shows monomers with alkyl, alkenyl, aryl, halogen, alkoxy, ester, amide, nitrile, and heterocyclic substituents on the alkene double bond.

Whether a vinyl monomer polymerizes by radical, anionic, or cationic initiators depends on the inductive and resonance characteristics of the substituent(s) present. The effect of the

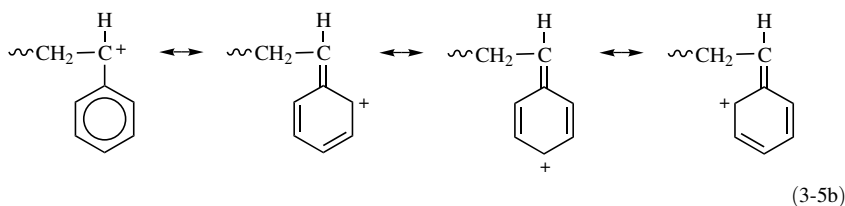
substituent manifests itself by its alteration of the electron-cloud density on the double bond and its ability to stabilize the possible radical, anion, or cation formed. Electron-donating substituents such as alkoxy, alkyl, alkenyl, and phenyl increase the electron density on the carbon-carbon double bond and facilitate its bonding to a cationic species. Further,



these substituents stabilize the cationic propagating species by resonance, for example, in the polymerization of vinyl ethers:



The alkoxy substituent allows a delocalization of the positive charge. If the substituent were not present (e.g., in ethylene), the positive charge would be localized on the single α -carbon atom. The presence of the alkoxy group leads to stabilization of the carbocation by delocalization of the positive charge over two atoms—the carbon and the oxygen. Similar delocalization effects occur with phenyl, vinyl, and alkyl substituents, for example, for styrene polymerization:

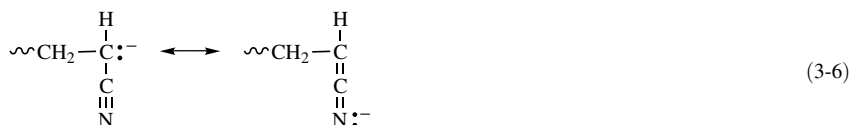


Thus monomers such as isobutylene, styrene, methyl vinyl ether, and isoprene undergo polymerization by cationic initiators. The effect of alkyl groups in facilitating cationic polymerization is weak, and it is only the 1,1-dialkyl alkenes that undergo cationic polymerization.

Electron-withdrawing substituents such as cyano and carbonyl (aldehyde, ketone, acid, or ester) facilitate the attack of an anionic species by decreasing the electron density on the double bond:

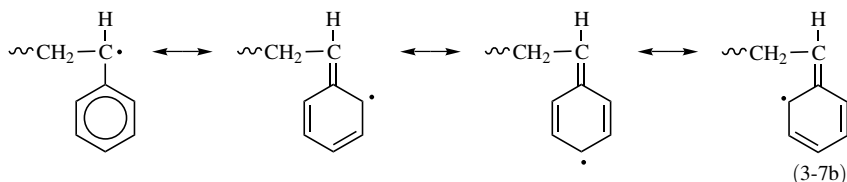


They stabilize the propagating anionic species by resonance, for example, for acrylonitrile polymerization:



Stabilization of the propagating carbanion occurs by delocalization of the negative charge over the α -carbon and the nitrogen of the nitrile group. Alkenyl and phenyl substituents, although electron-withdrawing inductively, can resonance stabilize the anionic propagating species in the same manner as a cyano group. Monomers such as styrene and 1,3-butadiene can, therefore, undergo anionic as well as cationic polymerization. Halogens withdraw electrons inductively and push electrons by resonance, but both effects are relatively weak and neither anionic nor cationic polymerization is appreciably facilitated for halogenated monomers such as vinyl chloride.

Contrary to the high selectivity shown in cationic and anionic polymerization, radical initiators bring about the polymerization of almost any carbon-carbon double bond. Radical species are neutral and do not have stringent requirements for attacking the π -bond or for the stabilization of the propagating radical species. Resonance stabilization of the propagating radical occurs with almost all substituents, for example

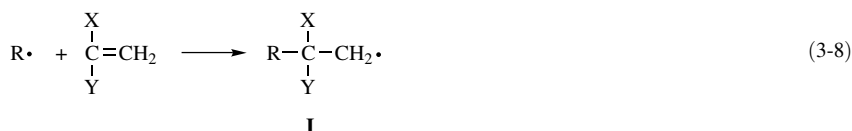


Thus, almost all substituents are able to stabilize the propagating radical by delocalization of the radical over two or more atoms. The remainder of this chapter will be concerned with the detailed characteristics of radical chain polymerization. Ionic chain polymerizations will be considered in Chap. 5.

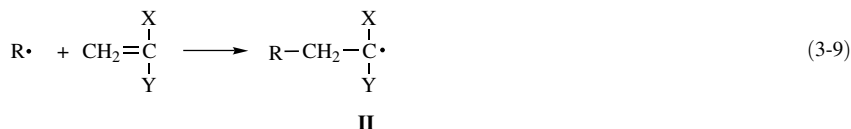
3-2 STRUCTURAL ARRANGEMENT OF MONOMER UNITS

3-2a Possible Modes of Propagation

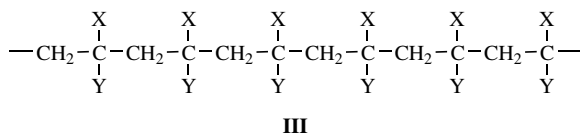
There are two possible points of attachment on monosubstituted ($X = \text{H}$) or 1,1-disubstituted monomers for a propagating radical—on either carbon 1



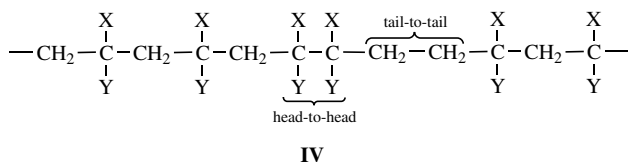
or carbon 2:



If each successive addition of monomer molecules to the propagating radical occurs in the same manner as Eq. 3-9 or Eq. 3-8, the final polymer product will have an arrangement of monomer units in which the substituents are on alternate carbon atoms:



This type of arrangement (**III**) is usually referred to as a *head-to-tail* (H-T) or 1,3-*placement* of monomer units. An inversion of this mode of addition by the polymer chain propagating alternately via Eqs. 3-9 and 3-8 would lead to a polymer structure with a 1,2-*placement* of substituents at one or more places in the final polymer chain. 1,2-Placement is usually referred to as *head-to-head* (H-H) placement.

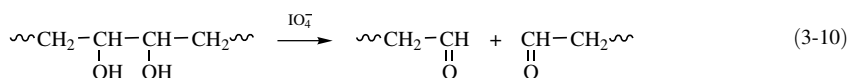


The head-to-tail placement would be expected to be overwhelmingly predominant, since successive propagations by Eq. 3-9 are favored on both steric and resonance grounds. The propagating radical (radical **II**) formed by attachment of a radical at carbon 2 is the more stable one. Radical **II** can be stabilized by the resonance effects of the X and Y substituents. The substituents cannot stabilize radical **I**, since they are not attached to the carbon bearing the unpaired electron. Further, the approach (and subsequent attachment) of a propagating radical at the unsubstituted carbon (carbon 2) of a monomer molecule is much less sterically hindered compared to the approach at the substituted carbon (carbon 1). A propagation proceeding with predominantly H-T placement is a *regioselective* process, that is, one orientation (H-T) is favored over another (H-H). The term *isoregic* has been used to indicate a polymer structure with exclusive head-to-tail placements. The terms *syndioregic* and *aregic* would be used for polymer structures with alternating and random arrangements, respectively, of H-T and H-H placements.

3-2b Experimental Evidence

These theoretical predictions have been experimentally verified for a number of polymers. The presence of no more than 1–2% head-to-head placement in various polymers of vinyl

esters such as poly(vinyl acetate) has been determined by hydrolysis of the polymer to poly(vinyl alcohol) and the periodate oxidation of the 1,2-glycol units [Hayashi and Ostu, 1969].

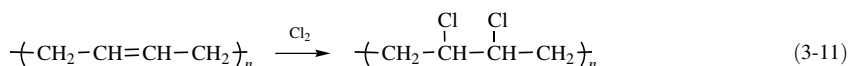


Although appropriate chemical reactions do not exist to detect the occurrence of head-to-head propagation in all but a few polymers, the use of high-resolution nuclear magnetic resonance spectroscopy (including ^1H , ^{13}C , and F^{19}) has greatly increased our knowledge in this area [Bovey and Mirau, 1996; Bovey et al., 1977]. It is now clear that H-T propagation is the predominant (>98–99%) mode of propagation in chain polymerization. For some polymers such as polystyrene there is no detectable H-H placement [Hensley et al., 1995]. The only exceptions occur when the substituents on the double bond are small (and do not offer appreciable steric hindrance to the approaching radical) and do not have a significant resonance-stabilizing effect, specifically when fluorine is the substituent. Thus, the extents of H-H placements in poly(vinyl fluoride), poly(vinylidene fluoride), poly(trifluoroethylene), and poly(chlorotrifluoroethylene) are about 10, 5, 12, and 2%, respectively [Cais and Kometani, 1984, 1988; Guiot et al., 2002; Ovenall and Uschold, 1991].

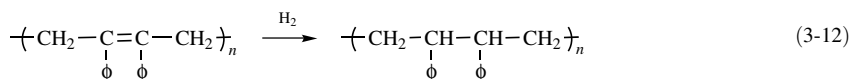
The effect of increasing the polymerization temperature is an increase in the extent of H-H placement, but the effect is small. Thus the H-H content in poly(vinyl acetate) increases from 1 to 2% when the temperature is increased from 40 to 100°C; the increase is from 10 to 14% for poly(trifluoroethylene) when the temperature is increased from –80 to 80°C.

3-2c Synthesis of Head-to-Head Polymers

Some polymers consisting entirely of head-to-head placements have been deliberately synthesized to determine if significant property differences exist compared to the head-to-tail polymers. The synthetic approach involves an appropriate choice of monomer for the particular H-H polymer. For example, H-H poly(vinyl chloride) is obtained by chlorination of 1,4-poly-1,3-butadiene,



and H-H polystyrene by hydrogenation of 1,4-poly-2,3-diphenylbutadiene,



[Kawaguchi et al., 1985; Vogl; 2000; Vogl et al., 1999].

3-3 RATE OF RADICAL CHAIN POLYMERIZATION

3-3a Sequence of Events

Radical chain polymerization is a chain reaction consisting of a sequence of three steps—*initiation*, *propagation*, and *termination*. The initiation step is considered to involve two

reactions. The first is the production of free radicals by any one of a number of reactions. The usual case is the homolytic dissociation of an initiator species **I** to yield a pair of radicals **R•**



where k_d is the rate constant for the catalyst dissociation. The second part of the initiation involves the addition of this radical to the first monomer molecule to produce the chain-initiating radical $\text{M}_1\cdot$



where **M** represents a monomer molecule and k_i is the rate constant for the initiation step (Eq. 3-14a). For the polymerization of $\text{CH}_2=\text{CHY}$, Eq. 3-14a takes the form



The radical **R•** is often referred to as an *initiator radical* or *primary radical* to distinguish it from the the chain-initiating species ($\text{M}_1\cdot$).

Propagation consists of the growth of $\text{M}_1\cdot$ by the successive additions of large numbers (hundreds and perhaps thousands) of monomer molecules according to Eq. 3-2. Each addition creates a new radical that has the same identity as the one previously, except that it is larger by one monomer unit. The successive additions may be represented by



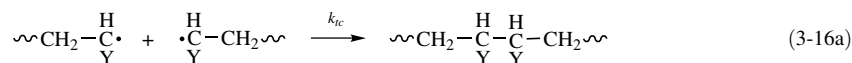
etc., etc.

or in general terms



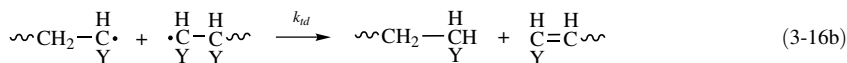
where k_p is the rate constant for propagation. Propagation with growth of the chain to high-polymer proportions takes place very rapidly. The value of k_p for most monomers is in the range 10^2 – 10^4 $\text{L mol}^{-1} \text{s}^{-1}$. This is a large rate constant—much larger than those usually encountered in step polymerizations (see Table 2-8).

At some point, the propagating polymer chain stops growing and terminates. Termination with the annihilation of the radical centers occurs by bimolecular reaction between radicals. Two radicals react with each other by *combination (coupling)* or, more rarely, by



disproportionation, in which a hydrogen radical that is *beta* to one radical center is transferred to another radical center. This results in the formation of two polymer molecules—

one saturated and one unsaturated:



Termination can also occur by a combination of coupling and disproportionation. The two different modes of termination can be represented in general terms by



where k_{tc} and k_{td} are the rate constants for termination by coupling and disproportionation, respectively. One can also express the termination step by



where the particular mode of termination is not specified and

$$k_t = ak_{tc} + (1-a)k_{td} \quad (3-19)$$

where a and $(1-a)$ are the fractions of termination by coupling and disproportionation, respectively.

The term *dead polymer* signifies the cessation of growth for the propagating radical. The propagation reaction would proceed indefinitely until all the monomer in a reaction system were exhausted if it were not for the strong tendency toward termination. Typical termination rate constants are in the range of 10^6 – 10^8 L mol⁻¹ s⁻¹ or orders of magnitude greater than the propagation rate constants. The much greater value of k_t (whether k_{tc} or k_{td}) compared to k_p does not prevent propagation because the radical species are present in very low concentrations and because the polymerization rate is dependent on only the one-half power of k_t (as will be discussed in Sec. 3-4a-2). (Polymerizations with little or no termination occur under special conditions—Sec. 3-15).

3-3b Rate Expression

Equations 3-13 through 3-19 constitute the detailed mechanism of a free-radical-initiated chain polymerization. The chain nature of the process resides in the propagation step (Eq. 3-15) in which large numbers of monomer molecules are converted to polymer for each initiating radical produced in the first step (Eq. 3-14). In order to obtain a kinetic expression for the rate of polymerization, it is necessary to assume that k_p and k_t are independent of the size of the radical. This assumption is inherent in the notation used in Eqs. 3-15 through 3-18. It is exactly the same assumption—the equal-reactivity assumption—that was employed in deriving the kinetics of step polymerization. Very small radicals are more reactive than propagating radicals, but this effect is not important because the effect of size vanishes at the dimer or trimer size [Gridnev and Ittel, 1996; Kerr, 1973]. There are limitations to the equal-reactivity assumption with respect to the sizes of propagating radicals, and this is discussed in Secs. 3-10 and 3-11b.

Monomer disappears by the initiation reaction (Eq. 3-14) as well as by the propagation reactions (Eq. 3-15). The *rate of monomer disappearance*, which is synonymous with the *rate of polymerization*, is given by

$$\frac{-d[M]}{dt} = R_i + R_p \quad (3-20)$$

where R_i and R_p are the rates of initiation and propagation, respectively. However, the number of monomer molecules reacting in the initiation step is far less than the number in the propagation step for a process producing high polymer. To a very close approximation the former can be neglected and the polymerization rate is given simply by the rate of propagation

$$\frac{-d[M]}{dt} = R_p \quad (3-21)$$

The rate of propagation, and therefore the rate of polymerization, is the sum of many individual propagation steps. Since the rate constants for all the propagation steps are the same, one can express the polymerization rate by

$$R_p = k_p[M\cdot][M] \quad (3-22)$$

where $[M]$ is the monomer concentration and $[M\cdot]$ is the total concentration of all chain radicals, that is, all radicals of size $M_1\cdot$ and larger.

Equation 3-22 for the polymerization rate is not directly usable because it contains a term for the concentration of radicals. Radical concentrations are difficult to measure quantitatively, since they are very low ($\sim 10^{-8} M$), and it is therefore desirable to eliminate $[M\cdot]$ from Eq. 3-22. In order to do this, the *steady-state* assumption is made that the concentration of radicals increases initially, but almost instantaneously reaches a constant, steady-state value. The rate of change of the concentration of radicals quickly becomes and remains zero during the course of the polymerization. This is equivalent to stating that the rates of initiation R_i and termination R_t of radicals are equal or

$$R_i = R_t = 2k_t[M\cdot]^2 \quad (3-23)$$

The steady-state assumption is not unique to polymerization kinetics. It is often used in developing the kinetics of many small-molecule reactions that involve highly reactive intermediates present at very low concentrations—conditions that are present in radical chain polymerizations. The theoretical validity of the steady-state assumption has been discussed [Kondratiev, 1969] and its experimental validity shown in many polymerizations. Typical polymerizations achieve a steady-state after a period, which may be at most a minute.

The right side of Eq. 3-23 represents the rate of termination. There is no specification as to whether termination is by coupling or disproportionation since both follow the same kinetic expression. The use of the factor of 2 in the termination rate equation follows the generally accepted convention for reactions destroying radicals in pairs. It is also generally used for reactions creating radicals in pairs as in Eq. 3-13. This convention is now the IUPAC-preferred convention. In using the polymer literature, one should be aware that the factor of 2 has not always been followed. Rearrangement of Eq. 3-23 to

$$[M\cdot] = \left(\frac{R_i}{2k_t} \right)^{1/2} \quad (3-24)$$

and substitution into Eq. 3-22 yields

$$R_p = k_p[M] \left(\frac{R_i}{2k_t} \right)^{1/2} \quad (3-25)$$

for the rate of polymerization. It is seen that Eq. 3-25 has the significant conclusion of the dependence of the polymerization rate on the square root of the initiation rate. Doubling the rate of initiation does not double the polymerization rate; the polymerization rate is increased only by the factor $\sqrt{2}$. This behavior is a consequence of the bimolecular termination reaction between radicals.

3-3c Experimental Determination of R_p

It is appropriate at this point to briefly discuss the experimental procedures used to determine polymerization rates for both step and radical chain polymerizations. R_p can be experimentally followed by measuring the change in any property that differs for the monomer(s) and polymer, for example, solubility, density, refractive index, and spectral absorption [Collins et al., 1973; Giz et al., 2001; McCaffery, 1970; Stickler, 1987; Yamazoe et al., 2001]. Some techniques are equally useful for step and chain polymerizations, while others are more appropriate for only one or the other. Techniques useful for radical chain polymerizations are generally applicable to ionic chain polymerizations. The utility of any particular technique also depends on its precision and accuracy at low, medium, and high percentages of conversion. Some of the techniques have the inherent advantage of not needing to stop the polymerization to determine the percent conversion, that is, conversion can be followed versus time on the same reaction sample.

3-3c-1 Physical Separation and Isolation of Reaction Product

This technique involves isolating (followed by drying and weighing) the polymer from aliquots of the polymerization system as a function of reaction time. Polymer is typically isolated by precipitation by addition of a nonsolvent. The technique is primarily useful for chain polymerizations, which consist of monomer and high-molecular-weight polymer, differing greatly in their solubility. It is not generally useful for step polymerization, since they consist of monomers and a range of different low-molecular-weight products (until very high conversions) whose solubility differences are typically not too different. Even when applicable, the technique is very time-consuming and requires great care to obtain accurate results.

A modification of this technique, applicable to many step polymerizations, involves the continuous monitoring of the small-molecule by-product. For example, for polyesterification between a diol and diacid above 100°C, water distills out of the reaction vessel and its volume can be measured by condensation and collection in a calibrated trap.

3-3c-2 Chemical and Spectroscopic Analysis

Chemical analysis of the unreacted monomer functional groups as a function of time is useful for step polymerizations. For example, polyesterification can be followed accurately by titration of the carboxyl group concentration with standard base or analysis of hydroxyl groups by reaction with acetic anhydride. The rate of chain polymerization of vinyl monomers can be followed by titration of the unreacted double bonds with bromine.

The disappearance of monomer or appearance of polymer can be followed by infrared (IR), ultraviolet (UV), and nuclear magnetic resonance (NMR) and other spectroscopies. One can follow the decrease in absorption signal(s) due to monomer and/or increase in absorption signal(s) due to polymer. For example, for styrene polymerization, proton NMR signals characteristic of the monomer, which decrease with conversion, include signals for the $\text{CH}_2=\text{CH}$ protons (5.23, 5.73, and 6.71 ppm); simultaneously, signals characteristic of the CH_2 and CH protons of polymer appear at 1.44 and 1.84 ppm, respectively. The accuracy of the spectroscopic technique is high when the monomer and polymer signals do not overlap. Spectroscopy allows the continuous monitoring of a polymerization without periodic sample removal for analysis. The polymerization is performed in a sample tube placed in the spectrometer and equilibrated at the desired reaction temperature [Aguilar et al., 2002]. Periodic spectral analysis allows one to follow conversion versus time. More elaborate instrumentation allows the simultaneous analysis of conversion and molecular weight versus time [Chauvin et al., 2002; Grassl and Reed, 2002].

3-3c-3 Other Techniques

Dilatometry utilizes the volume change that occurs on polymerization. It is an accurate method for some chain polymerizations because there is often a high-volume shrinkage when monomer is converted to polymer. For example, the density of poly(methyl methacrylate) is 20.6% lower than that of its monomer. Polymerization is carried out in a calibrated reaction vessel and the volume recorded as a function of reaction time. Dilatometry is not useful for the usual step polymerization where there is a small molecule by-product that results in no significant volume change on polymerization.

The heat of polymerization can be measured accurately by differential scanning calorimetry and is directly related to conversion. Other techniques that have been used include light scattering and refractive index.

3-4 INITIATION

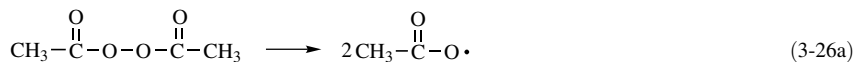
The derivation of Eq. 3-25 is general in that the reaction for the production of radicals (Eq. 3-13) is not specified and the initiation rate is simply shown as R_i . A variety of initiator systems can be used to bring about the polymerization. (The term *catalyst* is often used synonymously with *initiator*, but it is incorrect in the classical sense, since the initiator is consumed. The use of the term *catalyst* may be condoned since very large numbers of monomer molecules are converted to polymer for each initiator molecule that is consumed.) Radicals can be produced by a variety of thermal, photochemical, and redox methods [Bamford, 1988; Denisova et al., 2003; Eastmond, 1976a,b,c; Moad et al., 2002]. In order to function as a useful source of radicals an initiator system should be readily available, stable under ambient or refrigerated conditions, and possess a practical rate of radical generation at temperatures which are not excessive (approximately $<150^\circ\text{C}$).

3-4a Thermal Decomposition of Initiators

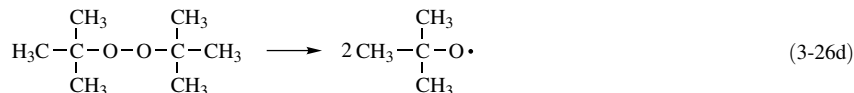
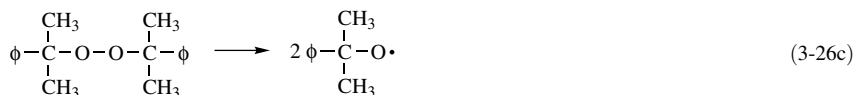
3-4a-1 Types of Initiators

The *thermal, homolytic dissociation* of initiators is the most widely used mode of generating radicals to initiate polymerization—for both commercial polymerizations and theoretical studies. Polymerizations initiated in this manner are often referred to as *thermally initiated* or

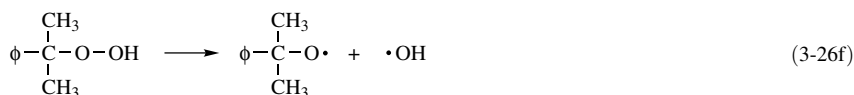
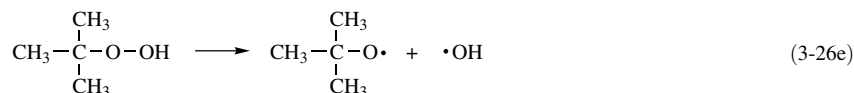
thermal catalyzed polymerizations. The number of different types of compounds that can be used as thermal initiators is rather limited. One is usually limited to compounds with bond dissociation energies in the range 100–170 kJ mol⁻¹. Compounds with higher or lower dissociation energies will dissociate too slowly or too rapidly. Only a few classes of compounds—including those with O–O, S–S, or N–O bonds—possess the desired range of dissociation energies. However, it is the peroxides which find extensive use as radical sources. The other classes of compounds are usually either not readily available or not stable enough. Several different types of peroxy compounds are widely used [Sheppard, 1988]. These are acyl peroxides such as acetyl and benzoyl peroxides



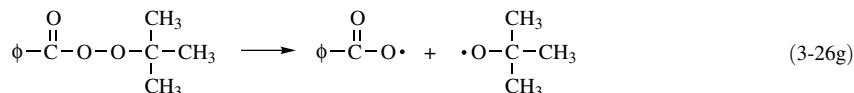
alkyl peroxides such as cumyl and *t*-butyl peroxides



hydroperoxides such as *t*-butyl and cumyl hydroperoxides



and peresters such as *t*-butyl perbenzoate:

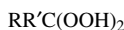
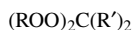


Other peroxides used to initiate polymerization are acyl alkylsulfonyl peroxides (**Va**), dialkyl peroxydicarbonates (**Vb**), diperoxyketals (**Vc**), and ketone peroxides (**Vd**).



Va

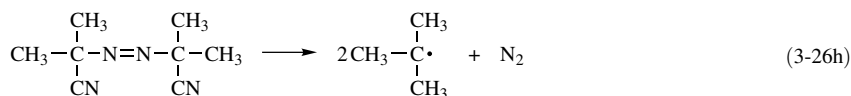
Vb



Vc

Vd

Aside from the various peroxy compounds, the main other class of compound used extensively as initiators are the azo compounds. 2,2'-Azobisisobutyronitrile (AIBN) is the most important member of this class of initiators, although other azo compounds such as



2,2'-azobis(2,4-dimethylpentanenitrile), 4,4'-azobis(4-cyanovaleric acid), and 1,1'-azobis(cyclohexanecarbonitrile) are also used [Sheppard, 1985]. The facile dissociation of azo compounds is not due to the presence of a weak bond as is the case for the peroxy compounds. The C–N bond dissociation energy is high ($\sim 290 \text{ kJ mol}^{-1}$), but the driving force for homolysis is the formation of the highly stable nitrogen molecule.

Among other initiators that have been studied are disulfides



and tetrazenes



[Oda et al., 1978; Sato et al., 1979a,b].

The various initiators are used at different temperatures depending on their rates of decomposition. Thus azobisisobutyronitrile (AIBN) is commonly used at $50\text{--}70^\circ\text{C}$, acetyl peroxide at $70\text{--}90^\circ\text{C}$, benzoyl peroxide at $80\text{--}95^\circ\text{C}$, and dicumyl or di-*t*-butyl peroxide at $120\text{--}140^\circ\text{C}$. The value of the decomposition rate constant k_d varies in the range $10^{-4} - 10^{-9} \text{ s}^{-1}$ depending on the initiator and temperature [Eastmond, 1976a,b,c]. Most initiators are used at temperatures where k_d is usually $10^{-4} - 10^{-6} \text{ s}^{-1}$. The great utility of peroxide and azo compounds results from the availability in stable form of many different compounds with a range of use temperatures.

The differences in the rates of decomposition of the various initiators are related to differences in the structures of the initiators and of the radicals produced. The effects of structure on initiator reactivity have been discussed elsewhere [Bamford, 1988; Eastmond, 1976a,b,c; Sheppard, 1985, 1988]. For example, k_d is larger for acyl peroxides than for alkyl peroxides since the $\text{RCOO}\cdot$ radical is more stable than the $\text{RO}\cdot$ radical and for $\text{R}-\text{N}=\text{N}-\text{R}$, k_d increases in the order $\text{R} = \text{allyl, benzyl} > \text{tertiary} > \text{secondary} > \text{primary}$ [Koenig, 1973].

The differences in the decomposition rates of various initiators can be conveniently expressed in terms of the *initiator half-life* $t_{1/2}$ defined as the time for the concentration of I to decrease to one half its original value. The rate of initiator disappearance by Eq. 3-13 is

$$\frac{-d[\text{I}]}{dt} = k_d[\text{I}] \quad (3-27)$$

which on integration yields

$$[\text{I}] = [\text{I}]_0 e^{-k_d t} \quad (3-28\text{a})$$

or

$$\ln \frac{[\text{I}]_0}{[\text{I}]} = k_d t \quad (3-28\text{b})$$

TABLE 3-2 Half-Lives of Initiators^{a,b}

Initiator	Half-Life at					
	50°C	70°C	85°C	100°C	130°C	175°C
Azobisisobutyronitrile	74 h	4.8 h	—	7.2 min	—	—
Benzoyl peroxide	—	7.3 h	1.4 h	20 min	—	—
Acetyl peroxide	158 h	8.1 h	1.1 h	—	—	—
<i>t</i> -Butyl peracetate	—	—	88 h	13 h	18 min	—
Cumyl peroxide	—	—	—	—	1.7 h	—
<i>t</i> -Butyl peroxide	—	—	—	218 h	6.4 h	—
<i>t</i> -Butyl hydroperoxide	—	—	—	338 h	—	4.81 h

^a Data from Brandrup and Immergut [1989], Brandrup et al. [1999], and Huyser [1970].

^b Half-life ($t_{1/2}$) values are for benzene or toluene solutions of the initiators.

where $[I]_0$ is the initiator concentration at the start of polymerization. $t_{1/2}$ is obtained as

$$t_{1/2} = \frac{0.693}{k_d} \quad (3-29)$$

by setting $[I] = [I]_0/2$. Table 3-2 lists the initiator half-lives for several common initiators at various temperatures.

3-4a-2 Kinetics of Initiation and Polymerization

The rate of producing primary radicals by thermal homolysis of an initiator R_d (Eqs. 3-13 and 3-26) is given by

$$R_d = 2fk_d[I] \quad (3-30)$$

where $[I]$ is the concentration of the initiator and f is the *initiator efficiency*. The initiator efficiency is defined as the fraction of the radicals produced in the homolysis reaction that initiate polymer chains. The value of f is usually less than unity due to wastage reactions. The factor of 2 in Eq. 3-30 follows the convention previously discussed for Eq. 3-23.

The initiation reaction in polymerization is composed of two steps (Eqs. 3-13 and 3-14) as discussed previously. In most polymerizations, the second step (the addition of the primary radical to monomer) is much faster than the first step. The homolysis of the initiator is the rate-determining step in the initiation sequence, and the rate of initiation is then given by

$$R_i = 2fk_d[I] \quad (3-31)$$

Substitution of Eq. 3-31 into Eq. 3-25 yields

$$R_p = k_p[M] \left(\frac{fk_d[I]}{k_t} \right)^{1/2} \quad (3-32)$$

3-4a-3 Dependence of Polymerization Rate on Initiator

Equation 3-32 describes the most common case of radical chain polymerization. It shows the polymerization rate to be dependent on the square root of the initiator concentration. This

dependence has been abundantly confirmed for many different monomer–initiator combinations over wide ranges of monomer and initiator concentrations [Eastmond, 1976a,b,c; Kamachi et al., 1978; Santee et al., 1964; Schulz and Blaschke, 1942; Vrancken and Smets, 1959]. Figure 3-1 shows typical data illustrating the square-root dependence on $[I]$. Deviations from this behavior are found under certain conditions. The order of dependence of R_p on $[I]$ may be observed to be less than one-half at very high initiator concentrations. However, such an effect is not truly a deviation from Eq. 3-32. It may be due to a decrease in f with increasing initiator concentration (Sec. 3-4g-2).

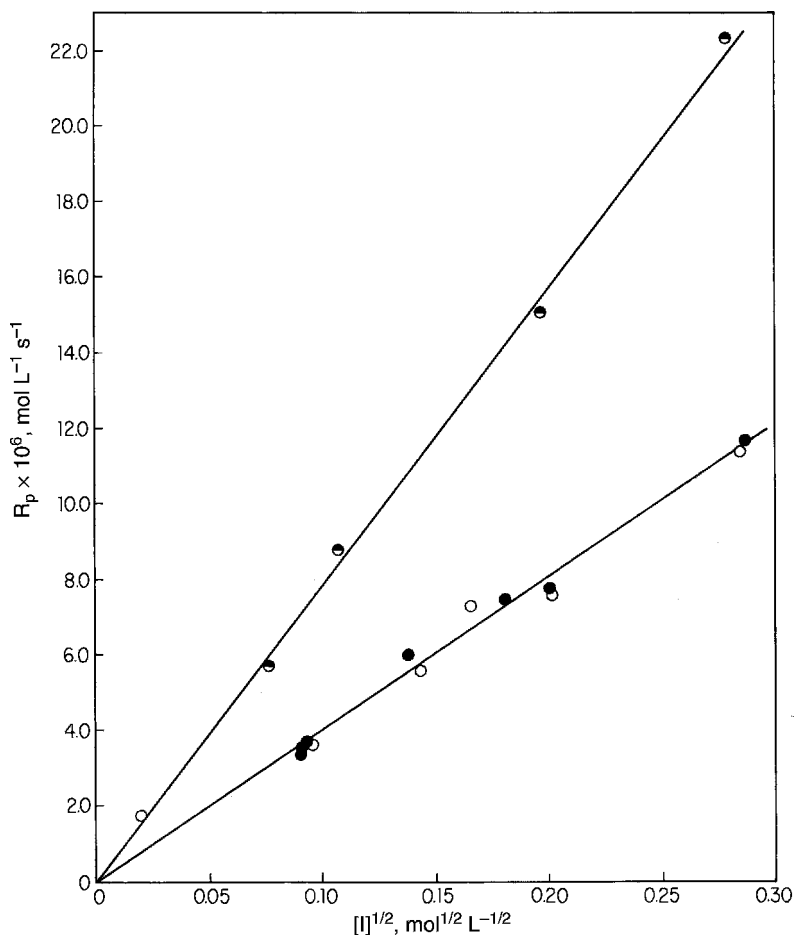


Fig. 3-1 Square root dependence of the polymerization rate R_p on the initiator concentration $[I]$. ● = Methyl methacrylate, benzoyl peroxide, 50°C. After Schulz and Blaschke [1942] (by permission of Akademische Verlagsgesellschaft, Geest and Portig K.-G., Leipzig). ○, ● = Vinyl benzoate, azobisisobutyronitrile, 60°C. After Santee et al. [1964] and Vrancken and Smets [1959] (by permission of Huthig and Wepf Verlag, Basel and Wiley-VCH, Weinheim).

Alternately, the termination mode may change from the normal bimolecular termination between propagating radicals to *primary termination*, which involves propagating radicals reacting with primary radicals [Berger et al., 1977; David et al., 2001; Ito, 1980]:



This occurs if primary radicals are produced at too high a concentration and/or in the presence of too low a monomer concentration to be completely and rapidly scavenged by monomer (by Eq. 3-14a). If termination occurs exclusively by primary termination, the polymerization rate is given by

$$R_p = \frac{k_p k_i [M]^2}{k_{tp}} \quad (3-33b)$$

Eq. 3-33b, derived by combining the rate expressions for Eqs. 3-14a, 3-15d, and 3-33a, shows that the polymerization rate becomes independent of the initiator concentration (but not k_i) and second-order in monomer concentration.

Primary termination and the accompanying change in the order of dependence of R_p on $[I]$ may also be found in the Trommsdorff polymerization region (Sec. 3-10). Situations also arise where the order of dependence of R_p on $[I]$ will be greater than one-half. This behavior may be observed in the Trommsdorff region if the polymer radicals do not undergo termination or under certain conditions of chain transfer or inhibition (Sec. 3-7).

Lower than one-half order dependence of R_p on R_i is also expected if one of the two primary radicals formed by initiator decomposition has low reactivity for initiation, but is still active in termination of propagating radicals. Modeling this situation indicates that the dependence of R_p on R_i becomes one-third order in the extreme of this situation where one of the primary radicals has no reactivity toward initiation, but still active for termination [Kaminsky et al., 2002].

3-4a-4 Dependence of Polymerization Rate on Monomer

The rate expression Eq. 3-32 requires a first-order dependence of the polymerization rate on the monomer concentration and is observed for many polymerizations [Kamachi et al., 1978]. Figure 3-2 shows the first-order relationship for the polymerization of methyl methacrylate [Sugimura and Minoura, 1966]. However, there are many polymerizations where R_p shows a higher than first-order dependence on $[M]$. Thus the rate of polymerization depends on the $\frac{3}{2}$ -power of the monomer concentration in the polymerization of styrene in chlorobenzene solution at 120°C initiated by *t*-butyl peresters [Misra and Mathiu, 1967]. The benzoyl peroxide initiated polymerization of styrene in toluene at 80°C shows an increasing order of dependence of R_p on $[M]$ as $[M]$ decreases [Horikx and Hermans, 1953]. The dependence is 1.18-order at $[M] = 1.8$ and increases to 1.36-order at $[M] = 0.4$. These effects may be caused by a dependence of the initiation rate on the monomer concentration. Equation 3-28 was derived on the assumption that R_i is independent of $[M]$. The initiation rate can be monomer-dependent in several ways. The initiator efficiency f may vary directly with the monomer concentration

$$f = f'[M] \quad (3-34)$$

which would lead (by substitution of Eq. 3-34 into Eqs. 3-31 and 3-32) to first-order dependence of R_i on $[M]$ and $\frac{3}{2}$ -order dependence of R_p on $[M]$. (This effect has been observed and

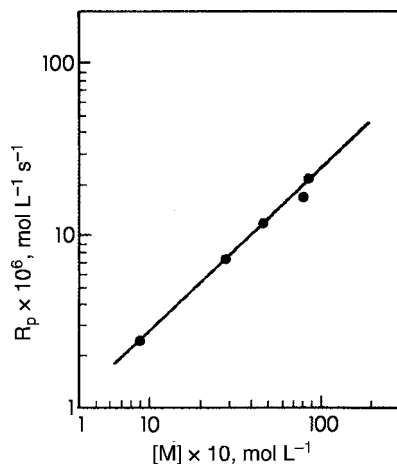


Fig. 3-2 First-order dependence of the polymerization rate R_p of methyl methacrylate on the monomer concentration $[M]$. The initiator is the *t*-butyl perbenzoate-diphenylthiourea redox system. After Sugimura and Minoura [1966] (by permission of Wiley-Interscience, New York).

is discussed in Sec. 3-4f.) The equivalent result arises if the second step of the initiation reaction (Eq. 3-14) were to become the rate-determining step instead of the first step (Eq. 3-13). This occurs when $k_d > k_i$ or when $[M]$ is low. It is also frequently encountered in polymerizations initiated photolytically or by ionizing radiation (Secs. 3-4c and 3-4d) and in some redox-initiated polymerizations (Sec. 3-4b).

In some systems it appears that the initiation step differs from the usual two-step sequence of Eqs. 3-13 and 3-14. Thus in the *t*-butyl hydroperoxide-styrene system only a minor part of the initiation occurs by the first-order homolysis reaction (Eq. 3-26f), which accounts for the complete decomposition of *t*-butyl hydroperoxide in the absence of styrene. Homolysis of the hydroperoxide occurs at a much faster rate in the presence of styrene than in its absence. The increased decomposition rate in the *t*-butyl hydroperoxide-styrene system occurs by a *molecule-induced homolysis* reaction which is first-order in both styrene and hydroperoxide [Walling and Heaton, 1965]. The initiation reaction may be written as



and results in a $\frac{3}{2}$ -order dependence of R_p on $[M]$. This initiation is probably best considered as an example of redox initiation (Sec. 3-4b).

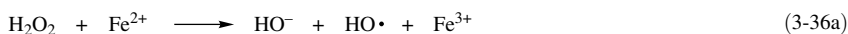
Other exceptions to the first-order dependence of the polymerization rate on the monomer concentration occur when termination is not by bimolecular reaction of propagating radicals. Second-order dependence of R_p on $[M]$ occurs for primary termination (Eq. 3-33a) and certain redox-initiated polymerizations (Sec. 3-4b-2). Less than first-order dependence of R_p on $[M]$ has been observed for polymerizations (Sec. 9-8a-2) taking place inside a solid under conditions where monomer diffusion into the solid is slower than the normal propagation rate [Odian et al., 1980] and also in some redox polymerizations (Sec. 3-4b-2) [Mapunda-Vlckova and Barton, 1978].

3-4b Redox Initiation

Many oxidation–reduction reactions produce radicals that can be used to initiate polymerization [Sarac, 1999]. This type of initiation is referred to as *redox initiation*, *redox catalysis*, or *redox activation*. A prime advantage of redox initiation is that radical production occurs at reasonable rates over a very wide range of temperatures, depending on the particular redox system, including initiation at moderate temperatures of 0–50°C and even lower. This allows a greater freedom of choice of the polymerization temperature than is possible with the thermal homolysis of initiators. Some redox polymerizations can be initiated photolytically as well as thermally. A wide range of redox reactions, including both inorganic and organic components either wholly or in part, may be employed for this purpose. Some redox systems involve direct electron transfer between reductant and oxidant, while others involve the intermediate formation of reductant-oxidant complexes; the latter are charge-transfer complexes in some cases.

3-4b-1 Types of Redox Initiators

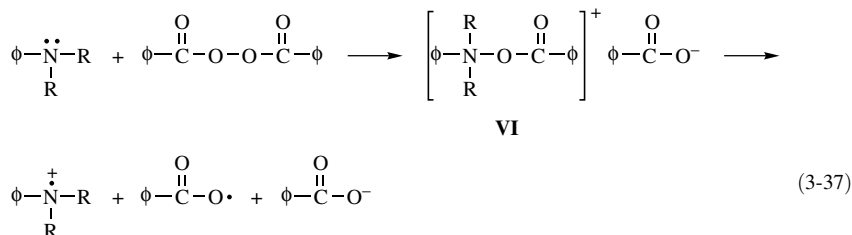
1. Peroxides in combination with a reducing agent are a common source of radicals; for example, the reaction of hydrogen peroxide with ferrous ion



Ferrous ion also promotes the decomposition of a variety of other compounds including various types of organic peroxides [Bamford, 1988].

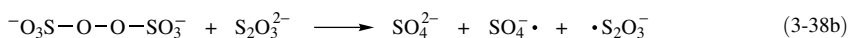
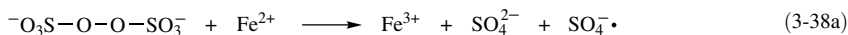


Other reductants such as Cr^{2+} , V^{2+} , Ti^{3+} , Co^{2+} , and Cu^+ can be employed in place of ferrous ion in many instances. Most of these redox systems are aqueous or emulsion systems. Redox initiation with acyl peroxides can be carried out in organic media by using amines as the reductant [Morsi et al., 1977; O'Driscoll et al., 1965]. An interesting system is the combination of benzoyl peroxide and an *N,N*-dialkylaniline. The difference in the rates of decomposition between such a redox system and the simple thermal homolysis of the peroxide alone is striking. The decomposition rate constant k_d for benzoyl peroxide in styrene polymerization is $1.33 \times 10^{-4} \text{ s}^{-1}$ at 90°C, while that for the benzoyl peroxide-*N,N*-diethylaniline redox system is $1.25 \times 10^{-2} \text{ L mol}^{-1} \text{ s}^{-1}$ at 60°C and $2.29 \times 10^{-3} \text{ L mol}^{-1} \text{ s}^{-1}$ at 30°C. The redox system has a much larger decomposition rate. Radical production in this redox system appears to proceed via an initial ionic displacement by the nitrogen of the aniline on the peroxide linkage



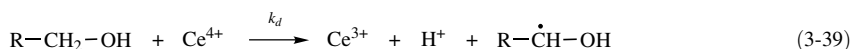
In support of this mechanism, the rate of initiation increases with increasing nucleophilicity of the amine. Initiation is by the $\phi\text{COO}\cdot$ radical. The amino cation–radical is generally not an effective initiator as shown by the absence of nitrogen in the polymer; it apparently disappears by some unknown side reactions such as dimerization and/or deprotonation. (However, there is some evidence that the cation–radical produced by the interaction of benzoyl peroxide and *N*-vinylcarbazole (NVC) initiates cationic polymerization of NVC simultaneous with the radical polymerization [Bevington et al., 1978].) Other types of peroxides also appear susceptible to this type of acceleration. Peroxide decomposition is also accelerated by transition metal ion complexes such as copper (II) acetylacetonate [Ghosh and Maity, 1978; Shahani and Indictor, 1978]. Zinc chloride accelerates the rate of decomposition of AIBN in methyl methacrylate by a factor of 8 at 50°C, with a corresponding increase in polymerization rate [Lachinov et al., 1977]. The mechanism may be analogous to the amine–peroxide system. The effect of ZnCl_2 and other metal ions on accelerating R_p is well established, although the mechanism in most cases appears to involve changes in k_p and/or due to complexation of the metal ions with the monomer and/or propagating radicals.

2. The combination of a variety of inorganic reductants and inorganic oxidants initiates radical polymerization, for example



Other redox systems include reductants such as HSO_3^- , SO_3^{2-} , $\text{S}_2\text{O}_3^{2-}$, and $\text{S}_2\text{O}_5^{2-}$ in combination with oxidants such as Ag^+ , Cu^{2+} , Fe^{3+} , ClO_3^- , and H_2O_2 .

3. Organic–inorganic redox pairs initiate polymerization, usually but not always by oxidation of the organic component, for example, the oxidation of an alcohol by Ce^{4+} ,



or by V^{5+} , Cr^{6+} , Mn^{3+} [Fernandez and Guzman, 1989; Misra and Bajpai, 1982; Nayak and Lenka, 1980].

4. There are some initiator systems in which the monomer itself acts as one component of the redox pair. Examples are thiosulfate plus acrylamide or methacrylic acid and *N,N*-dimethylaniline plus methyl methacrylate [Manickam et al., 1978; Tsuda et al., 1984].

3-4b-2 Rate of Redox Polymerization

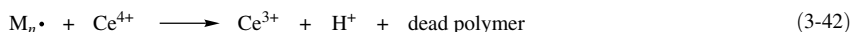
The kinetics of redox-initiated polymerizations generally fall into two categories depending on the termination mode. Many of these polymerizations proceed in the same manner as other polymerizations in terms of the propagation and termination steps; the only difference is the source of radicals for the initiation step. For these polymerizations where termination is by bimolecular reaction of propagating radicals, the initiation and polymerization rates will be given by appropriate expressions that are very similar to those developed previously:

$$R_i = k_d[\text{reductant}][\text{oxidant}] \quad (3-40)$$

$$R_p = k_p[\text{M}] \left(\frac{k_d[\text{reductant}][\text{oxidant}]}{2k_t} \right)^{1/2} \quad (3-41)$$

Equations 3-40 and 3-41 differ from those (Eqs. 3-31 and 3-32) discussed previously in that the factor of 2 is absent from the expression for R_i , since typically only one radical is produced per oxidant-reductant pair.

Some redox polymerizations involve a change in the termination step from the usual bimolecular reaction to monomolecular termination involving the reaction between the propagating radicals and a component of the redox system. This leads to kinetics that are appreciably different from those previously encountered. Thus, in the alcohol- Ce^{4+} system (Eq. 3-39), termination occurs according to



at high ceric ion concentrations. The propagating radical loses a hydrogen to form a dead polymer with a $\text{C}=\text{C}$ and group. The rates of initiation and termination are given by

$$R_i = k_d[\text{Ce}^{4+}][\text{alcohol}] \quad (3-43)$$

$$R_t = k_t[\text{Ce}^{4+}][\text{M}\cdot] \quad (3-44)$$

By making the usual steady-state assumption (i.e., $R_i = R_t$), one obtains the polymerization rate as

$$R_p = \frac{k_d k_p [\text{M}][\text{alcohol}]}{k_t} \quad (3-45)$$

In many redox polymerizations, monomer may actually be involved in the initiation process. Although not indicated above, this is the case for initiations described under item 3b; and, of course, for item 4. R_p will show a higher dependence on $[\text{M}]$ in these cases than indicated by Eqs. 3-41 and 3-45. First-order dependence of R_i on $[\text{M}]$ results in $\frac{3}{2}$ - and 2-order dependencies of R_p on $[\text{M}]$ for bimolecular and monomolecular terminations, respectively.

3-4c Photochemical Initiation

Photochemical or *photoinitiated* polymerizations occur when radicals are produced by ultraviolet and visible light irradiation of a reaction system [Oster and Yang, 1968; Pappas, 1988]. In general, light absorption results in radical production by either of two pathways:

1. Some compound in the system undergoes excitation by energy absorption and subsequent decomposition into radicals.
2. Some compound undergoes excitation and the excited species interacts with a second compound (by either energy transfer or redox reaction) to form radicals derived from the latter and/or former compound(s).

The term *photosensitizer* was originally used to refer to the second pathway, especially when it involved energy transfer, but that distinction has become blurred. The mechanism for photoinitiation in a reaction system is not always clear-cut and may involve both pathways. *Photosensitizer* is now used to refer to any substance that either increases the rate of photoinitiated polymerization or shifts the wavelength at which polymerization occurs.

Photoinitiation offers several advantages. Polymerization can be spatially directed (i.e., confined to specific regions) and turned on and off by turning the light source off and on.

The initiation rates can be very fast and are controlled by a combination of the source of radicals, light intensity, and temperature. Industrial photopolymerizations typically use solvent-free systems, which offer advantages for both economic and/or environmental considerations. The significant limitation of photopolymerization is that penetration of light energy through a thickness of material is low. However, photopolymerization is well suited for surface and other thin-layer applications in the printing and coatings industries [Decker, 1996; Fouassier, 1995; Pappas, 1988]. Applications include the ultrafast drying of varnishes, printing inks, and coatings (decorative and protective) for metal, paper, wood, and plastics; in photolithography for producing integrated and printed circuits; in holography and stereolithography; and in curing dental restorations, bone cements, and adhesive formulations. Photopolymerization can be used with heat-sensitive substrates, since polymerization is rapid even at ambient temperatures. Laser light sources are becoming important in applications that take advantage of their higher intensities, resulting in higher reaction rates, improved imaging resolution, and deeper penetration into substrates.

Photopolymerization is used in the photoimaging industry. The reaction system for photoimaging applications is referred to as a *photoresist*. The development of a printed circuit involves coating a copper-laminate substrate with the photoresist followed by irradiation through a mask with transparent areas corresponding to the desired copper circuitry. The unexposed areas are uncured and easily dissolved by solvent. Copper is then selectively etched away from below the unexposed areas. The copper below the exposed areas is protected by a polymer coating during the etching process. Finally, that polymer coating is removed to yield the desired copper printed circuit.

Many of these applications involve a combination of polymerization and crosslinking. Crosslinking usually involves monomers with two or more double bonds per molecule (Sec. 6-6a). Acrylate, unsaturated polyester-styrene, and dithiol-diene systems are used [Decker, 1996]. (Curing of epoxy resins and vinyl ethers by ionic photoinitiators is also practiced commercially; see Secs. 5-2a-4, 7-2b-7.) Another approach for producing photocrosslinked coatings is the crosslinking of preformed polymers. This requires the use of specially designed polymers with reactive functional groups (e.g., double bonds) and/or appropriate crosslinking agents.

3-4c-1 Bulk Monomer

The irradiation of some monomers results in the formation of an excited state M^* by the absorption of light photons (quanta):



The excited species undergoes homolysis to produce radicals



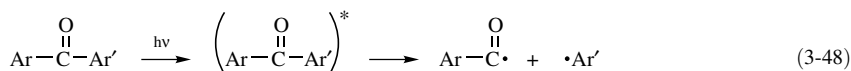
capable of initiating the polymerization of the monomer. The identities of the radicals $R\cdot$ and $R'\cdot$ are seldom well established. Nor is it clear that photolysis of a bulk monomer always results in the simple homolysis to yield two radicals per one monomer molecule as described by Eq. 3-47. Initiation by photolysis of a monomer is limited to those monomers where the double bond is conjugated with other groups (e.g., styrene, methyl methacrylate) such that absorption will occur above the vacuum UV region (200 nm) where light sources are readily available. However, unless absorption occurs above 300–325 nm, there is the practical

limitation of the need for quartz reaction vessels, since glass does not transmit appreciable amounts of energy at wavelengths below 300–325 nm. A further practical limitation for most monomers is that the efficiency of initiation (*quantum yield*) by photolysis of bulk monomer is almost always considerably less than the initiator systems described below.

3-4c-2 Irradiation of Thermal and Redox Initiators

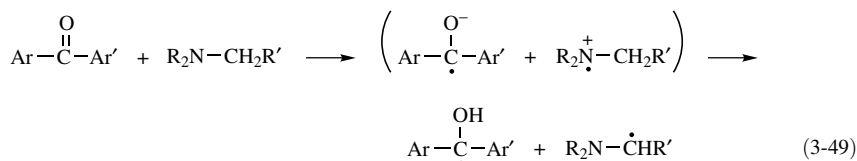
The various thermal and redox initiators described in Secs. 3-4a and 3-4b can also be used in photoinitiation. In the usual case irradiation yields the same radicals as described previously for thermal or redox initiation. However, not all thermal and redox initiators are equally useful as photoinitiators, since few of them absorb light in the practical wavelength region. On the other hand, the photochemical method allows the use of a wider range of compounds as initiators due to the higher selectivity of photolytic homolysis. For example, for compounds other than the thermal and redox initiators discussed previously, homolysis occurs at too high a temperature and usually results in the production of a wide spectrum of different radicals (and ions) as various bonds randomly break. A useful photoinitiator should absorb strongly in the wavelength range of the light source and possess a high quantum yield for radical production.

Although both aliphatic and aromatic ketones have been studied, the aromatic ketones are more useful in commercial practice, since their absorptions occur at longer wavelength (lower energy) and their quantum yields are higher [Ledwith, 1977; Pappas, 1988]. Ketones and their derivatives undergo homolysis by one or both (often simultaneously) of two processes: α -scission and electron transfer [Padon and Scranton, 1999]. α -Scission involves



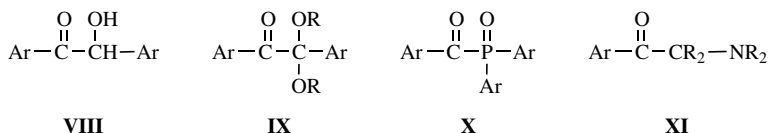
VII

bond scission at the bond between the carbonyl carbon and the α -carbon (Eq. 3-48) while electron transfer occurs only in the presence of an electron donor (RH) and involves electron transfer followed by proton transfer from the amine to the ketone:



Tertiary amines with an α -hydrogen are among the most effective electron donors; other electron donors include alcohols, amides, amino acids, and ethers. A third process, direct hydrogen atom transfer from RH to the ketone, is not common but does occur with some photoinitiators. The overall result is the same as the electron-transfer process. Although two radicals are produced by photolysis of the photoinitiator, only one of the radicals is typically active in initiation—the aroyl and amine radicals in Eqs. 3-48 and 3-49, respectively. The other radical may or may not initiate polymerization, but is active in termination. The decrease in photoinitiator concentration during polymerization is referred to as *photo-bleaching*.

Similar photolytic reactions occur with benzoin (**VIII**), benzyl ketals (**IX**), aroylphosphine oxides (**X**), and α -aminoalkylphenones (**XI**). These and related compounds are used



as commercial photoinitiators, usually together with an amine [Decker et al., 2001; Encinas et al., 1989a,b; Fouassier, 1995; Padon and Scranton, 1999; Pappas, 1988]. The relative amounts of α -scission and electron transfer vary with the initiator (which determines the relative stabilities of the radicals formed from the two processes) and also the electron donor used. The photoinitiator and electron donor are chosen to maximize energy absorption and radical yield.

Photoinitiation systems have been developed to take advantage of the lower cost of visible light sources compared to ultraviolet light sources. Many applications such as printing plates and lithography become more economical when using visible light. Visible light is preferable in biological applications (e.g., dental restorations and in vivo curing), since ultraviolet light is much more damaging to living cells. Many dyes and other compounds absorbing in the visible region have been used as photoinitiators, including methylene blue, eosin, ketocoumarins, cyanines, and fluorinated diaryl titanocenes. These compounds are used as part of a two- or three-component system. Two-component systems use an electron donor. Radicals are generated by the electron-transfer mechanism (Eq. 3-49). The dye-derived radical is inactive in polymerization, but active in termination. Three-component systems use an electron donor and a third component. The third component is often a diaryliodonium salt such as diaryliodonium chloride, $\text{Ar}_2\text{I}^+\text{Cl}^-$. The third component increases the efficiency of photopolymerization by reacting with the inactive dye radical to decrease the termination rate and increase the initiation rate by generating new radicals from fragmentation of the third component (e.g., $\text{Ar}_2\text{I}^+\text{Cl}^-$ generates aryl radicals and aryl iodide) [Padon and Scranton, 2000]. In many cases, the reaction of the third component with the inactive dye radical regenerates the dye, that is, photobleaching does not occur. Other mechanisms have also been proposed for the three-component systems [Padon and Scranton, 1999]. More recently, two-component dye systems with organoborates such as tetramethylammonium triphenylbutylborate in place of amines have been found to be highly active in photoinitiation.

3-4c-3 Rate of Photopolymerization

The rate of photochemical initiation is given by

$$R_i = 2\phi I_a \quad (3-50)$$

where I_a is the intensity of absorbed light in moles (called *einsteins* in photochemistry) of light quanta per liter-second and ϕ is the number of propagating chains initiated per light photon absorbed. ϕ is referred to as the *quantum yield for initiation*. The factor of 2 in Eq. 3-50 is used to indicate that two radicals are produced per molecule undergoing photolysis. The factor of 2 is not used for those initiating systems that yield only one radical instead of two. Thus the maximum value of ϕ is 1 for all photoinitiating systems. ϕ is synonymous with f in that both describe the efficiency of radicals in initiating polymerization. (The reader is cautioned that this definition of ϕ is not always used. An alternate approach is

to replace ϕ by $f\phi'$, where ϕ' is the number of radicals produced per light photon absorbed and f is the previously defined initiator efficiency. Also, quantum yields can be defined in terms of the quantum yield for reaction of the initiator species or quantum yield for monomer polymerized. These quantum yields are not synonymous with the quantum yield for initiation.)

An expression for the polymerization rate is obtained by combining Eqs. 3-50 and 3-25 to yield

$$R_p = k_p[M] \left(\frac{\phi I_a}{k_t} \right)^{1/2} \quad (3-51)$$

The absorbed light intensity I_a is obtained from a consideration of the Beer–Lambert law in the form

$$I'_a = I_0 - I_0 e^{-\alpha[A]D} \quad (3-52)$$

where I_0 is the incident light intensity at the outer surface of the reaction system and I'_a is the intensity of absorbed light on a layer at a distance D (cm) into the reaction system. I'_a is not the same as the quantity I_a in Eqs. 3-50 and 3-51. I_a is the volumetric light intensity (with units of $\text{mol cm}^{-3} \text{ s}^{-1}$ or, more often, $\text{mol L}^{-1} \text{ s}^{-1}$). I'_a and I_0 are surface area intensities (with units of $\text{mol cm}^{-2} \text{ s}^{-1}$). $[A]$ is the molar concentration of light-absorbing photoinitiator. α is the absorption coefficient of A and varies with wavelength and temperature. α has units of $\text{L mol}^{-1} \text{ cm}^{-1}$. (The molar absorptivity ϵ , formerly called the *extinction coefficient*, is often used instead of α . α and ϵ are related by $\alpha = \epsilon \ln 10 = 2.3\epsilon$ and result from the use of the base e instead of 10, respectively, in the Beer–Lambert law.)

I_a and, therefore, R_p vary with depth of penetration D into the reaction system [Calvert and Pitts, 1967; Terrones and Pearlstein, 2001]. The variation of I_a with D is obtained as the differential of I'_a with respect to D

$$I_a = \frac{dI'_a}{dD} = \alpha[A]I_0 10^3 e^{-\alpha[A]D} \quad (3-53)$$

The term 10^3 is a conversion factor (10^3 mL L^{-1}) that converts I_a from units of $\text{mol cm}^{-3} \text{ s}^{-1}$ to $\text{mol L}^{-1} \text{ s}^{-1}$. Combination of Eqs. 3-51 and 3-53 yields the polymerization rate as a function of D

$$R_p = k_p[M] \left(\frac{\phi \alpha [A] I_0 10^3 e^{-\alpha[A]D}}{k_t} \right)^{1/2} \quad (3-54)$$

R_p is the “local” polymerization rate—the rate at a layer located a distance D from the surface of the reaction system. Since R_p varies with the depth of penetration into the reaction system, it is useful to calculate the layer-averaged polymerization rate $\bar{R}_p$, the average polymerization rate for a thickness D of reaction system. $\bar{R}_p$ is obtained by integrating the local rate over the layer thickness D and dividing by D to give

$$\bar{R}_p = 2k_p[M] \left(\frac{\phi I_0 10^3}{\alpha[A]k_t} \right)^{1/2} \left(\frac{1 - e^{-\alpha[A]D/2}}{D} \right) \quad (3-55)$$

The light intensities delivered by light sources are usually expressed in units such as kcal s^{-1} , kJ s^{-1} , or erg s^{-1} , and it is necessary to convert them into the appropriate units of $\text{mol L}^{-1} \text{ s}^{-1}$ before using them in the preceding equations. This is accomplished by a

knowledge of the wavelength λ or frequency ν of the light energy employed. The energy in a mole (einstein) of light is $Nh\nu$ or Nhc/λ , where h is Planck's constant, c is the speed of light, and N is Avogadro's number.

3-4c-3-a Measurement of Absorbed Light. The use of Eqs. 3-54 and 3-55 may be avoided and Eq. 3-51 used instead by directly measuring I_a in a specific polymerization system. Measurement of light intensity is referred to as *actinometry*. Chemical, thermal, and electrical actinometers are used [Murov et al., 1993; Ranby and Rabek, 1975]. Thermal and electrical actinometers include photomultipliers, semiconductor photodetectors, and thermocouples that operate on the principle of converting photon energy to either electrical or thermal energy. The light intensity is measured by placing the electrical or thermal actinometer directly behind the reaction vessel and measuring the difference in intensity when the vessel is empty compared to when it holds the reaction system. A chemical actinometer involves using a chemical reaction whose quantum yield is known. The most frequently used chemical actinometer is probably potassium ferrioxalate. Irradiation of $K_3Fe(C_2O_4)_3$ as an aqueous acidified solution results in reduction of ferric ions to ferrous. Ferrous ions are followed by UV spectroscopy by forming the red-colored complex with 1,10-phenanthroline. Other chemical actinometers include uranyl oxalate (involving oxidation of oxalate ion) and benzophenone (reduction to benzhydrol). Chemical actinometry is performed in the same reaction vessels to be used for polymerization studies.

3-4c-3-b General Observations. If the term $\alpha[A]D$ is sufficiently small, the exponential term in Eq. 3-53 has a value of one and there is no variation of I_a and R_p with D . This occurs for very thin reaction systems with low photoinitiator concentration and small value of the absorption coefficient. Equation 3-54 becomes

$$R_p = k_p[M] \left(\frac{\phi\alpha[A]I_0 10^3}{k_t} \right)^{1/2} \quad (3-56)$$

under these conditions. Thus, R_p is first-order in $[M]$, $\frac{1}{2}$ -order in both light intensity and photoinitiator concentration when there is negligible attenuation of light intensity in traversing the reaction system. When the photoexcitation process involves monomer ($A = M$), the dependence of R_p on $[M]$ increases to $\frac{3}{2}$ -order. The dependence of R_p on $[M]$ decreases to $\frac{1}{2}$ -order in some systems with high monomer concentrations, such as in the photopolymerization of methyl methacrylate with ketone photoinitiators [Lissi et al., 1979]. With increasing $[M]$, monomer quenches the excited state for photoinitiation. Quenching is a generally observed phenomenon, leading to a lower than expected dependence of R_p on some component in the system that acts as the *quencher*. A quencher (which can be any compound present in the reaction system) undergoes energy transfer with the photoexcited species to dissipate the excitation energy.

For most practical photopolymerizations there is appreciable attenuation of light intensity with penetration and the dependence of polymerization rate on monomer, photoinitiator, and light intensity is more complex (see Eqs. 3-54 and 3-55 for exact definitions). Equation 3-54 is especially useful for analyzing the practical aspects of a photopolymerization. When polymerizing any specific thickness of reaction system it is important to know R_p at various depths (e.g., front, middle, and rear surfaces) than to know only the total R_p for that system thickness. If the thickness is too large, the polymerization rate in the rear (deeper) layers will be too low, and those layers will be only partially polymerized—the result would be detrimental because the product's properties (especially the physical properties) would be

nonuniform. This problem is more severe for reactions carried out at high values of $[A]$ and α because the variation of R_p with D is greater for larger values of $[A]$ and α [Lee et al., 2001]. Uniformity of polymerization is increased by using lower concentrations of photoinitiators with lower α values. However, there is a tradeoff between polymerization rate and uniformity of reaction.

The nonuniformity of polymerization with depth of penetration is less for photobleaching photoinitiators compared to photoinitiators that are regenerated. Photobleaching allows photon penetration deeper into the reaction system.

The nonuniformity of polymerization with depth of penetration is also minimized (but not completely overcome) by using a mixture of two photoinitiators (or one photoinitiator) with absorption bands at two different wavelength, one of which absorbs strongly (large α) and the other weakly (small α). The strong absorption band gives a high intensity at the surface of the reaction system, but the intensity rapidly decreases with penetration. The intensity of the weak absorption band is less effected by penetration and provides a more uniform intensity as a function of penetration. Dual photothermal initiation systems are also used. The specific photoinitiator initiates rapidly enough to generate sufficient heat to drive a thermal polymerization within the depth of the reaction system.

Performing photopolymerizations in air, which would simplify commercial practice, has a major complication due to two effects of oxygen. Oxygen acts as quencher of photoexcited states of molecules and also inhibits polymerization by its reaction with radicals (Sec. 3-7b). This problem can be avoided by performing the photopolymerization under an inert atmosphere (nitrogen, argon). Using a protective coating of a paraffin oil or some other compound has also been reported [Padon and Scranton, 2000]. These methods are usually avoided because of cost and other practical considerations. The use of an appropriate two-wavelength photoinitiator system overcomes the oxygen problem by having a higher intensity energy absorption in the surface layer.

3-4d Initiation by Ionizing Radiation

Radioactive sources and particle accelerators are used to initiate polymerizations. Electrons, neutrons, and α -particles (He^{2+}) are particulate radiations, while gamma and X rays are electromagnetic radiations. The interactions of these radiations with matter are complex [Chapiro, 1962; Wilson, 1974]. The chemical effects of the different types of radiation are qualitatively the same, although there are quantitative differences. Molecular excitation may occur with the subsequent formation of radicals in the same manner as in photolysis, but ionization of a compound C by ejection of an electron is more probable because of the higher



energies of these radiations compared to visible or ultraviolet light energy. (Ionizing radiations have particle or photon energies in the range 10 keV–100 meV (1–16,000 fJ) compared to 1–6 eV for visible–ultraviolet photons.) For this reason such radiations are termed *ionizing radiations*. The cation formed in Eq. 3-67 is a radical–cation $\text{C}^{\bullet+}$ formed by loss of a π -electron and has both radical and positive centers (Sec. 5-2a-6). The radical–cation can propagate at the radical and/or cationic centers depending on reaction conditions. The radical–cation can also dissociate to form separate radical and cationic species:



The initially ejected electron may be attracted to the cation B^+ with the formation of another radical:



Radicals may also be produced by a sequence of reactions initiated by the capture of an ejected electron by C



where C^- may or may not be an excited species depending on the energy of the electron.

The radiolysis of olefinic monomers results in the formation of cations, anions, and free radicals as described above. It is then possible for these species to initiate chain polymerizations. Whether a polymerization is initiated by the radicals, cations, or anions depends on the monomer and reaction conditions. Most radiation polymerizations are radical polymerizations, especially at higher temperatures where ionic species are not stable and dissociate to yield radicals. Radiolytic initiation can also be achieved using initiators, like those used in thermally initiated and photoinitiated polymerizations, which undergo decomposition on irradiation.

Radiation-initiated ionic polymerizations, however, have been established in a number of systems. This occurs under conditions where ionic species have reasonable stabilities and the monomer is susceptible to ionic propagation. Cationic polymerizations of isobutylene, vinyl ethers, epoxies, and styrene and anionic polymerization of acrylonitrile have been observed [Chapiro, 1962; Kubota et al., 1978; Wilson, 1974]. Ionic polymerizations have been observed at temperatures as high as 30–50°C, but lower temperatures are generally required, usually not because the ionic rates increase with decreasing temperature but because the radical contribution decreases. The role of reaction conditions has been well-established for styrene polymerization [Machi et al., 1972; Squire et al., 1972; Takezaki et al., 1978]. The dryness of the reaction system and the absence of any other species which can terminate ions (either those formed in the radiolytic reactions (Eqs. 3-57 through 3-62) or the ionic propagating species) is critical. Water and other similar compounds terminate ions by transferring a proton or negative fragment (see Chap. 5). Styrene monomer as normally purified and “dried” often has sufficient water present ($\sim 10^{-2}$ – 10^{-4} M) to prevent ionic polymerization—only radical polymerization occurs. With *superdried* monomer ($[H_2O] < 10^{-5}$ – 10^{-7} M), one observes a bimodal molecular weight distribution. This indicates the simultaneous occurrence of cationic and radical polymerizations since the two are known to yield different-molecular-weight polymers. With decreasing water concentration ($\sim < 10^{-7}$ – 10^{-10} M) the polymerization proceeds entirely by cationic propagation as evidenced by a unimodal MWD, which is characteristic of the cationic MWD. The extent of the ionic contribution relative to radical polymerization also increases with increasing radiation intensity, perhaps due to the rapid depletion of water at the higher intensities. Other evidence for the ionic contributions include kinetic and activation energy data.

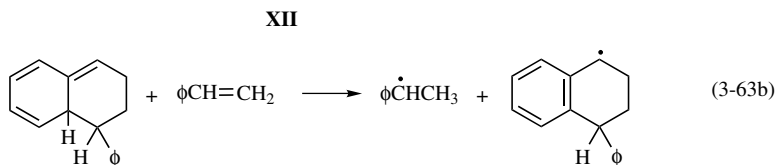
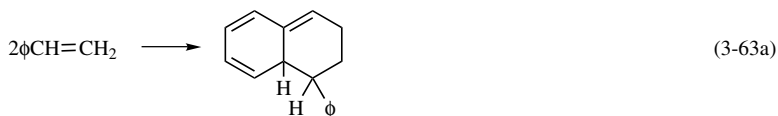
The kinetics of radiation-initiated polymerizations follow in a relatively straightforward manner those of photolytic polymerization. The initiation rate is determined by the radiation intensity and the concentration and susceptibility of the compound that radiolyzes to yield the initiating species (ionic and/or radical). The final expression for R_p is determined by the exact details of the initiation, propagation, and termination steps.

Radiation-initiated polymerization has achieved some commercial success. The most frequently used radiation is electrons, the technology is called *electron-beam (EB) technology*. Electrons as well as other ionizing radiations (except for α -particles) have a significant advantage over UV and visible radiation. The depth of penetration is much greater with less attenuation for ionizing radiations than for UV and visible. There are several areas of application for EB technology [Fouassier and Rabek, 1993]. Coatings and other thin reactions systems (involving mostly polymerization with crosslinking—Sec. 6-6a) are an area of application where EB competes directly against UV and visible light. EB is not used to the same extent as UV and visible because of the higher overall equipment costs and the perception that working with ionizing radiations is risky from a health-safety viewpoint. Other EB uses include the crosslinking of wire and cable insulation and packaging films (Sec. 9-2c). EB is the technology of choice in microelectronics fabrication.

3-4e Pure Thermal Initiation

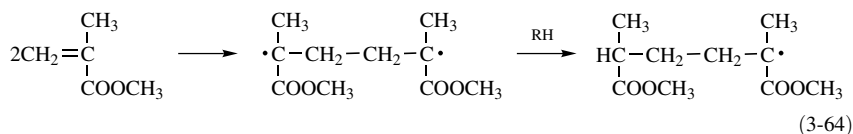
Many monomers appear to undergo a spontaneous polymerization when heated in the apparent absence of catalysts. On careful investigation few of these involve the thermal production of radicals from the monomer. In most cases the observed polymerizations are initiated by the thermal homolysis of impurities (including peroxides or hydroperoxides formed due to O_2) present in the monomer. Most monomers, when exhaustively purified (and in exhaustively purified reaction vessels), do not undergo a *purely thermal, self-initiated polymerization* in the dark. Only styrene has been unequivocally shown to undergo self-initiated polymerization. Methyl methacrylate was also considered to undergo self-initiated polymerization, but more recent work indicates that most, but not all, of the previously reported self-initiated polymerization was caused by adventitious peroxides that were difficult to exclude by the usual purification techniques [Lehrle and Shortland, 1988]. Other monomers that may be susceptible to self-initiated polymerization are substituted styrenes, acenaphthylene, 2-vinylthiophene, and 2-vinylfuran as well as certain pairs of monomers [Brand et al., 1980; Hall, 1983; Lingnau et al., 1980; Sato et al., 1977]. The rate of self-initiated polymerization is much slower than the corresponding polymerization initiated by thermal homolysis of an initiator such as AIBN, but far from negligible; for example, the self-initiated polymerization rate for neat styrene at 60°C is $1.98 \times 10^{-6} \text{ mol L}^{-1} \text{ s}^{-1}$ [Graham et al., 1979].

The initiation mechanism for styrene has been established [Graham et al., 1979; Kaufman, 1979; Kothe and Fischer, 2001; Mayo, 1968; Olaj et al., 1976, 1977a,b]. It involves the formation of a Diels–Alder dimer (XII) of styrene followed by transfer of a hydrogen atom from the dimer to a styrene molecule (Eq. 3-63). Whether formation of the



Diels–Alder dimer or its reaction with styrene is the rate-determining step in initiation is not completely established. The dependence of R_p on $[M]$ is closer to third-order than second-order, indicating that Eq. 3-63b is the slow step. The Diels–Alder dimer has not been isolated, but ultraviolet spectroscopy of the reaction system is entirely compatible with its presence. There are indications that the photopolymerization of neat styrene proceeds by a similar mechanism.

The initiation mechanism for methyl methacrylate appears to involve the initial formation of a biradical by reaction of two monomer molecules followed by hydrogen transfer from



some species in the reaction system to convert the biradical to a monoradical (Eq. 3-64) [Lingnau and Meyerhoff, 1984a,b]. Spontaneous polymerization is also observed in certain pairs of monomers such as styrene-acrylonitrile and maleimide–vinyl ether [Decker, 2000; Liu et al., 1995]. These are monomer pairs in which one double bond is electron-rich and the other is electron-poor (Sec. 6-3b-3).

3-4f Other Methods of Initiation

Electrolysis of monomer solutions has been studied as a means of initiating polymerization [Olaj, 1987; Otero and Mugarz, 1987]. Aqueous and various organic solvents (e.g., DMF, methylene chloride, methanol) have been employed in the presence of various inorganic compounds. The latter are used either to conduct current or participate in the initiation process. Depending on the components present, radicals and/or ions are formed when current is passed through the reaction system, and these initiate polymerization. Such polymerizations are referred to as *electroinitiated* or *electrolytic polymerizations*. An interesting example is the electrolysis of an acetonitrile solution of acrylamide containing tetrabutylammonium perchlorate [Samal and Nayak, 1988]. Radical polymerization occurs at the anode initiated by $\text{ClO}_4\cdot$ formed by oxidation of ClO_4^- . Anionic polymerization occurs at the cathode initiated by direct transfer of electrons to the monomer (Sec. 5-3a-2).

Plasma polymerization occurs when a gaseous monomer is placed in an electric discharge at low pressures under conditions where a plasma is created [Boenig, 1988; Yasuda, 1986]. A plasma consists of ionized gaseous molecules. In some cases, the system is heated and/or placed in a radiofrequency field to assist in creating the plasma. A variety of organic molecules including alkenes, alkynes, and alkanes undergo polymerization to high-molecular-weight products under these conditions. The propagation mechanisms appear to involve both ionic and radical species. Plasma polymerization offers a potentially unique method of forming thin polymer films for uses such as thin-film capacitors, antireflection coatings, and various types of thin membranes.

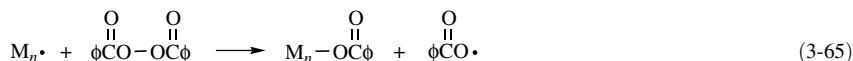
Sonication, the application of high-intensity ultrasound at frequencies beyond the range of human hearing (16 kHz), of a monomer results in radical polymerization. Initiation results from the effects of *cavitation*—the formation and collapse of cavities in the liquid. The collapse (implosion) of the cavities generates very high local temperatures and pressures. This results in the formation of excited states that leads to bond breakage and the formation of

radicals. Polymerization to high-molecular-weight polymer is observed but the conversions are low (<15%). The polymerization is self-limiting because of the high viscosity produced even at low conversion. High viscosity hinders cavitation and radical production [Price et al., 1992].

3-4g Initiator Efficiency

3-4g-1 Definition of f

When a material balance is performed on the amount of initiator that is decomposed during a polymerization and compared with that which initiates polymerization, it is apparent that the initiator is inefficiently used. There is wastage of initiator due to two reactions. One is the *induced decomposition of initiator* by the attack of propagating radicals on the initiator, for example



This reaction is termed *chain transfer to initiator* and is considered further in Sec. 3-6b. The induced decomposition of initiator does not change the radical concentration during the polymerization, since the newly formed radical ($\phi\text{COO}\cdot$) will initiate a new polymer chain. However, the reaction does result in a wastage of initiator. A molecule of initiator is decomposed without an increase in the number of propagating radicals or the amount of monomer being converted to polymer.

The second wastage reaction is that involving the side reaction(s) of the radicals formed in the primary step of initiator decomposition. Some of the radicals formed in the primary decomposition step, for example, in the reaction



undergo reactions to form neutral molecules instead of initiating polymerization. It is this wastage reaction that is referred to when discussing the initiator efficiency f . The initiator efficiency f is defined as the fraction of radicals formed in the primary step of initiator decomposition, which are successful in initiating polymerization. The initiator efficiency is considered exclusive of any initiator wastage by induced decomposition. The reader is cautioned, however, that reported literature values of f do not always make this distinction. Very frequently, the calculations of f neglect and do not correct for the occurrence of induced decomposition. Such f values may be considered as the “effective” or “practical” initiator efficiency in that they give the net or overall initiation efficiency of the initial catalyst concentration. The preferred method of quantitatively handling induced decomposition of initiator, however, is that which is discussed in Sec. 3-6b-3.

3-4g-2 Mechanism of $f < 1$: Cage Effect

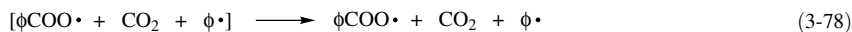
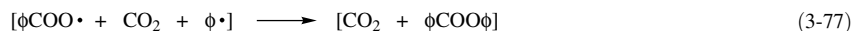
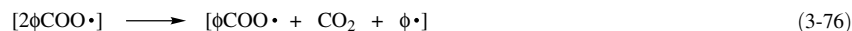
The values of f for most initiators lie in the range 0.3–0.8. To understand why the initiator efficiency will be less than unity, consider the following reactions that occur in

polymerizations initiated by benzoyl peroxide:



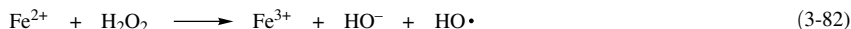
The brackets around any species indicate the presence of a solvent cage, which traps the radicals for some short period before they defuse apart. Equation 3-67 represents the primary step of initiator decomposition into two radicals, which are held within the solvent cage. The radicals in the solvent cage may undergo recombination (the reverse of Eq. 3-67), reaction with each other (Eq. 3-68), or reaction with monomer (Eq. 3-69), or may diffuse out of the solvent cage (Eq. 3-70). Once outside the solvent cage, the radicals may react with monomer (Eq. 3-71) or decompose according to Eq. 3-72 to yield a radical that may undergo various reactions (Eqs. 3-73 to 3-75). Reaction 3-72 probably also occurs within the solvent cage followed by diffusion of the two species.

Recombination of the primary radicals (Eq. 3-67) has no effect on the initiator efficiency. Initiation of polymerization occurs by Eqs. 3-69, 3-71, and 3-73. The initiator efficiency is decreased by the reactions indicated by Eqs. 3-68, 3-74, and 3-75, since their products are stable and cannot give rise to radicals. Of these reactions the decomposition within the solvent cage (Eq. 3-68) is usually much more significant than the others in decreasing the value of f . That this reaction is competitive with those leading to initiation of polymerization can be seen by considering the timescale of the various events [Koenig and Fischer, 1973; Noyes, 1961]. The average life of neighboring radicals is perhaps 10^{-10} – 10^{-9} s. Since rate constants for radical–radical reactions are in the range 10^7 L mol⁻¹ s⁻¹ and higher, and the concentration of radicals in the solvent cage is about 10 M , there is a reasonable probability that Reaction 3-68 will occur. Reaction 3-69 cannot compete effectively with Reaction 3-68, since radical addition reactions have much lower rate constants (10 – 10^5 L mol⁻¹ s⁻¹).



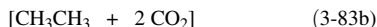
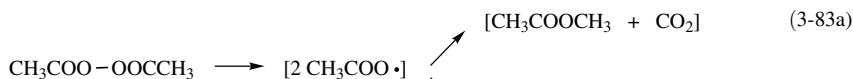
Reactions 3-76 and 3-79 coupled, respectively, with Reactions 3-78 and 3-81 do not lower f but do lower f when coupled, respectively, with Reactions 3-77 and 3-80. The radicals that escape the solvent cage (Eqs. 3-78 and 3-81) then react as per Eqs. 3-71 through 3-75.

Lowering of f by reactions analogous to Eq. 3-68 is referred to as the *cage effect* [Bamford, 1988; Koenig and Fischer, 1973; Martin, 1973]. It is a general phenomenon observed in almost all initiation systems. About the only exceptions are the initiation systems such as

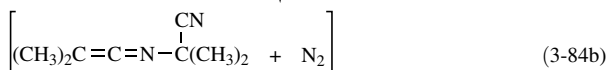
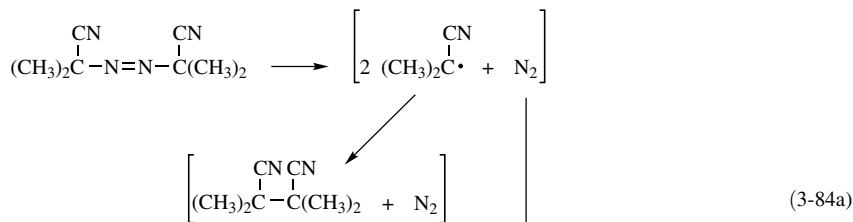


which do not produce radicals in pairs. However, even in some such instances the radical may be capable of reacting with a nonradical species in the solvent cage.

Acetoxy radicals from acetyl peroxide undergo partial decarboxylation and radical combination within the solvent cage leads to stable products incapable of producing radicals:

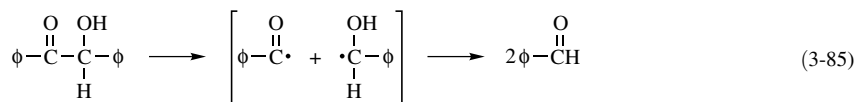


The homolysis of AIBN occurs in a concerted process with simultaneous breakage of the two C–N bonds to yield nitrogen and 2-cyano-2-propyl radicals. Reaction of the radicals with each other can occur in two ways to yield tetramethylsuccinodinitrile and dimethyl-*N*-(2-cyano-2-isopropyl)ketenimine:



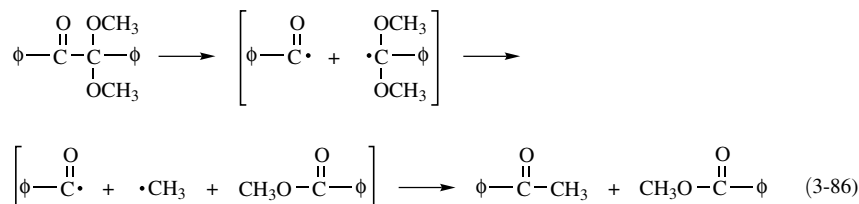
A minor reaction of 2-cyano-2-propyl radicals is disproportionation to methacrylonitrile and isobutyronitrile [Moad et al., 1984; Starnes et al., 1984]. This presents a complication for polymerizations carried out to high conversions where the methacrylonitrile concentration is significant since methacrylonitrile undergoes copolymerization with many monomers.

The cage effect has also been well documented as the cause of lowered ϕ values in photo-initiation [Berner et al., 1978; Braun and Studenroth, 1979]. Benzoin photolysis yields benzaldehyde:



The photolysis of benzildimethylketal yields benzoyl and benzylketal radicals in the primary cleavage. The latter radical undergoes decay within the cage to yield methyl benzoate and

methyl radical. Coupling of the methyl and benzoyl radicals decrease f :



The initiator efficiency and quantum yield for initiation are generally independent of monomer concentration and of the radical coupling reactions occurring outside the solvent cage (Eqs. 3-74, 3-75). The prime reason for $f < 1$ is the reactions occurring within the solvent cage. Once a radical has diffused out of the solvent cage, the reaction with monomer (Eq. 3-71) occurs predominantly in preference to other reactions [Fink, 1983]. Even if Reaction 3-72 occurs this will be followed by Reaction 3-73 in preference to the two radical combination reactions (Eqs. 3-74, 3-75). The preference for initiation of polymerization arises from the much greater monomer concentrations (10^{-1} – 10 M) compared to the radical concentrations (10^{-7} – 10^{-9} M) that are normally present in polymerization systems. However, one can observe a variation of f with the monomer concentration at low monomer concentrations. Figure 3-3 shows this effect in the AIBN initiation of styrene polymerization. The initiator efficiency increases very rapidly with $[M]$ and a limiting value is quickly reached. Theoretical predictions [Koenig and Fischer, 1973] indicate that an effect of $[M]$ on f would be expected at monomer concentrations below 10^{-1} – 10^{-2} M, and this is the general observation. f is affected at lower concentrations as one increases the initiation rate, since the radical–radical reactions become more probable. An example is the photopolymerization of methyl methacrylate using benzoin methyl ether [Carlbom and Pappas, 1977],

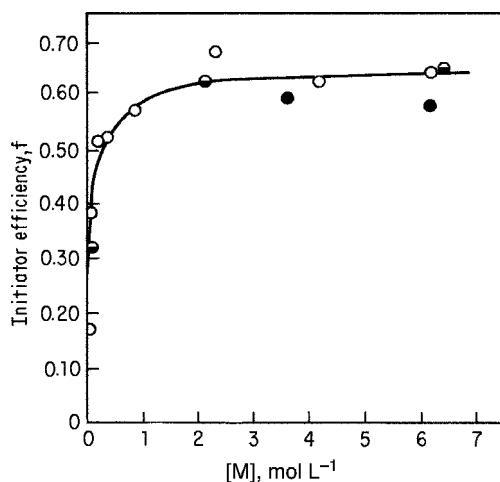


Fig. 3-3 Effect of styrene concentration on the initiator efficiency of azobisisobutyronitrile. ●, ○ and ◐ refer to experiments with initiator concentrations of 0.20, 0.50, and 1.00 g L⁻¹, respectively. After Bevington [1955] (by permission of Faraday Society, and Royal Society of Chemistry, London).

where ϕ decreases from 0.65 to 0.30 as the concentration of the photosensitizer increases from $10^{-3} M$ to $4 \times 10^{-2} M$.

The initiator efficiency varies to differing extents depending on the identities of the monomer, solvent, and initiator. f decreases as the viscosity of the reaction medium increases. With increasing viscosity, the lifetimes of radicals in the solvent cage are increased—leading to greater extents of radical–radical reactions within the solvent cage. The effect of viscosity has been observed when viscosity was altered by using different solvents. The effect can be quite large, for example, f for bis-azo-1,1'-cyclohexane nitrile at 0°C decreases from 0.22 in benzene to 0.086 in diethyl phthalate [Fischer et al., 1969]. f has also been observed to decrease during the course of a polymerization, since both $[M]$ and viscosity increase with conversion [Russell et al., 1988]. For example, f for AIBN in the polymerization of styrene decreases from 0.75 at conversions up to 30% to 0.20 at 90–95% conversion [Solomon and Moad, 1987]. In some cases f varies with solvent as a result of the solvent reacting with radicals before the radicals can initiate polymerization. The initiator efficiencies of AIBN, benzoyl peroxide, and *t*-butyl hydroperoxide are lower in carbon tetrachloride or 1-chlorooctane than in aromatic solvents [Nozaki and Bartlett, 1946; Shahani and Indictor, 1978; Walling, 1954]. Reactions of radicals with solvents are discussed further in Sec. 3-6. The change in initiator efficiency with solvent may in a few instances be due to a solvation effect, for example, the specific solvation of electrophilic radicals by electron-donor solvents [Martin, 1973]. The initiator efficiency for any particular initiator may also vary for different monomers. Thus the value of f for AIBN in the polymerizations of methyl methacrylate, vinyl acetate, styrene, vinyl chloride, and acrylonitrile ranged from 0.6 to 1.0, increasing in that order [Arnett and Peterson, 1952]. This order is a consequence of the relative rates with which radicals add to the different monomers.

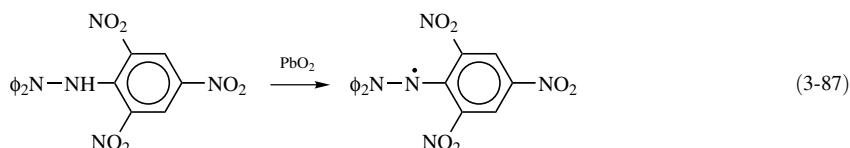
3-4g-3 Experimental Determination of f

Various methods are employed for the experimental evaluation of the initiator efficiency. (These methods are generally also applicable to determining ϕ for photopolymerization). One method involves the determination and comparison of both the initiator decomposition and the production of polymer molecules. The initiator decomposition is best determined during an actual polymerization. Independent measurement of initiator decomposition in the absence of monomer can give erroneous results. The rates of decomposition of initiator can be quite different for pure initiator as compared to initiator in the presence of monomer, since f varies with monomer concentration. Also in some cases monomer is involved in the initiation step [e.g., molecule-induced homolysis (Eq. 3-35), certain redox initiations described in Sec. 3-4b-1]. AIBN decomposition can be followed relatively easily by following the evolution of nitrogen. Measurement of the polymer number-average molecular weight allows a determination of f by comparison of the number of radicals produced with the number of polymer molecules obtained. This method requires a knowledge of whether termination occurs by coupling or disproportionation, since the former results in two initiator fragments per polymer molecule and the latter in only one. The occurrence of induced decomposition must be taken into account in calculating the number of radicals produced. Induced decomposition is negligible for azonitriles but occurs to an appreciable extent with many peroxides.

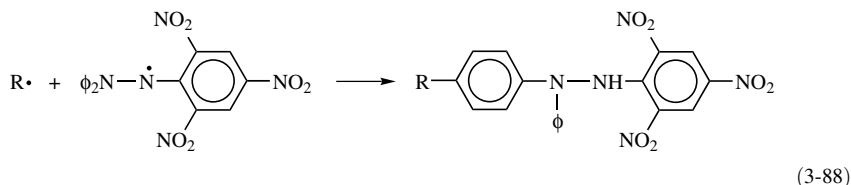
The second method is a variation of the first in which the number of initiator fragments in the polymer is determined by direct analysis of the polymer end groups. The analysis is relatively difficult to perform accurately because of the low concentration of the end groups. For a 50,000-molecular-weight polymer, the end groups constitute only $\sim 0.1\%$ of the total

weight of the sample. The use of isotopically labeled initiators such as ^{14}C -labeled AIBN and benzoyl peroxide and ^{35}S -labeled potassium persulfate is a sensitive method for determining the number of initiator fragments [Bonta et al., 1976]. Isotopically labeled initiators also allow a quantitative analysis of the initiator radicals in systems where their identities are not clear-cut. For example, the use of benzoyl peroxide with ^{14}C in the carbonyl carbon shows that $\phi\text{COO}\cdot$ is responsible for 98% of initiation of styrene polymerization at 80°C , but this drops to about 60% (with $\phi\cdot$ initiating 40% of the propagating chains) at 30°C [Berger et al., 1977].

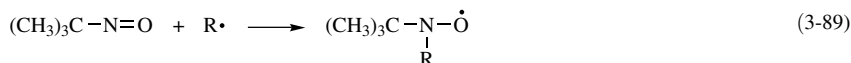
A third method involves the use of radical scavengers, which count the number of radicals in a system by rapidly stopping their growth. Three groups of radical scavengers are used [Bamford, 1988; Koenig and Fischer, 1973]. The first group consists of stable radicals such as 2,2-diphenylpicrylhydrazyl (DPPH) obtained by oxidation of diphenylpicrylhydrazine:



The DPPH radical terminates other radicals, probably by the reaction

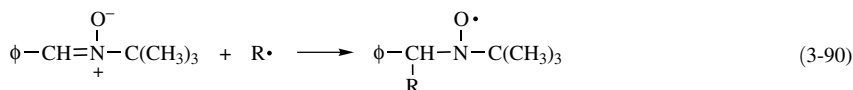


The reaction can be easily followed spectrophotometrically, since the DPPH radical is deep violet and the product is usually light yellow or colorless. Other stable radicals include TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy), 1,3,5-triphenylverdazyl, and galvinoxyl [Areizaga and Guzman, 1988; Braun and Czerwinski, 1987]. A second group reacts by fast hydrogen or halogen transfer and consists of thiols, iodine, bromine, and dihydroanthracene. The third group, consisting of molecules that react with radicals, includes duroquinone and *p*-benzoquinone [Janzen, 1971]. Nitroso and nitron compounds have been found to be highly useful [Evans, 1979; Sato et al., 1977]. These compounds, called *spin traps*, react with radicals to form stable radicals. 2-Methyl-2-nitrosopropane (**XIII**) and phenyl-*N*-*t*-butylnitron (**XIV**) have been used extensively:



XIII

XV



XIV

XVI

Electron spin resonance (ESR) spectroscopy can be advantageously used to measure the radical concentrations of the nitroxide radicals (**XV** and **XVI**) produced, since these are much more stable than the $R\cdot$ radicals. Of greater importance, ESR can be used to determine the structure of $R\cdot$, since the ESR of the nitroxide radical is quite sensitive to the structure of R . (For this purpose, nitroso spin traps are more useful, since the R group in the nitroxide radical is nearer to the lone electron.) This can allow a determination of the structures of radicals first formed in initiator decomposition, the radicals that actually initiate polymerization (if they are not identical with the former) as well as the propagating radicals [Rizzardo and Solomon, 1979; Sato et al., 1975].

The radical scavenging methods require the general caution that the stoichiometry of the reaction between scavenger and radical must be established. A problem with some scavengers is that their reaction with radicals may not be quantitative. The DPPH radical is an extremely efficient scavenger in many systems. It completely stops vinyl acetate and styrene polymerizations even at concentrations below $10^{-4} M$ [Bartlett and Kwart, 1950]. However, the scavenging effect of DPPH is not universally quantitative for all monomers.

A fourth method is the dead-end polymerization technique, which allows the simultaneous determination of k_d [Catalgil and Baysal, 1987; Reimschuessel and Creasy, 1978; Stickler, 1979]. *Dead-end polymerization* refers to a polymerization in which the initiator concentration decreases to such a low value that the half-life of the propagating polymer chains approximates that of the initiator. Under such circumstances the polymerization stops short of completion, and one observes a limiting conversion of monomer to polymer at infinite reaction time. Consider a dead-end polymerization initiated by the thermal homolysis of an initiator. Equations 3-28a and 3-32 can be combined and rearranged to yield

$$\frac{-d[M]}{[M]} = k_p \left(\frac{fk_d[I]_0}{k_t} \right)^{1/2} e^{-k_d t/2} dt \quad (3-91)$$

which on integration leads to

$$-\ln \frac{[M]}{[M]_0} = -\ln(1-p) = 2k_p \left(\frac{f[I]_0}{k_t k_d} \right)^{1/2} (1 - e^{-k_d t/2}) \quad (3-92)$$

where p is the extent of conversion of monomer to polymer and is defined by $([M]_0 - [M])/[M]_0$. At long reaction times ($t \rightarrow \infty$), $[M]$ and p reach the limiting values of $[M]_\infty$ and p_∞ , respectively, and Eq. 3-92 becomes

$$-\ln \frac{[M]_\infty}{[M]_0} = -\ln(1-p_\infty) = 2k_p \left(\frac{f[I]_0}{k_t k_d} \right)^{1/2} \quad (3-93)$$

Dividing Eq. 3-92 by Eq. 3-93, rearranging, and then taking logarithms of both sides leads to

$$-\ln \left[1 - \frac{\ln(1-p)}{\ln(1-p_\infty)} \right] = \frac{k_d t}{2} \quad (3-94)$$

The value of k_d is then found from the slope of a plot of the left side of Eq. 3-94 versus time. Figure 3-4 shows the plot for the AIBN-initiated polymerization of isoprene at three temperatures [Gobran et al., 1960]. Since k_d is determined, f can be obtained from either Eq. 3-32 or 3-93 if the ratio $k_p/k_t^{1/2}$ is known from other studies.

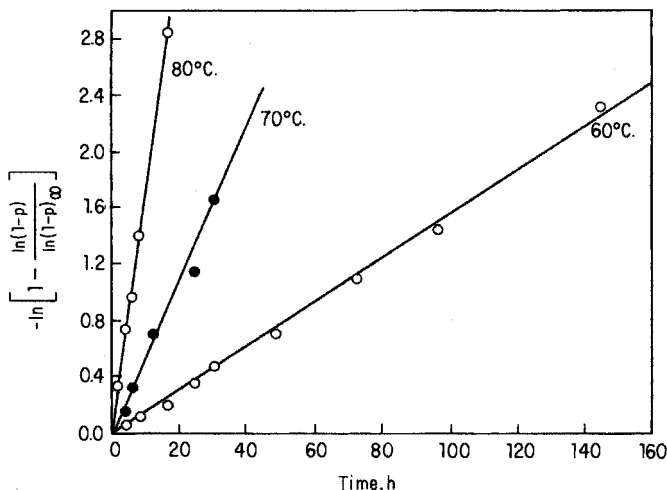


Fig. 3-4 Dead-end polymerization of isoprene initiated by azobisisobutyronitrile. After Gobran et al. [1960] (by permission of Wiley-Interscience, New York).

Equation 3-92 is also useful for determining the time needed to reach different extents of conversion for actual polymerization systems where both $[M]$ and $[I]$ decrease with time.

3-4h Other Aspects of Initiation

There are two possible modes of addition of a primary radical from initiator to the double bond of a monomer: *head* and *tail additions*, corresponding to Eqs. 3-8 and 3-9, respectively. Tail addition is favored over head addition for the same reasons head-to-tail propagation is favored over head-to-head propagation (Sec. 3-2a). This expectation is generally verified in the few systems which have been experimentally examined [Bevington, 1988; Moad et al., 1982, 1984; Solomon and Moad, 1987]. Tail addition occurs exclusively in the AIBN and *t*-butyl peroxide initiated polymerizations of styrene and the AIBN-initiated polymerization of vinyl chloride; there is no detectable head addition. The ratio of tail : head additions varies from 20 : 1 to 13 : 1, depending on the reaction conditions, for the benzoyl-peroxide-initiated polymerization of styrene. The extent of head addition increases for monomers where there is a smaller difference in stability between the two possible radicals. The tail : head ratio is about 5–6 for the *t*-butyl peroxide initiated polymerization of vinyl acetate. The various results, especially those with vinyl acetate, show that the selectivity between tail and head additions in the initiation step is not as great as the selectivity between head-to-tail and head-to-head additions in propagation, presumably because the typical primary radical is more reactive than the typical propagating radical.

The initiation process appears more complicated than described above, although data are not available in more than a few systems. The benzoyl peroxide initiated polymerization of styrene involves considerable substitution of initiator radicals on the benzene ring for polymerizations carried out at high conversions and high initiator concentrations. About one-third of the initiator radicals from *t*-butyl peroxide abstract hydrogen atoms from the α -methyl groups of methyl methacrylate, while there is no such abstraction for initiator radicals from benzoyl peroxide or AIBN.