INITIATORS, FREE-RADICAL

1. Introduction

Free-radical initiators are chemical substances that, under certain conditions, initiate chemical reactions by producing free radicals:

$$\mathrm{I} \longrightarrow \mathrm{I}\cdot \qquad \text{initiator} \quad \text{radical} \tag{1}$$

Initiators contain one or more labile bonds that cleave homolytically when sufficient energy is supplied to the molecule. The energy must be greater than the bond dissociation energy (BDE) of the labile bond. Radicals are reactive chemical species possessing a free (unbonded or unpaired) electron. Radicals may also be positively or negatively charged species carrying a free electron (ion radicals). Initiator-derived radicals are very reactive chemical intermediates and generally have short lifetimes, ie, half-life times less than 10^{-3} s (1).

The principal commercial initiators used to generate radicals are peroxides and azo compounds. Lesser amounts of carbon–carbon initiators and photoinitiators, and high-energy ionizing radiation are also employed commercially to generate radicals. *N*-alkoxyamines as free-radical initiators or employ atom or group radical transfer facilitated by transition metals.

2. Free-Radical Formation and Use

There are three general processes for supplying the energy necessary to generate radicals from initiators: thermal processes, microwave or ultraviolet (uv) radiation processes, and electron transfer (redox) processes. Radicals can also be produced in high-energy radiation processes. Initiators are sometimes called radical catalysts. However, initiators are not true catalysts because they are consumed in amounts ranging from substoichiometric up to stoichiometric or greater when they are employed as initiators in chemical reactions. True catalysts such as enzymes are not consumed in the chemical reaction they catalyze.

Once formed, radicals undergo two basic types of reactions: propagation reactions and termination reactions. In a propagation reaction, a radical reacts to form a covalent bond and to generate a new radical. The three most common propagating reactions are atom abstraction, β-scission, and addition to carbon–carbon double bonds or aromatic rings. In a termination reaction, two radicals interact in a mutually destructive reaction in which both radicals form covalent bonds and reaction ceases. The two most common termination reactions are coupling and disproportionation. Because the propagation reaction is a chain reaction, it has become the most significant aspect of commercial free-radical chemistry. Radical chain reactions are involved in many commercial processes.

Radicals are employed widely in the polymer industry, where their chain-propagating behavior transforms vinyl monomers into polymers and copolymers. The mechanism of addition polymerization involves all three types of reactions discussed above, ie, initiation, propagation by addition to carbon–carbon double bonds, and termination:

Initiation $$\mathrm{I \longrightarrow I\cdot} \tag{2}$$

$$\mathrm{I\cdot + M \longrightarrow I{-}M\cdot} \tag{3}$$

Propagation $$\mathrm{I{-}M\cdot} + n\mathrm{M \longrightarrow I{-}M}_n\mathrm{{-}M\cdot} \tag{4}$$

Termination $$2\,\mathrm{I{-}M}_n\mathrm{{-}M\cdot \longrightarrow I{-}M}_n\mathrm{{-}M{-}M{-}M}_n\mathrm{{-}I} \tag{5}$$

$$2\,\mathrm{I{-}M}_n\mathrm{{-}M\cdot \longrightarrow I{-}M}_n\mathrm{{-}M' + I{-}M}_n\mathrm{{-}M''} \tag{6}$$

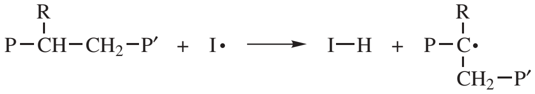
In these equations I is the initiator and I· is the radical intermediate, M is a vinyl monomer, I—M· is an initial monomer radical,I—M_nM· is a propagating polymer radical, and M′ and M″ are polymer end groups that result from termination by disproportionation. Common vinyl monomers that can be homo- or copolymerized by radical initiation include ethylene, butadiene, styrene, vinyl chloride, vinyl acetate, acrylic and methacrylic acid esters, acrylonitrile, *N*-vinylimidazole, *N*-vinyl-2-pyrrolidinone, and others (2).

Two other important commercial uses of initiators are in polymer cross-linking and polymer degradation. In a cross-linking reaction, atom abstraction, usually a hydrogen abstraction, occurs, followed by termination by coupling of two polymer radicals to form a covalent cross-link:

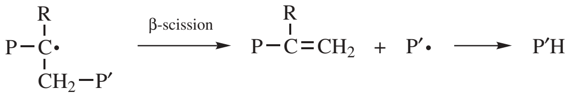
$$\mathrm{P{-}H + I\cdot \longrightarrow I{-}H + P\cdot} \tag{7}$$

$$\mathrm{2P\cdot \longrightarrow P{-}P} \tag{8}$$

P—H is a polymer with covalently attached hydrogen, I· is the initiating radical, and P—P is a cross-linked polymer. Cross-linking is a commercially important reaction of thermoplastics (such as polyethylene) and elastomers. In polymer degradation, hydrogen abstraction is followed by β-scission that results in breakage of the polymer chain:



$$\mathrm{P{-}\overset{R}{C}H{-}CH_2{-}P' + I\bullet \longrightarrow I{-}H + P{-}\underset{CH_2-P'}{\overset{R}{C}}\bullet} \tag{9}$$



$$\mathrm{P{-}\underset{CH_2-P'}{\overset{R}{C}}\bullet \xrightarrow{\beta\text{-scission}} P{-}\overset{R}{C}{=}CH_2 + P'\bullet \longrightarrow P'H} \tag{10}$$

I· is the initiating radical,P′· is the chain-propagating polymer radical that subsequently abstracts a hydrogen atom from another polymer molecule, P−CHR−CH_2−P′ is the polymer before, and P−CR=CH_2 and P′−H are polymer chains after degradation. Polymer degradation is important in facilitating the commercial processing (molding and extruding) of polypropylene (the degradation is more commonly called controlled rheology or vis-breaking). In the β-scission reaction the first-formed radical cleaves to a polymer radical and to an electronically neutral molecule (polymer with an unsaturated end group) by scission of a carbon−carbon bond β to the atom bearing the initial radical center.

Other common radical-initiated polymer processes include curing of resins, eg, unsaturated polyester–styrene blends; curing of rubber; grafting of vinyl monomers onto polymer backbones; and telomerizations.

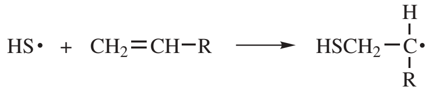
A typical example of a nonpolymeric chain-propagating radical reaction is the anti-Markovnikov addition of hydrogen sulfide to a terminal olefin. The mechanism involves alternating abstraction and addition reactions in the propagating steps:

Initiation

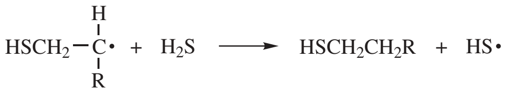
$$\mathrm{I} \longrightarrow \mathrm{I}\cdot \qquad (11)$$

$$\mathrm{I}\cdot + (\mathit{excess})\ \mathrm{H_2S} \longrightarrow \mathrm{I{-}H} + \mathrm{HS}\cdot \qquad (12)$$

Propagation



$$\mathrm{HS}\cdot + \mathrm{CH_2{=}CH{-}R} \longrightarrow \mathrm{HSCH_2{-}}\overset{\mathrm{H}}{\underset{\mathrm{R}}{\mathrm{C}}}\cdot \qquad (13)$$



$$\mathrm{HSCH_2{-}}\overset{\mathrm{H}}{\underset{\mathrm{R}}{\mathrm{C}}}\cdot + \mathrm{H_2S} \longrightarrow \mathrm{HSCH_2CH_2R} + \mathrm{HS}\cdot \qquad (14)$$

Termination

$$\mathrm{HS}\cdot \longrightarrow \text{nonradical sulfur compounds} \qquad (15)$$

Other nonpolymeric radical-initiated processes include oxidation, autoxidation of hydrocarbons, chlorination, bromination, and other additions to double bonds. The same types of initiators are generally used for initiating polymerization and nonpolymerization reactions. Radical reactions are extensively discussed in the chemical literature (3–20).

2.1. Structure–Reactivity Relationships. Much has been written about the structure reactivity of radicals. No single unifying concept has satisfactorily explained all radical reactions reported in the literature. A longstanding correlation of structure and reactivity involves comparisons of the energies required to homolytically break covalent bonds to hydrogen. It is assumed that this energy, the hydrogen bond dissociation energy (BDE), reflects the stability and the reactivity of the radical coproduced with the hydrogen atom (21–24). However, this assumption should really be limited to radical reactivity and selectivity in hydrogen atom abstraction reactions, and can be particularly misleading for reactions with polar transition states, in which radicals can behave either as nucleophiles or electrophiles (25). Solvent interacations with transition-state species can also influence the reactivity (26–30). Nevertheless, the correlation of radical reactivity with BDE is quite useful. Table 1 shows some general BDE values for the formation of various carbon and oxygen radicals from various precursors. According to the theory, the higher the BDE, the higher the reactivity and the lower the stability of the radical formed by removal of a hydrogen atom. Thus bulky *tert*-alkyl radicals are more stable and less reactive then less bulky secondary alkyl radicals that in turn are more stable and less reactive than primary alkyl radicals. Hydroxyl radicals are the most reactive radicals listed. Methyl radicals are more reactive than other primary alkyl radicals and are about as reactive as alkoxy radicals. Lower stability and increased reactivity correspond to less discriminating radical behavior, resulting in faster and less-selective radical reactions with other molecules. In organic systems, this reaction is usually hydrogen atom abstraction. Consequently, methyl radicals and oxy radicals (carboxy, alkoxy, hydroxy) are considered good hydrogen atom-abstracting radicals, and are suitable for cross-linking, grafting, and degradation reactions. Enhanced stability and reduced reactivity correspond to more discriminating radical behavior, resulting in slower and more selective subsequent reactions. Therefore, reactions other than hydrogen abstraction are favored. Substituted carbon radicals, such as the ethyl radical, are ineffective hydrogen-abstracting radicals; thus these radicals are more likely to react with carbon–carbon double bonds. Initiators that generate these types of radicals are suitable for vinyl monomer polymerizations that avoid undesirable side reactions (cross-linking, grafting, etc).

The BDE theory does not explain all observed experimental results. Addition reactions are not adequately handled at all, mostly owing to steric and electronic effects in the transition state. Thus it is important to consider both the reactivities of the radical and the intended coreactant or environment in any attempt to predict the course of a radical reaction (31). Application of frontier molecular orbital theory may be more appropriate to explain certain reactions (32,33). Radical reactivities have been studied by ESR spectroscopy (34–36) and modeling based on general reactivity and radical polarity (37). Recent radical trapping studies have provided considerable insight into the course of free-radical reactions, particularly addition polymerizations, using radical traps such as 2,4-diphenyl-4-methyl-1-pentene (α-methylstyrene dimer, MSD) (38–44) and 1,1,3,3-tetramethyl-2,3-dihydro-1*H*-isoindol-2-yloxyl (45–49).

The choice of an initiator for a given radical process depends on the reaction conditions and the reactivity of the initiator. These two factors must be balanced so that the reaction is successful. Knowing the decomposition be- havior of initiators is important to proper selection. The stabilities or reactivities of initiators such as organic peroxides and aliphatic azo compounds are significantly affected by structural variations close to the labile bond or bonds, ie, the oxygen–oxygen bond in peroxides and the carbon–nitrogen bonds in aliphatic azo compounds. The reactivity differences, resulting from structural differences between initiators, are due to several electronic and steric factors. Alkyl and aryl substituents stabilize carbon radicals through resonance and field effects. These substituent effects on radical stability are reversed for initiator stability. Initiators that decompose to produce highly alkylated or arylated carbon radicals are less stable (more reactive) than those that decompose to less alkylated or arylated carbon radicals. Electronic factors introduced by electron-donating or electron-withdrawing substituents can also affect initiator stability–reactivity; electron-donating substituents stabilize, whereas electron-withdrawing groups destabilize incipient carbon radicals. Initiators with bulky groups on either side of the labile, radical-forming bonds are less stable (more reactive) than initiators with less bulky groups since decomposition to radicals relieves ground-state steric strain (50).

2.2. Activation Parameters. Thermal processes are commonly used to break labile initiator bonds in order to form radicals. The amount of thermal energy necessary varies with the environment, but absolute temperature, T, is usually the dominant factor. The energy barrier, the minimum amount of energy that must be supplied, is called the activation energy, E_a. A third important factor, known as the frequency factor, A, is a measure of bond motion freedom (translational, rotational, and vibrational) in the activated complex or transition state. The relationships of A, E_a, and T to the initiator decomposition rate (k_d) are expressed by the Arrhenius first-order rate equation (eq. 16), where R is the gas constant, and A and E_a are known as the activation parameters.

$$k_d = Ae^{(-E_a/RT)} \text{or } \ln k_d = \ln A - E_a/RT \tag{16}$$

Increasing temperature increases initiator decomposition rate. When a single labile bond is broken in the rate-determining step, the frequency factor is high. When multiple bonds are broken, the activated complex is restricted, the frequency factor is low, and the rate of decomposition is reduced (assuming no change in activation energy). Generally, slower rates of decomposition of the initiator mean higher activation energy values. Steric and electronic factors affect the activation energy of the initiator. Factors that enhance the stabilities of the incipient radicals reduce the activation energy and thus increase the decomposition rate.

The activation parameters for an initiator can be determined at normal atmospheric pressure by plotting ln k_d vs $1/T$ using initiator decomposition rates obtained in dilute solution (0.2 M or lower) at several temperatures. Rate data from dilute solutions are required in order to avoid higher-order reactions such as induced decompositions. The intercept for the resulting straight line is ln A and the slope of the line is $-E_a/R$, therefore both A and E_a can be calculated. Activation parameters can also be determined by differential scanning calorimetry (DSC) (51), although consideration must be given to the influence of decomposition products on the values obtained.

2.3. Initiator Half-Life. Once these activation parameters have been determined for an initiator, half-life times at a given temperature, ie, the time required for 50% decomposition at a selected temperature, and half-life temperatures for a given period, ie, the temperature required for 50% decomposition of an initiator over a given time, can be calculated. In selecting appropriate initiators for radical applications such as vinyl monomer polymerizations and polyolefin cross-linking, care must be exercised in the use of calculated half-life data for temperatures, pressures, and solvents different than those used in determining the activation parameters. Half-life data are useful for comparing the activity of one initiator with another when the half-life data are determined in the same solvent and at the same concentration and, preferably, when the initiators are of the same class. Because producers of initiators and their customers roughly correlate the thermal stability of initiators with temperature, it is useful to express this stability in terms of 1- and 10-h half-life temperatures, ie, the temperatures at which 50% of the initiator has decomposed in 1 and 10 h, respectively. An extensive compilation of rate data for initiators is available (52). Half-life temperatures are usually provided in manufacturers' product catalogs (53,54). Rate data for commercial organic peroxide initiators are often available from special manufacturers' half-life bulletins (55).

Although a variety of methods for generating radicals by one or more of these three methods are reported in the literature, commercial initiators are primarily organic and inorganic peroxides, aliphatic azo compounds, certain organic compounds with labile carbon–carbon bonds, and photoinitiators.

3. Peroxides

3.1. Organic Peroxides.

Organic peroxides are compounds possessing one or more oxygen–oxygen bonds. They have the general structure ROOR′ or ROOH, and decompose thermally by the initial cleavage of the oxygen–oxygen bond to produce two radicals:

$$\mathrm{ROOR'} \longrightarrow \mathrm{RO\cdot} + \mathrm{\cdot OR'} \tag{17}$$

Depending on the peroxide class, the rates of decompositions of organic peroxides can be enhanced by specific promoters or activators, which significantly decrease the energy necessary to break the oxygen–oxygen bond. Such accelerated decompositions occur well below a peroxide's normal application temperatures and usually result in generation of only one useful radical, instead of two. An example is the decomposition of hydroperoxides with multivalent metals (M), commonly iron, cobalt, or vanadium:

$$\mathrm{ROOH} + \mathrm{M}^{+n} \longrightarrow \mathrm{RO\cdot} + \mathrm{HO}^{-} + \mathrm{M}^{+(n+1)} \tag{18}$$

Solvent polarity also affects the rate of peroxide decomposition (56). Most peroxides decompose faster in more polar or polarizable solvents. This is true even if the peroxide is not generally susceptible to higher-order decomposition reactions. This phenomenon is illustrated by various half-life data for *tert*-butyl peroxypivalate [927-07-1]. The 10-h half-life temperature for *tert*-butyl peroxypivalate varies from 62°C in decane (nonpolar) to 55°C in benzene (polarizable) and 53°C in methanol (polar).

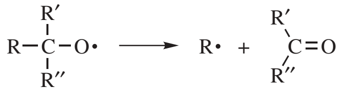
Following radical generation, the radicals produced (RO· and R′O·) can initiate the desired reaction. However, when the radicals are generated in commercial applications, they are surrounded by a solvent, monomer, or polymer "cage." When the cage is solvent, the radical must diffuse out of this cage to react with the desired substrate. When the cage is monomer, the radical can react with the cage wall or diffuse out of the cage. When the cage is polymer, reaction with the polymer can occur in the cage. Unfortunately, other reactions can occur within the cage and can adversely affect efficiency of radical generation and radical reactivity. If the solvent reacts with the initiator radical, then solvent radicals may participate in the desired reaction.

Two secondary propagating reactions often accompany the initial peroxide decomposition: radical-induced decompositions and β-scission reactions. These intermolecular and intramolecular radical reactions compete kinetically with the desired reaction. Both reactions affect the reactivity and efficiency of the initiation process. Peroxydicarbonates and hydroperoxides are particularly susceptible to radical-induced decompositions. In radical-induced decomposition, a radical in the system reacts with undecomposed peroxide, eg:

$$R'\cdot + ROOR \longrightarrow ROR' + RO\cdot \qquad (19)$$

Radical-induced decomposition is an inefficient method of generating radicals, since the peroxide is induced to decompose without adding radicals to the system. Such decompositions are suppressed in vinyl monomer polymerizations, since the vinyl monomers quickly and efficiently scavenge radicals. In nonscavenging environments, eg, in nonolefinic solvents, induced decompositions occur with those peroxides that are susceptible, and they become more pronounced as the peroxide concentration increases. Whereas the homolysis of organic peroxides is a first-order reaction, the radical-induced decomposition is generally a higher-order reaction. Therefore, in those peroxide systems where induced decomposition is occurring, decomposition rates are significantly higher than the true first-order decomposition rates.

The other secondary propagation reaction that occurs during initiation is β-scission, as shown in equations 20 and 21:



$$R{-}\overset{R'}{\underset{R''}{C}}{-}O\cdot \longrightarrow R\cdot + (R')(R'')C{=}O \qquad (20)$$

$$R{-}\overset{O}{\overset{\|}{C}}{-}O\cdot \longrightarrow R\cdot + CO_2 \qquad (21)$$

Although reaction **21** is a β-scission reaction, it is more commonly termed decarboxylation. In both reactions, the energetics and other properties of the radicals are changed. The initially formed oxygen radicals become carbon radicals. The earlier discussion of relative BDEs for the two types of radicals is applicable here. Steric and temperature effects are also important in β-scission. In equation **20**, the newly formed alkyl radical R· is generally derived from the bulkiest alkyl group of the alkoxy radical, and it is usually the most stable radical. An exception here is the phenyl radical, which does not form upon β-scission of α-cumyloxy radicals, owing to its high energy. Instead, β-scission of the α-cumyloxy radical gives methyl radical and acetophenone. For *tert*-alkoxy radicals, the difference in generation of a *tert*-butoxy radical or a *tert*-amyloxy radical from a *tert*-alkyl peroxide can make a significant difference in the course of the resulting radical reaction. β-Scission of the *tert*-butoxy radical produces a methyl radical having about the same energy (as indicated by BDE) and reactivity as a *tert*-butoxy radical. β-Scission of the *tert*-amyloxy radical produces an ethyl radical having significantly lower energy and reactivity than the *tert*-amyloxy radical.

In equation **21**, only one alkyl radical is possible; however, the rate of β-scission is greatly influenced by the bulk of the R group. As with β-scission of α-cumyloxy radicals, benzoyloxy radicals do not decarboxylate as readily as other acyloxy radicals, owing to formation of high-energy phenyl radicals. If the R group is sufficiently bulky, decarboxylation occurs simultaneously with scission of the oxygen–oxygen bond. Increased temperatures enhance β-scission. For more thermally stable peroxides, the higher decomposition temperatures result in increased β-scission. Solvent interaction with the transition state for β-scission also facilitates the reaction (26–30).

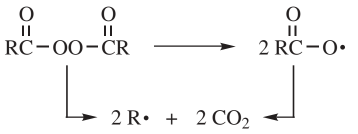
Approximately 100 different organic peroxide initiators, in well over 300 formulations (liquid, solid, paste, powder, solution, dispersion), are commercially produced throughout the world, primarily for the polymer and resin industries. Considerable published literature exists that describes the synthesis, chemical properties, and utility of organic peroxides (57–68). A multiclient study covers the commercial producers and users of organic peroxides as well as other initiators, and their commercial markets and applications (69).

The eight classes of organic peroxides that are produced commercially for use as initiators are listed in Table 2. Included are the 10-h half-life temperature ranges (nonpromoted) for the members of each peroxide class.

Peroxide half-life data provide useful guidance for comparing the activity of one peroxide with another in a given application, if the previously discussed limitations of half-life data are considered. Several producers of organic peroxides provide customers with extensive half-life data on commercial and developmental organic peroxides (56,70). In addition, customer guidance is provided for selection of organic peroxides for various commercial applications, eg, vinyl monomer polymerizations, curing of unsaturated polyester resins, cross-linking of elastomers and polyolefins, and reactive extrusion, based on peroxide type and half-life criteria. This information is available in a manufacturer's half-life bulletin and associated personal computer interactive software (56), and in many available application-focused brochures (71–77).

Table 2 shows that commercial organic peroxides are available with 10-h half-life temperature activity varying from about room temperature to about 130°C. Organic peroxide classes such as diacyl peroxides and peroxyesters show a strong correlation between structural variation and 10-h half-life temperature activity. Other organic peroxide classes, eg, peroxydicarbonates and monoperoxycarbonates, show very little change in activity with structural variation. The diperoxyketals and dialkyl peroxides show a moderate change in activity with variation in peroxide structures. In the cases of hydroperoxides and ketone peroxides, precise half-life data are difficult to obtain owing to the susceptibilities of these thermally stable peroxide classes to induced decompositions and transition-metal catalysis. Furthermore, radicals are usually generated from these two classes of peroxides at lower temperatures using activators (or promoters), and first-order decomposition rates have no significance. Although the low temperature acyl sulfonyl peroxide, acetyl cyclohexanesulfonyl peroxide (ACSP) [3179-56-4] (with a 10-h half-life temperature of 42°C), is still used to some extent commercially, it is only produced captively; hence its peroxide class was not included in Table 2.

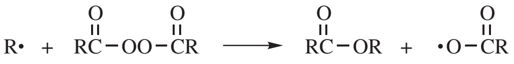
3.2. Diacyl Peroxides. Table 3 lists several commercial diacyl peroxides and their corresponding 10-h half-life temperatures, determined in benzene and other solvents (78). Although diacyl peroxides cleave at the oxygen–oxygen bond, decarboxylation can occur, either simultaneously or subsequently (eq. 22):



$$\mathrm{R\overset{O}{\overset{\|}{C}}{-}OO{-}\overset{O}{\overset{\|}{C}}R \longrightarrow 2\,R\overset{O}{\overset{\|}{C}}{-}O\cdot}$$
$$\mathrm{R\overset{O}{\overset{\|}{C}}{-}OO{-}\overset{O}{\overset{\|}{C}}R \longrightarrow 2\,R\cdot + 2\,CO_2 \longleftarrow 2\,R\overset{O}{\overset{\|}{C}}{-}O\cdot}$$

(22)

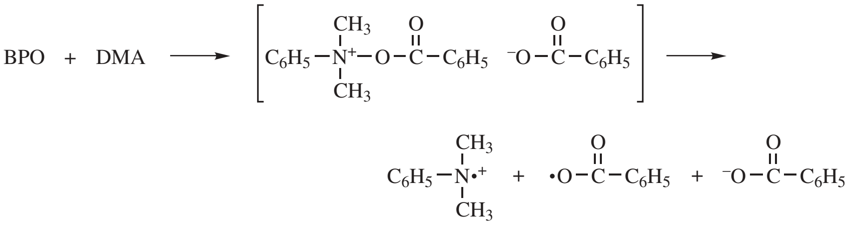
The extent of decarboxylation primarily depends on temperature, pressure, and the stability of the incipient R· radical. The more stable the R· radical, the faster and more extensive the decarboxylation. With many diacyl peroxides, decarboxylation and oxygen–oxygen bond scission occur simultaneously in the transition state. Acyloxy radicals are known to form initially only from diacetyl peroxide [110-22-5] and from dibenzoyl peroxides (because of the relative instabilities of the corresponding methyl and phenyl radicals formed upon decarboxylation). Diacyl peroxides derived from non-α-branched carboxylic acids, eg, dilauroyl peroxide, may also initially form acyloxy radical pairs; however, these acyloxy radicals decarboxylate very rapidly and the initiating radicals are expected to be alkyl radicals. Diacyl peroxides are also susceptible to induced decompositions:



$$\mathrm{R\cdot + R\overset{O}{\overset{\|}{C}}{-}OO{-}\overset{O}{\overset{\|}{C}}R \longrightarrow R\overset{O}{\overset{\|}{C}}{-}OR + \cdot O{-}\overset{O}{\overset{\|}{C}}R} \qquad (23)$$

Diacyl peroxides are used in a broad spectrum of applications, including curing of unsaturated polyester resin compositions, cross-linking of elastomers, production of poly(vinyl chloride), polystyrene, and polyacrylates, and in many nonpolymeric addition reactions. The activities of acyloxy radicals in vinyl monomer polymerization (79–80) and under high-pressure conditions (81–82) have been investigated.

Aromatic diacyl peroxides such as dibenzoyl peroxide (BPO) [94-36-0] may be used with promoters to lower the useful decomposition temperatures of the peroxides, although usually with some sacrifice to radical generation efficiency. The most widely used promoter is dimethylaniline (DMA). The BPO–DMA combination is used for hardening (curing) of unsaturated polyester resin compositions, eg, body putty in auto repair kits. Here, the aromatic *tert*-amine promoter attacks the BPO to initially form *N*-benzoyloxydimethylanilinium benzoate (ion pair), which subsequently decomposes at room temperature to form a benzoate ion, a dimethylaniline radical cation, and a benzoyloxy radical that, in turn, initiates the curing reaction (83):

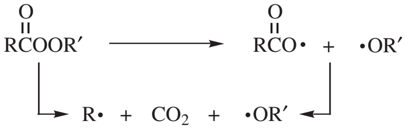


$$\mathrm{BPO + DMA \longrightarrow \left[C_6H_5{-}\underset{CH_3}{\overset{CH_3}{N^+}}{-}O{-}\overset{O}{\overset{\|}{C}}{-}C_6H_5 \quad {}^{-}O{-}\overset{O}{\overset{\|}{C}}{-}C_6H_5 \right] \longrightarrow}$$
$$\mathrm{C_6H_5{-}\underset{CH_3}{\overset{CH_3}{N^{\cdot +}}} + \cdot O{-}\overset{O}{\overset{\|}{C}}{-}C_6H_5 + {}^{-}O{-}\overset{O}{\overset{\|}{C}}{-}C_6H_5} \qquad (24)$$

Whereas the BPO–DMA redox system works well for curing of unsaturated polyester blends, it is not a very effective system for initiating vinyl monomer polymerizations, and therefore it generally is not used in such applications (83). However, combinations of amines (eg, DMA) and acyl sulfonyl peroxides (eg, ACSP) are very effective initiator systems at 0°C for high-conversion suspension polymerizations of vinyl chloride (84). BPO has also been used in combination with ferrous ammonium sulfate to initiate emulsion polymerizations of vinyl monomers via a redox reaction (85). Decompositions of BPO using other promoters have been reported, including organoaluminum compounds (86), chromium(II) acetate (87), nitroxyl radicals (88), tin(II) chloride with *o*-sulfonic benzoylimide (89), benzoyl thiourea [614-23-3] (90), and other reducing agents (91).

3.3. tert-Alkyl Peroxyesters. Table 4 lists several commercial *tert*-alkyl peroxyesters and their corresponding 10-h half-life temperatures (determined in dodecane and other solvents) (92). Only *tert*-alkyl peroxyesters are commercially available. As illustrated in Table 2, the peroxyester class offers the broadest range of temperature activity of any of the peroxide classes.

Peroxyesters undergo single- or multiple-bond scission to generate acyloxy and alkoxy radicals, or alkyl and alkoxy radicals and carbon dioxide:



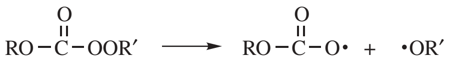
$$\begin{array}{ccc} R\overset{\overset{O}{\|}}{C}OOR' & \longrightarrow & R\overset{\overset{O}{\|}}{C}O\cdot + \cdot OR' \\ \downarrow & & \downarrow \\ \hookrightarrow & R\cdot + CO_2 + \cdot OR' & \longleftarrow \end{array} \qquad (25)$$

Acyloxy radicals can decarboxylate, as noted above for the diacyl peroxides. The alkoxy radicals (R′O·) can undergo the β-scission reaction leading to greater radical reaction selectivity. Variation of the R group or the R′ group provides a convenient means of altering the relative activity of peroxyesters. For example, increasing the steric bulk of either or both of R and R′ generally lowers the thermal stability of a peroxyester. Thermal stability decreases as follows: for $R, CH_3 > RCH_2 > R_2CH > R_3C$. For R′, $\mathit{tert} - \text{butyl} > \mathit{tert} - \text{amyl} > \mathit{tert} - \text{octyl} > \alpha - -\text{cumyl} > 3 - \text{hydroxy} - 1, 1 - \text{dimethylbutyl}$. By way of example, *tert*-butyl peroxyacetate [107-71-1] is more thermally stable than 3-hydroxy-1,1-dimethylbutyl peroxyneodecanoate [95718-78-8]. Although other factors affect thermal stability, the trends shown can be used to qualitatively predict peroxyester reactivity trends. The order of activity of the R′ group in peroxyesters is also observed in other *tert*-alkylperoxy-containing compounds. The mechanism of decomposition of *tert*-alkyl peroxypivalates has been studied by use of a nitroxyl compound to trap the radicals formed (93). The behavior of peroxyesters under pressure has been investigated (94–97).

Peroxyesters, particularly those with α-hydrogens or conjugated double bonds, are susceptible to induced decomposition under certain conditions, but they are generally less susceptible than diacyl peroxides. Lower molecular weight peroxyesters that have some water solubility can be hydrolyzed.

The more selective nature of the radicals produced by *tert*-amyl peroxyesters and other *tert*-amyl peroxides has led to their use in commercial polymer applications requiring discriminating radicals, such as polyol grafting and high solids acrylic resin production (99,100). *tert*-Amyl peroxides have been replacing aliphatic α-cyanoazo initiators in these applications. Owing to their diverse structures and associated reactivities, peroxyesters are also used in many other applications, including polymerization of ethylene, vinyl chloride, styrene and acrylate esters, and curing of unsaturated polyester resins.

3.4. Monoperoxycarbonates. Some commercially available *OO-tert*-alkyl *O*-alkyl monoperoxycarbonates and their corresponding 10-h half-life temperature (determined in dodecane) are listed in Table 2 (92). Monoperoxycarbonates are related to peroxyesters and also generate alkoxy radicals, ·OR′, which again as above can undergo β-scission.



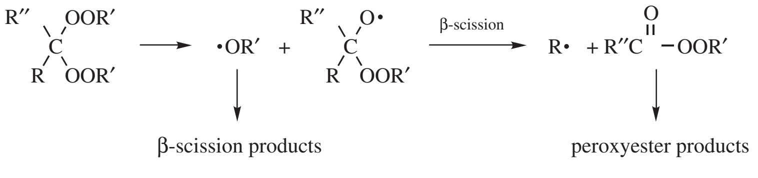
$$\mathrm{RO{-}\overset{O}{\overset{\|}{C}}{-}OOR'} \longrightarrow \mathrm{RO{-}\overset{O}{\overset{\|}{C}}{-}O\bullet} + \bullet\mathrm{OR'} \qquad (26)$$

Changing the structure of R′ affects the activity of monoperoxycarbonates as previously discussed for peroxyesters. The other cogenerated radical is an alkoxycarbonyloxy radical. The nature of the R group has practically no effect on the reactivity of monoperoxycarbonates having the same *OO-tert*-alkyl group. The 10-h half-life temperature remains at 100°C for almost all *OO-tert*-butyl *O*-alkyl monoperoxycarbonates.

Monoperoxycarbonates are similar in thermal stability to *t*-alkyl peroxybenzoates and can be used in application where there is concern that benzene will be formed as a byproduct of peroxybenzoate initiation. For example, *OO-tert*-butyl *O*-(2-ethylhexyl) monoperoxycarbonate [34443-12-4], with a 10-h half-life temperature of 99°C can be used in place of *tert*-butyl peroxybenzoate with a 10-h half-life temperature of 104°C for the polymerization of styrene with only slight changes in reaction conditions.

Recently, poly(monoperoxycarbonates) have been introduced for the commercial polymerization of vinyl monomers (101). They provide improved productivity in existing polymerization processes. Perhaps more interesting are possibilities of forming polymers with enhanced molecular weight and enhanced properties due to the formation of polyradical initiating species.

3.5. Diperoxyketals. Some commercially available di(*tert*-alkylperoxy)-ketals and their corresponding 10-h half-life temperatures (determined in dodecane) are listed in Table 5 (102). Diperoxyketals thermally decompose by cleavage of only one oxygen–oxygen bond initially, usually followed by β-scission of the resulting alkoxy radicals (103–106). For acyclic diperoxyketals, β-scission produces an alkyl radical and a peroxyester.



(27)

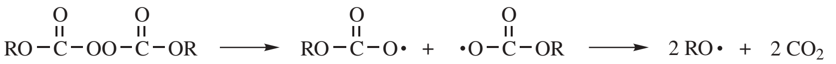
Owing to similarity of thermal stability, the peroxyester decomposes, as discussed previously. Cyclic diperoxyketals such as 1,1-di(*tert*-butylperoxy)cyclohexane cleave the cycloalkyl ring during β-scission to give an alkyl radical with an attached peroxyester group. The effect, after peroxyester decomposition, is the production of two monoradicals ($\cdot OR'$), a diradical ($\cdot R'{-}R\cdot$), and carbon dioxide. Because of the generation of diradicals, cyclic diperoxyketals such as 1,1-di(*tert*-butylperoxy)cyclohexane are effective in enhancing polymer molecular weight or increasing polymer productivity when employed as initiators in commercial vinyl monomer polymerizations (108,109). Diperoxyketals are used commercially in styrene polymerizations, curing of elastomers, and in elevated temperature curing of unsaturated polyester resin compositions. *tert*-Amyl diperoxyketals are good initiators for acrylics, especially in the preparation of high-solids coatings resins (110).

3.6. Di(tert-alkyl) Peroxides. Some commercially available dialkyl peroxides and their corresponding 10-h half-life temperatures in dodecane are listed in Table 6 (111). Dialkyl peroxides initially cleave at the oxygen–oxygen bond to generate alkoxy radical pairs:

$$R_3C{-}OO{-}CR_3 \longrightarrow 2R_3C{-}O\cdot \xrightarrow{\beta\text{–scission}} 2R\cdot + 2R_2C{=}O \qquad (28)$$

Because high temperatures are required to decompose dialkyl peroxides at useful rates, β-scission of the resulting alkoxy radicals is more rapid and more extensive than for most other peroxide types. When methyl radicals are produced from alkoxy radicals, the dialkyl peroxide precursors are very good initiators for cross-linking, grafting, and degradation reactions. When higher alkyl radicals such as ethyl radicals are produced, the dialkyl peroxides are useful in vinyl monomer polymerizations. The behavior of di(*tert*-butyl) peroxide [110-54-4] under high pressure has been investigated (112,113).

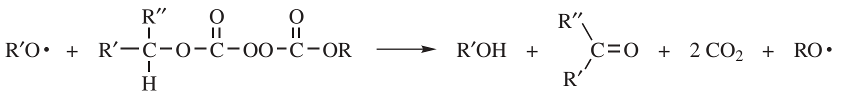
3.7. Dialkyl Peroxydicarbonates. Some commercially available dialkyl peroxydicarbonates and their corresponding 10-h half-life temperatures (determined in trichloroethylene solutions) are listed in Table 7 (114). These peroxides are active at low temperatures and initially undergo homolytic cleavage to produce alkoxycarbonyloxy radical pairs that may subsequently decarboxylate to produce alkoxy radicals:



$$RO{-}\overset{O}{\overset{\|}{C}}{-}OO{-}\overset{O}{\overset{\|}{C}}{-}OR \longrightarrow RO{-}\overset{O}{\overset{\|}{C}}{-}O\cdot + \cdot O{-}\overset{O}{\overset{\|}{C}}{-}OR \longrightarrow 2\,RO\cdot + 2\,CO_2 \qquad (29)$$

Table 7 shows that the nature of the alkyl group, whether primary alkyl, secondary alkyl, or cycloalkyl, does not affect the 10-h half-life temperatures of dialkyl peroxydicarbonates in trichloroethylene (TCE) [79-01-6]. All peroxydicarbonates have about the same 10-h half-life temperature in TCE (48–50°C).

As a peroxide class, dialkyl peroxydicarbonates are very susceptible to radical-induced decompositions:



$$R'O\cdot + R'{-}\underset{H}{\overset{R''}{C}}{-}O{-}\overset{O}{\overset{\|}{C}}{-}OO{-}\overset{O}{\overset{\|}{C}}{-}OR \longrightarrow R'OH + \begin{matrix} R'' \\ & C{=}O \\ R' \end{matrix} + 2\,CO_2 + RO\cdot \qquad (30)$$

Decomposition rate studies on dialkyl peroxydicarbonates in various solvents reveal dramatic solvent effects that primarily result from the susceptibility of peroxydicarbonates to induced decompositions. These studies show a decreasing order of stability of peroxydicarbonates in solvents as follows: TCE > saturated hydrocarbons > aromatic hydrocarbons > ketones (69). Decomposition rates are lowest in TCE where radicals are scavenged before they can induce the decomposition of peroxydicarbonate molecules.

Peroxydicarbonates are efficient polymerization initiators for most vinyl monomer polymerizations, especially for monomers such as acrylates, ethylene, and vinyl chloride. They are particularly good initiators for less reactive monomers such as those containing allyl groups. They are also effective for curing of unsaturated polyester molding resins. In order to increase the shipping and handling safety of peroxydicarbonates, stabilized formulations have been developed and commercialized (115–120).

3.8. tert-Alkyl Hydroperoxides. Some commercially available *tert*-alkyl hydroperoxides (121) are listed in Table 8. Hydroperoxides can decompose thermally to initially form alkoxy and hydroxy radicals:

$$\mathrm{ROOH} \longrightarrow \mathrm{RO\cdot} + \mathrm{\cdot OH} \tag{31}$$

However, because of the high-temperature nature of this class of peroxides (10-h half-life temperatures of 133–172°C) and their extreme sensitivities to radical-induced decompositions and transition-metal activation, hydroperoxides have very limited utility as thermal initiators. The acid-promoted decomposition to produce radicals has been reported (122). The oxygen-hydrogen bond in hydroperoxides is weak [368 – 377 kJ/mol (88.0–90.1 kcal/mol) BDE] and is susceptible to attack by higher-energy radicals:

$$\mathrm{ROOH} + \mathrm{R'\cdot} \longrightarrow \mathrm{R'{-}H} + \mathrm{ROO\cdot} \tag{32}$$

Further reactions of the alkylperoxy radical (ROO·) depend on the environment but generally cause generation of other radicals that can attack undecomposed hydroperoxide, thus perpetuating the induced decomposition chain. Radicals also can attack undecomposed peroxide by radical displacement on the oxygen–oxygen bond:

$$\mathrm{R'\cdot} + \mathrm{ROOH} \longrightarrow \mathrm{R'OH} + \mathrm{\cdot OH} \text{ or } \mathrm{R'OH} + \mathrm{RO\cdot} \tag{33}$$

This is basically the same type of induced decomposition that occurs with other peroxide classes, eg, the dialkyl peroxydicarbonates and diacyl peroxides.

Hydroperoxides are more widely used as initiators in low temperature applications (at or below room temperature) where transition-metal (M) salts are employed as activators. The activation reaction involves electron-transfer (redox) mechanisms:

$$\mathrm{ROOH} + \mathrm{M}^{+n} \longrightarrow \mathrm{RO\cdot} + \mathrm{OH}^- + \mathrm{M}^{+(n+1)} \tag{34}$$

$$\mathrm{ROOH} + \mathrm{M}^{+(n+1)} \longrightarrow \mathrm{ROO\cdot} + \mathrm{H}^+ + \mathrm{M}^{+n} \tag{35}$$

Either oxidation state of a transition metal (Fe, Mn, V, Cu, Co, etc) can activate decomposition of the hydroperoxide. Thus a small amount of transition-metal ion can decompose a large amount of hydroperoxide. Trace transition-metal contamination of hydroperoxides is known to cause violent decompositions. Because of this fact, transition-metal promoters should never be premixed with the hydroperoxide. Trace contamination of hydroperoxides (and ketone peroxides) with transition metals or their salts must be avoided.

Transition-metal ions also react with the generated radicals to convert the radicals to ions:

$$\mathrm{RO\cdot} + \mathrm{M}^{+n} \longrightarrow \mathrm{RO}^{-} + \mathrm{M}^{+(n+1)} \tag{36}$$

This reaction is one example of several possible radical transition-metal ion interactions. The significance of this and similar reactions is that radicals are destroyed and are no longer available for initiation of useful radical reactions. Consequently, the optimum use levels of transition metals are very low. Although the hydroperoxide decomposes quickly when excess transition metal is employed, the efficiency of radical generation is poor.

3.9. Ketone Peroxides. These materials are mixtures of compounds with hydroperoxy groups and are composed primarily of the two structures shown in Table 2. Ketone peroxides are marketed as solutions in inert solvents such as dimethyl phthalate. They are primarily employed in room-temperature-initiated curing of unsaturated polyester resin compositions (usually containing styrene monomer) using transition-metal promoters such as cobalt naphthenate. Ketone peroxides contain the hydroperoxy (−OOH) group and thus are susceptible to the same hazards as hydroperoxides. By far the most popular commercial ketone peroxide is methyl ethyl ketone peroxide [1338-23-4]. Smaller quantities of ketone peroxides such as methyl isobutyl ketone peroxide [28056-59-9], cyclohexanone peroxide [12262-58-7], and 2,4-pentanedione peroxide [37187-22-7] are used commercially (123).

The cyclic trimer ketone peroxides (eg, methyl ethyl ketone peroxide cyclic trimer [24748-23-0]) have been selectively prepared in dilute solution (in a safety solvent due to the shock sensitivity of the pure peroxside) for use as unpromoted, thermal initiators (124,125). They have been shown to effectively modify polyolefins under certain conditions in a manner similar to dialkyl peroxides.

Selection of organic peroxides for various commercial applications has been reviewed (55,126,127), particularly for vinyl chloride polymerizations (72). Recent innovations in peroxide technology include new promoted systems (128,129), peroxide-containing surfactants (130–133), and peroxides bonded to inorganic fillers (134).

4. Inorganic Peroxides

Inorganic peroxide–redox systems have been employed for initiating emulsion homo- and copolymerizations of vinyl monomers. These systems include hydrogen peroxide–ferrous sulfate, hydrogen peroxide–dodecyl mercaptan, potassium peroxydisulfate–sodium bisulfite, and potassium peroxydisulfate–dodecyl mercaptan (85,135). Potassium peroxydisulfate, $K_2S_2O_8$ [7727-21-2] (or the corresponding sodium or ammonium salt), is an inorganic peroxide that is used widely in emulsion polymerization (eg, latexes, rubbers, etc), usually in combination with a reducing agent. Without reducing agents, the peroxydisulfate ion decomposes to give sulfate ion radicals:

$$S_2O_8^{2-} \longrightarrow 2{\cdot}SO_4^- \qquad (37)$$

With transition-metal activators, the initiation process is postulated as:

$$S_2O_8^{2-} + Fe^{2+} \longrightarrow Fe^{3+} + {\cdot}SO_4^- + SO_4^{2-} \qquad (38)$$

The reaction with mercaptans is believed to generate initiating sulfur radicals:

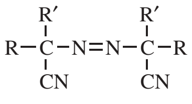
$$K_2S_2O_8 + 2\ RSH \longrightarrow 2\ KHSO_4 + 2\ RS{\cdot} \qquad (39)$$

Hydrogen peroxide, in combination with reducing agents (transition metals), also is used in those applications where its high water and low oil solubility is not a problem or is easily overcome.

4.1. Peroxide Safety. When handling and using peroxide initiators, care should be exercised since they are thermally sensitive and decompose (sometimes violently) when exposed to excessive temperatures, especially when they are in their pure or highly concentrated states. However, they are useful as initiators because of their thermal instability. What may be a safe temperature for one peroxide can be an unsafe temperature for another, since peroxide initiators encompass a wide activity range. Because some peroxides are shock or friction sensitive in the pure state, they are generally desensitized by formulating them into solutions, pastes, or powders with inert diluents and dispersions or emulsions with aqueous diluent. All manufacturers' literature should be carefully scrutinized and the peroxide safety literature should be reviewed before handling and using specific peroxide initiator compositions (71–78,92,102,111, 114,121,123,127,136–140).

5. Azo Compounds

Generally, the commercially available azo initiators are of the symmetrical azonitrile type:



$$R-\underset{\displaystyle CN}{\overset{\displaystyle R'}{C}}-N=N-\underset{\displaystyle CN}{\overset{\displaystyle R'}{C}}-R$$

The symmetrical azonitriles are solids with limited solubilities in common solvents (141,142). Some commercial aliphatic azo compounds and their 10-h half-life temperatures are listed in Table 9.

Azo initiators decompose thermally by cleavage of the two carbon–nitrogen bonds, either stepwise or simultaneously, to form two alkyl radicals and a nitrogen molecule:

$$R{-}N{=}N{-}R' \longrightarrow R\cdot + N_2 + \cdot R' \qquad (40)$$

In commercial azo initiators, *tert*-alkyl-type radicals are generated, which are generally more stable than most of the radicals generated from peroxide initiators. Thus when azonitriles are used as initiators for vinyl monomer polymerizations, the primary initiator radicals generally do not abstract hydrogens from polymer backbones as can sometimes occur when peroxide initiators are employed. Therefore branch grafting is suppressed and linear polymers having reduced long-chain branching are obtained.

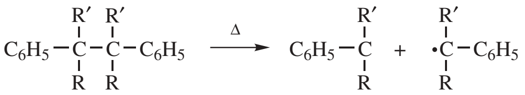
Azonitriles are not susceptible to radical-induced decompositions (142) and their decomposition rates are not usually affected by other components of the environment. Cage recombination of the alkyl radicals occurs when azo initiators are used, and results in the formation of toxic tetrasubstituted succinonitrile derivatives (142). This can be a significant drawback to the use of azo initiators. In contrast to some organic peroxides, azonitrile decomposition rates show only minor solvent effects (141,142) and are not affected by transition metals, acids, bases, and many other contaminants. Thus azonitrile decomposition rates are predictable. Azonitriles can be used as thermal initiators for curing resins that contain a variety of extraneous materials since cure rates are not affected. In addition to curing of resins, azonitriles are used for polymerization of commercial vinyl monomers.

tert-Amyl peroxides are viable commercial alternatives to azo initiators and can produce low-energy ethy radicals that are similar in initiating and hydrogen-abstracting properties to those produced by aliphatic azo compounds. *tert*-Amyl peroxides have been replacing aliphatic azo compounds in many commercial polymer applications, eg, production of high solids acrylic resins (99,100).

Care should be exercised in handling and using azo initiators in their pure and highly concentrated states because they are thermally sensitive and can decompose rapidly when overheated. Although azonitriles are generally less sensitive to contaminants, the same cautions that apply to peroxides also should be applied to handling and using azo initiators. The manufacturers' safety literature should be read carefully (141). The potential toxicity hazards of decomposition products must be considered when using azonitriles. Such hazards are present primarily when pure or highly concentrated azonitrile solutions are decomposed in poorly ventilated areas. The chemistry of aliphatic azo compounds has been reviewed (15,143–146).

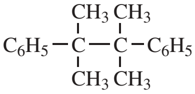
6. Carbon–Carbon Initiators

Carbon–carbon initiators are hexasubstituted ethanes that undergo carbon–carbon bond scission when heated to produce radicals. The thermal stabilities of the hexasubstituted ethanes decrease rapidly with increasing size of the alkyl groups (147). The 10-h half-life temperature range of this class of initiators is very broad, extending from about 100°C to well above 600°C. An extensive compilation of half-life data on carbon–carbon initiators has been published (147). The commercially available carbon–carbon initiators are tetrasubstituted 1,2-diphenylethanes that undergo homolyses to generate low-energy, *tert*-aralkyl radical pairs:



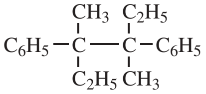
$$C_6H_5-\underset{R}{\overset{R'}{C}}-\underset{R}{\overset{R'}{C}}-C_6H_5 \xrightarrow{\Delta} C_6H_5-\underset{R}{\overset{R'}{C}} + \cdot\underset{R}{\overset{R'}{C}}-C_6H_5 \qquad (41)$$

Three carbon–carbon initiators are currently available commercially, 2,3-dimethyl-2,3-diphenylbutane [1889-67-4] (**1**), 3,4-dimethyl-3,4-diphenylhexane [10192-93-5] (**2**), and poly(1,4-diisopropylbenzene) [25822-43-9] (**3**).



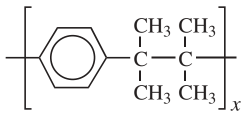
$$C_6H_5-\underset{CH_3}{\overset{CH_3}{C}}-\underset{CH_3}{\overset{CH_3}{C}}-C_6H_5$$

(**1**)



$$C_6H_5-\underset{C_2H_5}{\overset{CH_3}{C}}-\underset{CH_3}{\overset{C_2H_5}{C}}-C_6H_5$$

(**2**)



(**3**)

Initiators (**1**) and (**2**) have 10-h half-life temperatures of 237 and 201°C, respectively. It has been reported that, unlike organic peroxides and aliphatic azo compounds, carbon–carbon initiators (**1**) and (**2**) undergo endothermic decompositions (54). These carbon–carbon initiators are useful commercially as fire-retardant synergists in fire-resistant expandable polystyrenes (148). Accelerators for the thermal decomposition of diphenylethane initiators have been reported (149).

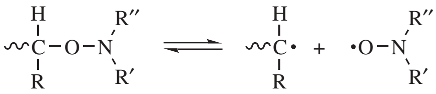
7. Initiators for Mediated Radical Reactions

Recently, there has been considerable interest in controlling the generation of free radicals in polymerization reactions both initially and throughout the course of the reaction (150). There are many reasons for this: controlling the polydispersity of the polymer formed ($M_n/M_w < 1.5$), control of polymer end groups, prevention of side reactions, preparation of block copolymers, chemical control of the reaction kinetics, design of new polymer architectures, and controlled graft modification of polyolefins (151,152).

Early work to control radical polymerization involved initiators that generated one radical capable of initiating a polymer-forming chain reaction and one radical that reversibly reacted with the propagating polymer radical. This reversible termination established an equilibrium between propagating and dormant polymer chains, and retarded irreversible termination reactions such as coupling and disproportionation. An initiator that provided mediated polymerization was called an *iniferter*, a combination of *ini*tiator, trans*fer* agent, and *ter*minator. Known photochemical iniferters are sulfides and disulfides (particularly thiuram disulfides, eg, tetraethylthiuram disulfide [97-77-8]). Thermal iniferters can be carbon–carbon initiators (eg, tetraphenylethanes, *vide supra*) and certain azo compounds (eg, phenylazotriphenylmethane [981-18-0]). Using iniferters, telomers, block copolymers, and other polymer architectures have been prepared using free-radical reactions (153,154).

More recently, refinements and new approaches for controlling radical polymerization have been described (155). Two of the most studied methods feature either stable counter-radicals, eg, nitroxy-mediated polymerization (NMP), or reversible activation of carbon–halogen bonds by transition metal species in a process called atom-transfer radical polymerization (ATRP).

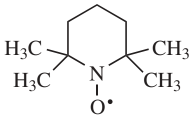
In NMP, the nitroxyl radicals, either alone or in the presence of additional modifiers, react reversibly with the propagating polymer radical to establish an equilibrium between active and dormant propagating radicals present in the system (156):



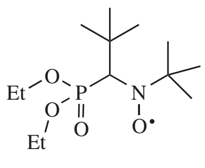
$$\sim\!\overset{\mathrm{H}}{\underset{\mathrm{R}}{\mathrm{C}}}-\mathrm{O}-\mathrm{N}\begin{smallmatrix}\mathrm{R}''\\ \mathrm{R}'\end{smallmatrix} \rightleftharpoons \sim\!\overset{\mathrm{H}}{\underset{\mathrm{R}}{\mathrm{C}}}\cdot + \cdot\mathrm{O}-\mathrm{N}\begin{smallmatrix}\mathrm{R}''\\ \mathrm{R}'\end{smallmatrix} \qquad (42)$$

New monomer units are thus added to the active radicals of the growing chain in a controlled manner, and when the monomer is completely consumed the usual termination reactions (coupling and disproportionation) are prevented by the presence of the nitroxyl, allowing the polymer chain to continue "living." Thus, in effect, each growing polymer chain becomes a polymerization initiator for continued reaction according to the equilibrium between dormant and active species, which is controlled by the structures of the polymer and nitroxyl radicals, the solvent and the temperature (157–164). The resulting product from nitroxyl-mediated polymerization of a single monomer can be used as a macroinitiator for copolymerizing one or more new monomers resulting in block copolymers or other designed molecular architectures.

NMP can be achieved in either of two ways: (a) by adding a stable nitroxyl radical to the polymerization reaction initiated by traditional initiators (peroxides or azo compounds) to generate an alkoxyamine *in situ*, or (b) by preparing an alkoxyamine to be used as the initiator. Two widely studies examples of stable nitroxyl radicals are 2,2,6,6-tetramethylpiperidinyl-1-oxyl (**4**, TEMPO) [2564-83-2] or 4-substituted derivatives thereof or *N*-*tert*-butyl-*N*-[1-(diethylphosphono)-2,2-dimethylpropyl]nitroxide (**5**) [188526-94-5] (165–172).



(**4**) (TEMPO)

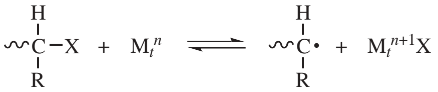


(**5**)

Many mono- and poly(*N*-alkoxyamines) have been synthesized and investigated in NMP reactions (161,173–185). Halogen-terminated polymers have been converted into alkoxyamine macroinitiators (186).

NMP has been studied mostly for polymerization of styrene and acrylates. It is limited in its application due to the equilibrium conditions, particularly high temperature, required to achieve a reasonable polymerization rate. A variation of this system does not use conventional free-radical initiators, using instead only the nitroxyl compound, an alkyl or aryl metal compound (such as an alkyl aluminum), and an appropriate strongly binding ligand (187). Nitroxyl-mediated polymerizations can be promoted by organic acids (188,189), organic salts (190), and acylating agents (191).

In ATRP, the growing polymer radical is deactivated to prevent termination reactions by reversible transfer of an atom or group (eg, halogen) between the propagating polymer radical and a transition metal compound, thus providing controlled, equilibrium concentrations of growing polymer chains and dormant chains:



$$\sim\!\overset{\displaystyle H}{\underset{\displaystyle R}{C}}-X + M_t^{n} \rightleftharpoons \sim\!\overset{\displaystyle H}{\underset{\displaystyle R}{C}}\cdot + M_t^{n+1}X \qquad (43)$$

In this equation M_t^n represents a transition metal of valence n and X represents a halogen atom. The most studied system of this type involves three components: an alkyl or aryl halide, a metal catalyst, and specific ligands (192–195), eg, 1-phenylethyl chloride [672-65-1], copper(I) chloride, and 2,2′-bipyridine [366-18-7]. In these systems, concentrations of propagating and dormant species must be carefully controlled for successful polymerization and narrow polydispersity to be achieved. The concept of “reverse” ATRP, involving conventional peroxide and azo initiators and the oxidized form of the metal catalyst [eg, copper(II) chloride] has also been reported (196). Like NMP, ATRP has been studied mostly for the polymerization of styrene and acrylic monomers, although other monomers have been polymerized successfully, eg, vinylidene difluoride (197). Other metal catalysts have been reported, such as bis(ortho-chelated) arylnicke(II) complexes (198) and porphyrin cobalt(III) organometallic complexes (199).

Various other approaches to mediated radical polymerization have been investigated. A living system has been reported wherein borinate radicals react reversibly with the growing chain and are generated by autoxidation of trialkylboranes through an alkylperoxyborane intermediate (200). Organochromium/macrocyclic polyamine systems and peroxide/trialkylphosphite systems (201) have also been investigated. Photochemical-mediated systems involving polymerization of acrylate monomer using alkyl cobaloximes as photoinitiators have been reported (202).

8. Other Radical Generating Systems

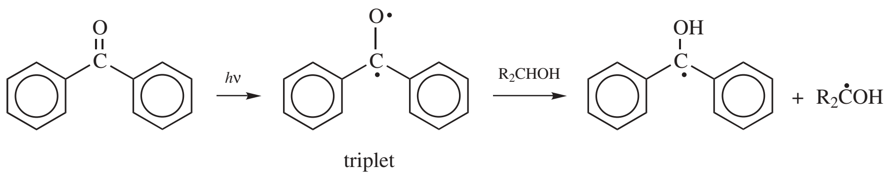
There are many chemical methods for generating radicals reported in the literature that involve unconventional initiators (91, 203–224). Most of these radical-generating systems cannot broadly compete with the use of conventional initiators in industrial polymer applications owing to cost or efficiency considerations. However, some systems may be well-suited for initiating specific radical reactions or polymerizations, eg, grafting of monomers to cellulose using ceric ion (225).

9. Initiation through Radiation and Photoinitiators

High-energy ionizing radiation sources (eg, x-rays, γ-rays, α-particles, β-particles, fast neutrons, and accelerator-generated electrons) can generate radical sites on organic substrates (226). If the substrate is a vinyl monomer, radical polymerization can occur (227). If the substrate consists of a polymer and a vinyl monomer, then polymer cross-linking, degradation, grafting of the monomer to the polymer, and polymerization of the monomer can all occur (228). Radical polymerizations of vinyl monomers with ionized plasma gases have been reviewed (229). Ultrasonic polymerization of vinyl monomers using special initiators (eg, dodecanethiol) has been described (230).

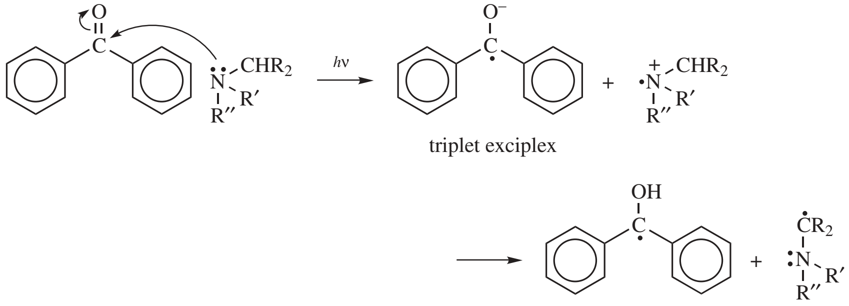
Initiation of radical reactions with uv radiation is widely used in industrial processes (231). In contrast to high-energy radiation processes where the energy of the radiation alone is sufficient to initiate reactions, initiation by uv irradiation usually requires the presence of a photoinitiator, ie, a chemical compound or compounds that generate initiating radicals when subjected to uv radiation. There are two types of photoinitiator systems: those that produce initiator radicals by intermolecular hydrogen abstraction and those that produce initiator radicals by photocleavage (232–239).

In the case of intermolecular hydrogen abstraction, a hydrogen (H) atom donor is required. Typical donors have an active H atom positioned alpha to an oxygen or nitrogen, eg, alcohols (R_2CHOH), ethers (R_2CHOR), and *tert*-amines (R_2CHNR_2), or an active H atom directly attached to sulfur, eg, thiols (RSH). Some of the commercial photoinitiators that undergo intermolecular H abstraction from the H atom donor upon excitation by uv radiation are listed in Table 10. A reaction illustrating this photoinitiation pr ocess is given below for benzophenone (photoinitiator) and an alcohol (H atom donor):



(44)

Upon exposure to uv light, ground-state benzophenone is excited to the triplet state (a diradical), which abstracts an alpha H atom from the alcohol, resulting in the formation of two separate initiating radicals. With amine H atom donors, an electron transfer may precede the H transfer, as in triplet exciplex formation between benzophenone and amine (eq. 46):



(45)

Some commercial photoinitiators (Table 11) undergo a photocleavage to form two initiating radical fragments directly, eg, benzoin ethers:

In many photoinitiated processes, a photosensitizer may be used. A photosensitizer absorbs light and subsequently transfers the absorbed energy to an energy acceptor, which then can produce initiator radicals by H abstraction or by photocleavage. The energy-transfer agent (photosensitizer) usually undergoes no net change. A variety of photosensitizers have been used such as eosin, chlorophyll, methylene blue, and thioxanthone. In photosensitized processes, the energy acceptor often is referred to as a co-initiator. These co-initiators do not absorb light but accept energy from the excited photosensitizer, which distinguishes them from the photoinitiators listed in Tables 10 and 11. Typical co-initiators that undergo H abstraction are the H donors mentioned above. An example of a co-initiator undergoing photocleavage is quinoline-8-sulfonyl chloride [18704-37-5] photosensitized by thioxanthone (233).

The peroxide and azo thermal initiators also are photochemically unstable and have been used as radical sources at well below their normal thermal decomposition temperatures. However, their industrial use as photoinitiators has been limited because their light-absorption characteristics frequently are unsuitable and because of the obvious potential complication owing to their slow thermal decomposition, which leads to poor shelf-life and nonreproducible photoactivity in given formulations (237).

10. Economic Aspects

The principal worldwide producers of organic peroxide initiators (trade names and available Internet addresses) are Atofina Chemicals Inc. (Lupersol, Luperox http://www.atofinachemicals.com); Akzo Nobel (Trigonox, Perkadox, Cadox, Cadet, Laurox, Liladox, Kenodox, Lucidol, Butanox, Cyclonox, http://www.polymerchemicals.com); Degussa-Hüls AG (formerly LaPorte companies), which includes Aztec Peroxides, Inc. (in the U.S.) (Aztec) and Peroxid-Chemie GmbH (in Europe) (Interox) (http://www.degussa.com, http://www.laporteplc.com); Crompton Corp. (formerly Witco Corp.) (Esperox, Esperal, USP, Quickset, Hi Point, http://www.witco.com); Nippon Oil & Fats Co. (Nyper, Perbutyl, Percumyl, Perhexa, Permek, Peroyl, http://www.nof.co.jp); The Norac Company, Inc. (Benox, Norox, http://www.norac.com); and Hercules Inc. (DiCup, VulCup, http://www.herc.com). Worldwide the three leading producers of organic peroxides are Akzo Nobel, Atofina Chemicals Inc., and Degussa-Hüls (formerly LaPorte). Sales volumes and value are difficult to estimate due to the many initiator formulations and dilutions that are available. Particularly for dialkyl peroxides, there are many small formulators and distributors that purchase a peroxide from a primary manufacturer and formulate it for a particular end-use application. Approximate U.S. sales of organic peroxide initiators in 2000 were $\sim 45 \times 10^6$ kg, valued at $\sim \$250 \times 10^6$; worldwide sales were $\sim 80 \times 10^6$ kg valued at $\sim \$500 \times 10^6$.

The principal worldwide producers of organic azo initiators (trade names, Internet address) are: DuPont (Vazo, http://www.dupont.com/vazo/), Atofina Chemical, Inc. (AZDN, http://www.atofinachemicals.com), and Wako Pure Chemical Industries, Ltd. (Wako, http://www.wako-chem.co.jp/egaiyo/). The worldwide market for organic azo initiators is small, being only about 10% of the market for organic peroxide initiators.

Ciba Speciality Chemicals, Inc. (Darocur, Irgacure, http://www.cibasc.com) and Sartomer (distributor of Lamberti s.p.a. Esacure$^{\mathrm{TM}}$ photoinitiators, http://www.sartomer.com, http://www.esacure.com) are significant suppliers of photoinitiators. Ciba Specialty Chemicals supplies alkoxyamines (Chimassorb). Nitroxyl radicals are available from Aldrich and Degussa-Hüls. Sales figures on photoinitiators are not readily available. The market for these initiators has been reviewed (240). Because most of the consumption of organic peroxides and azo initiators is in the developed countries, market growth in 2000 and beyond is expected to be modest, ie, 2–3% annually.

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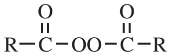
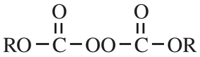
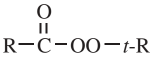
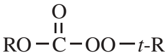
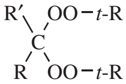
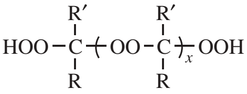
Table 1. **Bond Dissociation Energies**

Precursor	BDE, kJ/mol[a]
$(R)_3C—H$	381
$(R)_2$ CH—H	406
$RCH_2—H$	418
$CH_3—H$	439
RO—H	439
RCOO—H	444
$C_6H_5—H$	469
HO—H	498

[a] To convert kJ/mol to kcal/mol, divide by 4.184.

Table 2. **Commercial Organic Peroxide Classes**[a]

Organic peroxide class	Structure	10-h $t_{1/2}$[b,c], °C
Diacyl peroxides	 $R-\overset{O}{\overset{\Vert}{C}}-OO-\overset{O}{\overset{\Vert}{C}}-R$	21–75
Dialkyl peroxydicarbonates	 $RO-\overset{O}{\overset{\Vert}{C}}-OO-\overset{O}{\overset{\Vert}{C}}-OR$	49–51[d]
tert-Alkyl peroxyesters	 $R-\overset{O}{\overset{\Vert}{C}}-OO-t\text{-}R$	38–107
OO-*tert*-Alkyl *O*-alkyl monoperoxycarbonates	 $RO-\overset{O}{\overset{\Vert}{C}}-OO-t\text{-}R$	99–100
Di(*tert*-alkylperoxy)ketals	 $\begin{matrix} R' & & OO-t\text{-}R \\ & C & \\ R & & OO-t\text{-}R \end{matrix}$	92–110
Di-*tert*-alkyl peroxides	$t-R—OO—t-R$	115–128
tert-Alkyl hydroperoxides	$t-R—OO—H$	—[e]
Ketone peroxides[a,d]	 $HOO-\underset{R}{\overset{R'}{C}}\left(OO-\underset{R}{\overset{R'}{C}}\right)_x OOH$ + other structures	—[e]

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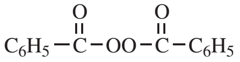
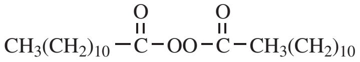
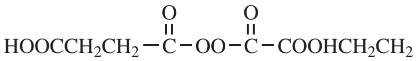
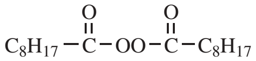
[a] $x = 0$ or 1.

[b] Temperature at which $t_{1/2} = 10$ h.

[c] In benzene, unless otherwise noted.

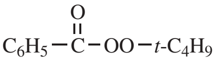
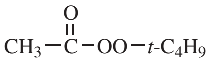
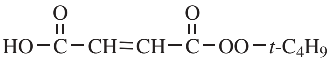
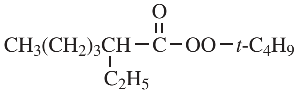
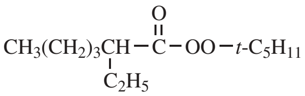
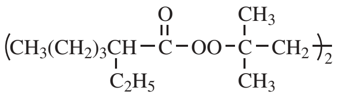
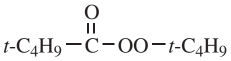
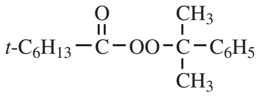
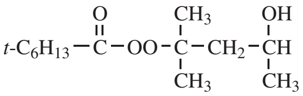
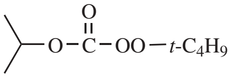
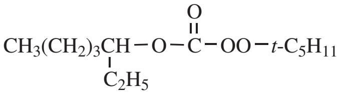
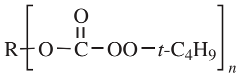
Table 3. **Commercial Diacyl Peroxides**

Name	CAS Registry number	Structure	10-h $t_{1/2}$, °C[a]	Solvent
Dibenzoyl peroxide	[94-36-0]	 $C_6H_5-\overset{\overset{O}{\parallel}}{C}-OO-\overset{\overset{O}{\parallel}}{C}-C_6H_5$	73	benzene
Dilauroyl peroxide	[105-74-8]	 $CH_3(CH_2)_{10}-\overset{\overset{O}{\parallel}}{C}-OO-\overset{\overset{O}{\parallel}}{C}-CH_3(CH_2)_{10}$	72 62	TCE[b] benzene
Succinic acid peroxide	[123-23-9]	 $HOOCCH_2CH_2-\overset{\overset{O}{\parallel}}{C}-OO-\overset{\overset{O}{\parallel}}{C}-COOHCH_2CH_2$	64 66	TCE acetone
Diisononanoyl peroxide	[58499-37-9]	 $C_8H_{17}-\overset{\overset{O}{\parallel}}{C}-OO-\overset{\overset{O}{\parallel}}{C}-C_8H_{17}$	61	TCE

[a] Temperature at which $t_{1/2} = 10$ h.

[b] TCE is trichloroethylene.

Table 4. **Commercial tert-Alkyl Peroxyesters**

Name	CAS Registry number	Structure	10-h $t_{1/2}$, °C[a,b]
tert-Butyl peroxybenzoate	[614-45-9]	 $C_6H_5-\overset{O}{\overset{\Vert}{C}}-OO-t\text{-}C_4H_9$	104
tert-Butyl peroxyacetate	[107-71-1]	 $CH_3-\overset{O}{\overset{\Vert}{C}}-OO-t\text{-}C_4H_9$	102
tert-Butyl peroxymaleate	[1931-62-0]	 $HO-\overset{O}{\overset{\Vert}{C}}-CH=CH-\overset{O}{\overset{\Vert}{C}}-OO-t\text{-}C_4H_9$	87[c]
tert-Butyl 2-ethylperoxyhexanoate	[3006-82-4]	 $CH_3(CH_2)_3\underset{C_2H_5}{\underset{\vert}{CH}}-\overset{O}{\overset{\Vert}{C}}-OO-t\text{-}C_4H_9$	77
tert-Amyl 2-ethylperoxyhexanoate	[686-31-7]	 $CH_3(CH_2)_3\underset{C_2H_5}{\underset{\vert}{CH}}-\overset{O}{\overset{\Vert}{C}}-OO-t\text{-}C_5H_{11}$	75
2,5-Di(2-ethylhexanoylperoxy) 2,5-dimethylhexane	[13052-09-0]	 $\left(CH_3(CH_2)_3\underset{C_2H_5}{\underset{\vert}{CH}}-\overset{O}{\overset{\Vert}{C}}-OO-\overset{CH_3}{\overset{\vert}{\underset{CH_3}{\underset{\vert}{C}}}}-CH_2\right)_2$	73
tert-Butyl peroxypivalate	[927-07-1]	 $t\text{-}C_4H_9-\overset{O}{\overset{\Vert}{C}}-OO-t\text{-}C_4H_9$	62
α-Cumyl peroxyneoheptanoate	[104852-44-0]	 $t\text{-}C_6H_{13}-\overset{O}{\overset{\Vert}{C}}-OO-\overset{CH_3}{\overset{\vert}{\underset{CH_3}{\underset{\vert}{C}}}}-C_6H_5$	43[d]
3-Hydroxy-1,1-dimethylbutyl peroxyneodecanoate	[95718-78-8]	 $t\text{-}C_6H_{13}-\overset{O}{\overset{\Vert}{C}}-OO-\overset{CH_3}{\overset{\vert}{\underset{CH_3}{\underset{\vert}{C}}}}-CH_2-\overset{OH}{\overset{\vert}{\underset{CH_3}{\underset{\vert}{CH}}}}$	37[d]
OO-tert-Butyl *O*-(isopropyl) monoperoxycarbonate	[2372-21-6]		100
OO-tert-Amyl *O*-(2-ethylhexyl) monoperoxycarbonate	[70833-40-8]	 $CH_3(CH_2)_3\underset{C_2H_5}{\underset{\vert}{CH}}-O-\overset{O}{\overset{\Vert}{C}}-OO-t\text{-}C_5H_{11}$	98
Polyether poly(*OO-tert*-butyl monoperoxycarbonate)	[confidential]	 $R\left[O-\overset{O}{\overset{\Vert}{C}}-OO-t\text{-}C_4H_9\right]_n$	100[e]

[a] Temperature at which $t_{1/2} = 10$ h.

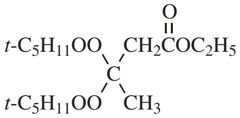
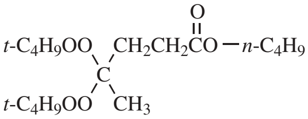
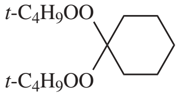
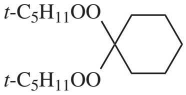
[b] In dodecane, unless otherwise noted.

[c] In acetone.

[d] In trichloroethylene (TCE).

[e] In ethylbenzene.

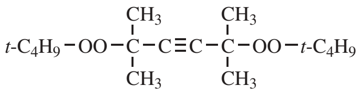
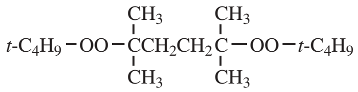
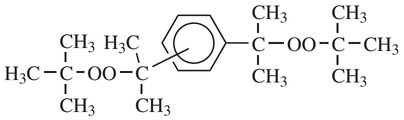
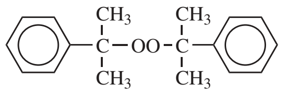
Table 5. **Commercial Diperoxyketals**

Name	CAS Registry number	Structure	10-h $t_{1/2}$, °C[a,b]
Ethyl 3,3-di (*tert*-amylperoxy) butyrate	[67567-23-1]		112
n-Butyl 4,4-di (*tert*-butylperoxy) valerate	[995-33-5]		109
1,1-Di (*tert*-butylperoxy) cyclohexane	[3006-86-8]		97
1,1-Di (*tert*-amylperoxy) cyclohexane	[15667-10-4]		93

[a] Temperature at which $t_{1/2} = 10$ h.

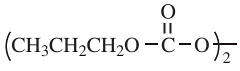
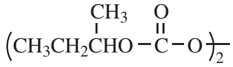
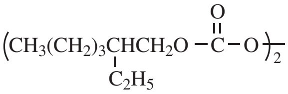
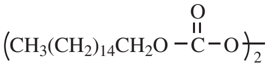
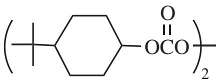
[b] In dodecane.

Table 6. **Commercial Dialkyl Peroxides**

Name	CAS Registry number	Structure	10-h $t_{1/2}$, °C[a,b]
2,5-Di (*tert*-butylperoxy)-2,5-dimethyl-3-hexyne	[1068-27-5]	 $t\text{-}C_4H_9-OO-\overset{CH_3}{\underset{CH_3}{C}}-C\equiv C-\overset{CH_3}{\underset{CH_3}{C}}-OO-t\text{-}C_4H_9$	131
2,5-Di(*tert*-butylperoxy)-2,5-dimethylhexane	[78-63-7]	 $t\text{-}C_4H_9-OO-\overset{CH_3}{\underset{CH_3}{C}}CH_2CH_2\overset{CH_3}{\underset{CH_3}{C}}-OO-t\text{-}C_4H_9$	120
1,3(4)-Bis (2-(*tert*-butylperoxy)-1-methylethyl) benzene	[25155-25-3]		119
Di(*tert*-butyl) peroxide	[110-54-4]	$t-C_4H_9—OO—t-C_4H_9$	129
Di(*tert*-amyl) peroxide	[10508-09-5]	$t-C_5H_{11}—OO—t-C_5H_{11}$	123
Dicumyl peroxide	[80-43-3]		117

[a] Temperature at which $t_{1/2} = 10$ h.
[b] In dodecane.

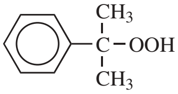
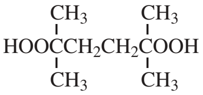
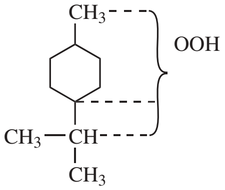
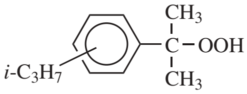
Table 7. **Commercial Dialkyl Peroxydicarbonates**

Name	CAS Registry number	Structure	10-h $t_{1/2}$, °C[a,b]
Di(*n*-propyl) peroxydicarbonate	[16066-38-9]	 $\left(CH_3CH_2CH_2O-\overset{\overset{O}{\|}}{C}-O\right)_2$	50
Di(*sec*-butyl) peroxydicarbonate	[19910-65-7]	 $\left(CH_3CH_2\overset{\overset{CH_3}{\vert}}{C}HO-\overset{\overset{O}{\|}}{C}-O\right)_2$	50
Di(2-ethylhexyl) peroxydicarbonate	[16111-62-9]	 $\left(CH_3(CH_2)_3\underset{\underset{C_2H_5}{\vert}}{C}HCH_2O-\overset{\overset{O}{\|}}{C}-O\right)_2$	49
Di(*n*-hexadecyl) peroxydicarbonate	[26322-14-5]	 $\left(CH_3(CH_2)_{14}CH_2O-\overset{\overset{O}{\|}}{C}-O\right)_2$	50
Di(4-*tert*-butylcyclohexyl) peroxydicarbonate	[15520-11-3]		48

[a] Temperature at which $t_{1/2} = 10$ h.

[b] In trichloroethylene (TCE).

Table 8. **Commercial *tert*-Alkyl Hydroperoxides**

Name	CAS Registry number	Structure
tert-Butyl hydroperoxide	[75-91-2]	$t{-}C_4H_9OOH$
tert-Amyl hydroperoxide	[3425-61-4]	$t{-}C_5H_{11}OOH$
α-Cumyl hydroperoxide	[80-15-9]	
2,5-Dihydroperoxy-2,5-dimethylhexane	[3025-88-5]	 $HOO\overset{CH_3}{\underset{CH_3}{C}}CH_2CH_2\overset{CH_3}{\underset{CH_3}{C}}OOH$
para-Menthane hydroperoxide[a]	[26762-92-5]	
m/*p*-Isopropyl-α-cumyl hydroperoxide	[98-49-7]	

[a] The -OOH group may be attached to any of the three positions indicated.

Table 9. **Commercial Azo Initiators**

Name	CAS Registry number	Structure	10-h $t_{1/2}$, °C[a]	Solvent
2,2′-Azobis[4-methoxy-2, 4-dimethylpentanenitrile]	[15545-97-8]		33	toluene
2,2′-Azobis[2,4-dimethylpentanenitrile]	[4419-11-8]		52	toluene
2,2′-Azobis[isobutyronitrile]	[78-67-1]		64	toluene
2,2′-Azobis[2-methylbutyronitrile]	[13472-08-7]		67	trimethylbenzene
1,1′-Azobis[cyclohexanecarbonitrile]	[2094-98-6]		88	toluene
4,4′-Azobis[4-cyanovaleric acid]	[2638-94-0]		66	water

Table 9 (*Continued*)

Name	CAS Registry number	Structure	10-h $t_{1/2}$, °C[a]	Solvent
Dimethyl 2,2′-azobis[2-methylpropionate]	[2589-57-3]		66	toluene
Azobis[2-acetoxy-2-propane]	[40888-97-9]		189	benzene
2,2′-Azobis[2-amidinopropane] dihydrochloride	[2997-92-4]		56	toluene

[a] Temperature at which $t_{1/2} = 10$ h.

Table 10. **Photoinitiators that Abstract Hydrogen**

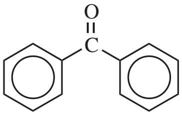
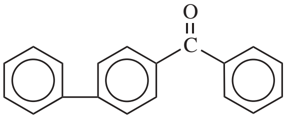
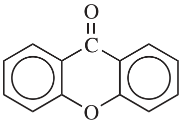
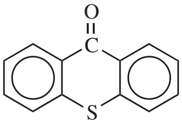
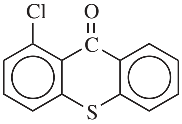
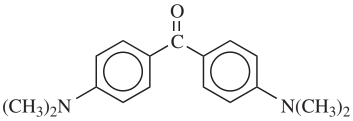
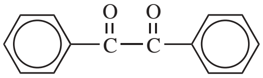
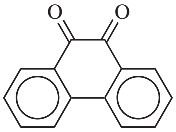
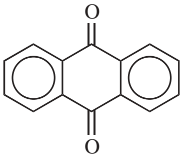
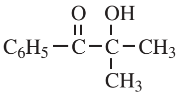
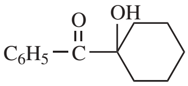
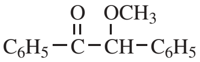
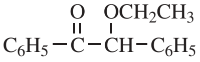
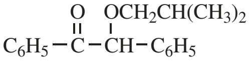
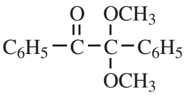
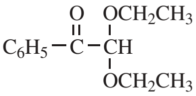
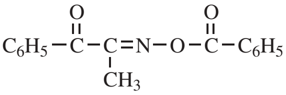
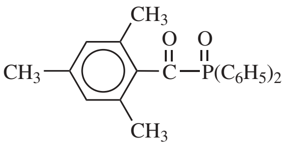
Name	CAS Registry number	Structure
Benzophenone	[119-61-9]	
4-Phenylbenzophenone	[2128-93-0]	
Xanthone	[90-47-1]	
Thioxanthone	[492-22-8]	
2-Chlorothioxanthone	[86-39-5]	
4,4′-Bis(*N*,*N*′-dimethylamino)-benzophenone (Michler's ketone)	[90-94-8]	
Benzil	[134-81-6]	
9,10-Phenanthraquinone	[84-11-7]	
9,10-Anthraquinone	[84-65-1]	

Table 11. **Photoinitiators That Undergo Photocleavage**

Name	CAS Registry number	Structure
α,α-Dimethyl-α-hydroxyacetophenone	[7473-98-5]	 $C_6H_5-\overset{O}{\overset{\|}{C}}-\underset{CH_3}{\overset{OH}{C}}-CH_3$
1-(1-Hydroxycyclohexyl)-phenylmethanone	[947-19-3]	
Benzoin methyl ether	[3524-62-7]	 $C_6H_5-\overset{O}{\overset{\|}{C}}-\overset{OCH_3}{CH}-C_6H_5$
Benzoin ethyl ether	[574-09-4]	 $C_6H_5-\overset{O}{\overset{\|}{C}}-\overset{OCH_2CH_3}{CH}-C_6H_5$
Benzoin isobutyl ether	[22499-12-3]	 $C_6H_5-\overset{O}{\overset{\|}{C}}-\overset{OCH_2CH(CH_3)_2}{CH}-C_6H_5$
α,α-Dimethoxy-α-phenylacetophenone	[24650-42-8]	 $C_6H_5-\overset{O}{\overset{\|}{C}}-\underset{OCH_3}{\overset{OCH_3}{C}}-C_6H_5$
α,α-Diethoxyacetophenone	[6175-45-7]	 $C_6H_5-\overset{O}{\overset{\|}{C}}-\underset{OCH_2CH_3}{\overset{OCH_2CH_3}{CH}}$
1-Phenyl-1,2-propanedione, 2-(*O*-benzoyl) oxime	[17292-57-8]	 $C_6H_5-\overset{O}{\overset{\|}{C}}-\underset{CH_3}{C}=N-O-\overset{O}{\overset{\|}{C}}-C_6H_5$
Diphenyl(2,4,6-trimethyl-benzoyl)phosphine	[75980-60-8]	
α-Dimethylamino-α-ethyl-α-benzyl-3,5-dimethyl-4-morpholinoacetophenone	[119313-12-1]