

ADDITION POLYMERIZATION

Prof.Dr.Salah Sh. Hashim

- 1-Free Radical Polymerisation
 - 2- Cationic Polymerisation
 - 3- Anionic polymerisation
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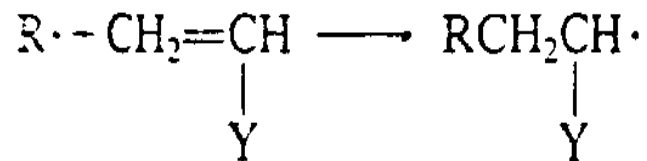
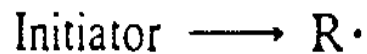
MONOMERS

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	-	+	+

FREE RADICAL POLYMERISATION

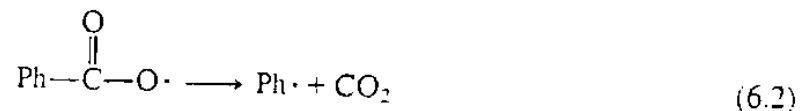
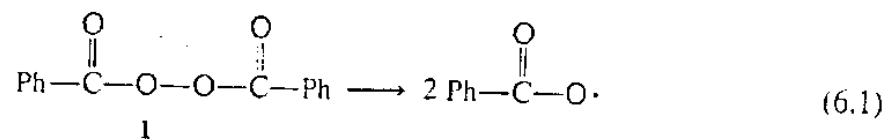
Step 1: Initiation

The first step in the chain polymerisation process ,initiation occurs when the free radical catalyst reacts with a double bonded carbon monomer

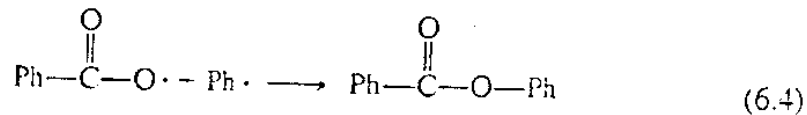
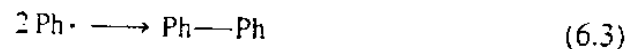


PEROXIDES

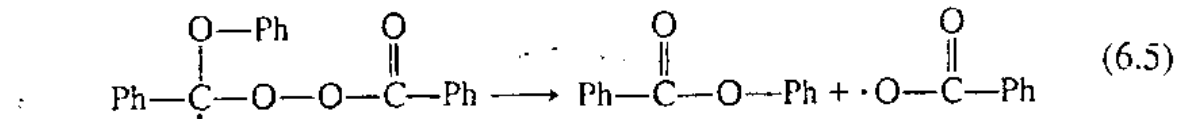
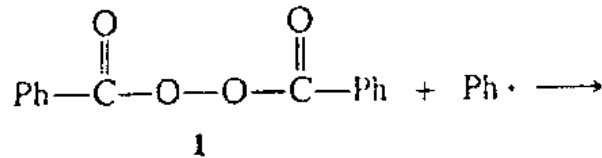
- Of the various types of initiators, peroxides (ROOR) and hydroperoxides (ROOH) are most widely used. They are thermally unstable and decompose into radicals at a temperature and rate dependent on structure. The most commonly used peroxide is benzoyl peroxide (1), which undergoes thermal homolysis to form benzoyloxy radicals (reaction 6.1).* The benzoyloxy radicals may undergo a variety of reactions besides adding to monomer, including recombination (reverse of 6.1), decomposition to phenyl radicals and carbon dioxide (6.2),



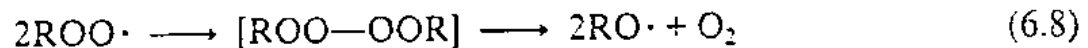
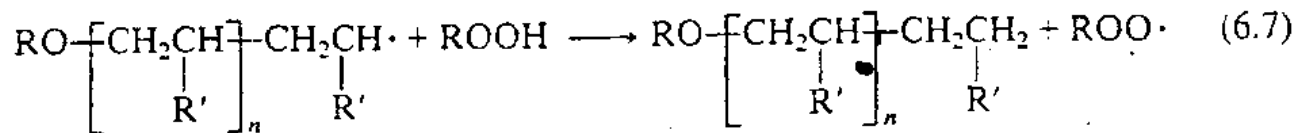
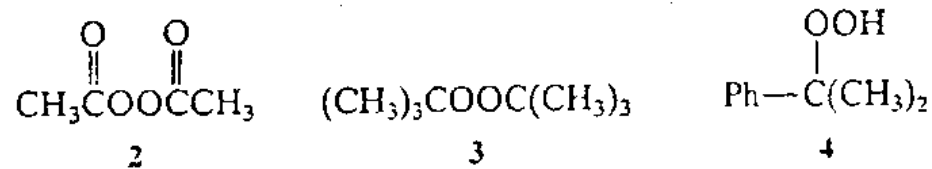
and radical combination (6.3 and 6.4). These secondary reactions occur because of the confining effect of solvent molecules (the *cage effect*), and as a result, the concentration of initiator radicals is depleted. Induced decomposition (6.5) is another "wastage" reaction.



*Ph = phenyl. For radical structures such as the benzoyloxy radical, only the unpaired electron is shown. A more complete representation would include lone pair electrons and contributing resonance structures.



Two other common initiators are diacetyl peroxide (2) and di-*t*-butyl peroxide (3). Hydroperoxides such as cumyl hydroperoxide (4) decompose to form alkoxy and hydroxy radicals (6.6). Because hydroperoxides contain an active hydrogen atom, induced decomposition occurs readily, for example, by a chain-end radical (6.7). Peroxy radicals may also combine with subsequent formation of oxygen (6.8).



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

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

or

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

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

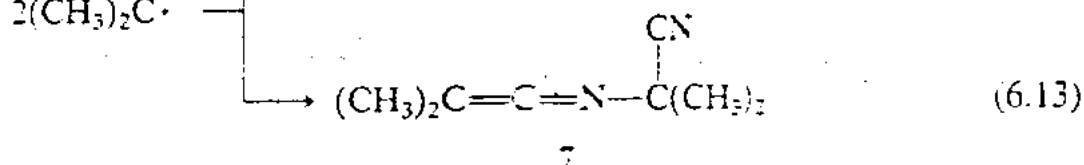
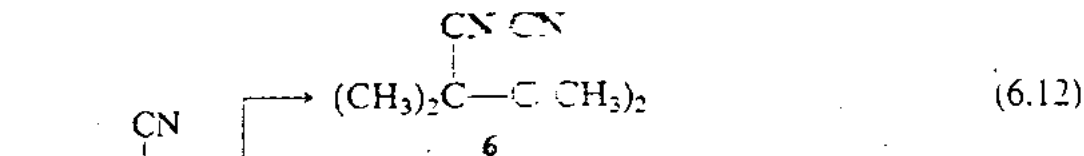
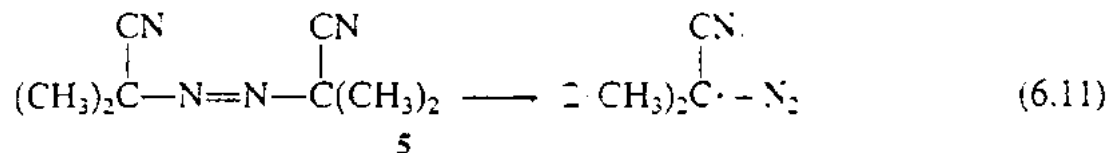
$$t_{1/2} = \frac{0.693}{k_d} \quad (3-29)$$

Type/Example	Formula	Temperature (°C) for 1/10 of 10h
<i>Diacetyl peroxides</i>		
Diacetyl peroxide		69
Dibenzoyl peroxide		72
<i>Dialkyl peroxides</i>		
Di-t-butyl peroxide		126
Di-cumyl peroxide		117
<i>Peroxyesters</i>		
t-Butyl peroxyacetate		102
t-Butyl peroxybenzoate		105
<i>Hydroperoxides</i>		
Cumyl hydroperoxide		158
<i>Peroxydicarbonates</i>		
Di-isopropyl peroxydicarbonates		46
<i>Ketone peroxides</i>		
Methyl ethyl ketone peroxides		105

AZO COMPOUNDS

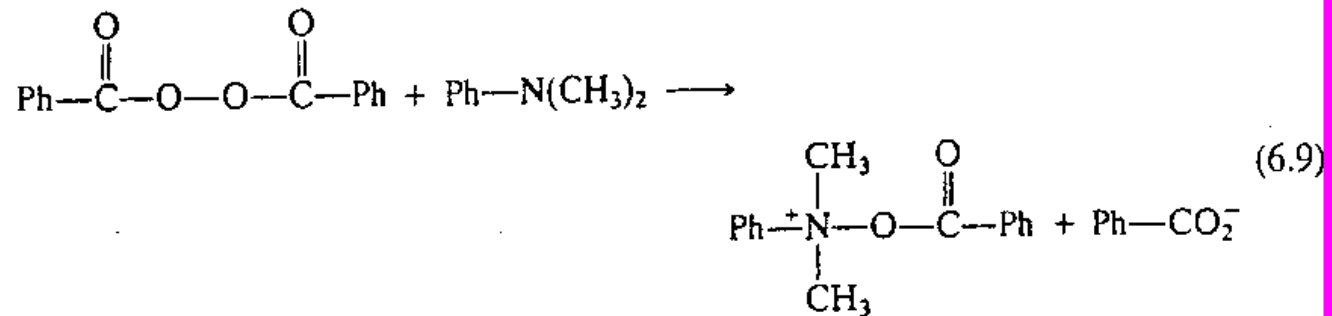
6.2.2 Azo Compounds

The most commonly used azo compounds are those having cyano groups on the carbons attached to the azo linkage—for example, α,α' -azobis(isobutyronitrile) (**5**), which decomposes at relatively low temperatures (half-life 1.3 hours at 50°C). The driving force for decomposition is formation of nitrogen and the resonance-stabilized cyanopropyl radical (6.11). As with peroxide decomposition, the initially formed radicals can combine in the solvent cage to deplete initiator concentration. Combination leads to both tetramethylsuccinonitrile (**6**) (6.12) and the ketenimine (**7**) (6.13).

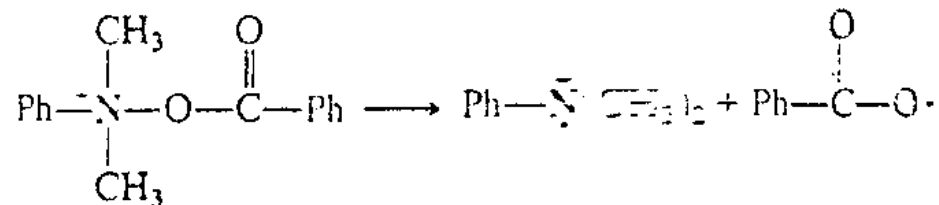


PROMOTERS

Decomposition of peroxides can frequently be induced at lower temperatures by the addition of *promoters*. For example, addition of N,N-dimethylaniline to benzoyl peroxide causes the latter to decompose rapidly at room temperature. Kinetics studies^{8,9} indicate that the decomposition involves formation of an unstable ionic intermediate (6.9) that reacts further to give benzoyloxy radical and a radical cation (6.10). The radical cation apparently undergoes reactions other than addition to monomer, since polymers formed by this method contain no nitrogen.



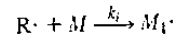
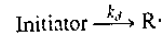
Free Radical Polymerization



KINETICS

Initiation proceeds in two steps: decomposition of initiator to yield initiator radicals, followed by addition of $R\cdot$ to monomer, M , to give a new radical, $M_1\cdot$.

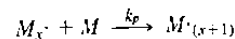
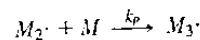
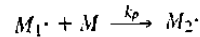
Initiation



Rate constants for the two reactions are k_d and k_i .

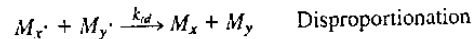
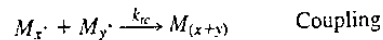
In the initial propagation step (rate constant k_p), $M_1\cdot$ adds to another monomer molecule to form a new radical, $M_2\cdot$, which, in turn, adds to M to form $M_3\cdot$, and so on.

Propagation



As was mentioned above, termination occurs principally by radical coupling or disproportionation, where k_{tc} and K_{td} are the respective rate constants.

Termination



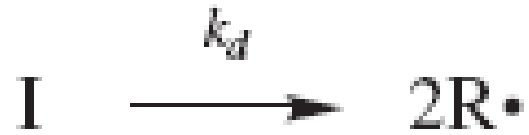
Assuming the rate of initiator decomposition is very slow relative to that of addition of initiator radical to monomer (reasonable, given the high reactivity of free radicals), and taking into account the fact that two initiator radicals are formed with each decomposition, the expression for initiation rate, R_i , is

$$R_i = \frac{-d[M\cdot]}{dt} = 2fk_d [I]$$

where $[M\cdot]$ is the total concentration of chain radicals, $[I]$ is the molar concentration of initiator, and f is the *initiator efficiency*, that is, the fraction of initiator radicals that actually start a polymer chain and are not consumed in the wastage reactions discussed in Section 6.2. Thus,

$$f = \frac{\text{radicals that initiate a polymer chain}}{\text{radicals formed from initiator}}$$

Efficiency is determined most conveniently by measuring the end groups arising from the addition of initiator radicals (by using isotopically labeled initiator, for example) and com-



$$R_i = 2fk_d[I]$$

$$R_p = k_p[M\cdot][M]$$

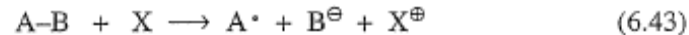
$$R_i = R_t = 2k_t[M\cdot]^2$$

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

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

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

REDOX INITIATORS

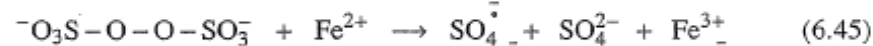


can occur with any molecule AB if the reducing agent X is sufficiently strong to split the A-B bond. For practical purposes, the A-B bond in redox systems must be relatively weak and this limits the choice of such materials. Some of the common redox systems are described below.

Water soluble peroxides and persulfates, in combination with a reducing agent such as ferrous (Fe^{2+}) and thiosulfate ($S_2O_3^{2-}$) ions, are a common source of radicals in aqueous and emulsion systems. An example of such a redox system has hydrogen peroxide as the oxidant and Fe^{2+} as the reductant:

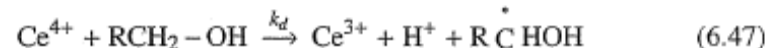


Another redox system commonly used consists of persulfate as the oxidant and Fe^{2+} or $S_2O_3^{2-}$ as the reductant (Rudin, 1982; Odian, 1991):



An equimolar mixture of $K_2S_2O_8$ and $FeSO_4$ at $10^\circ C$ produces radicals about 100 times as fast as an equal concentration of the persulfate alone at $50^\circ C$. Other redox systems with persulfate include reductants such as HSO_3^- and SO_3^{2-} .

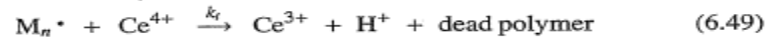
A combination of inorganic oxidant and organic reductant may initiate polymerization by oxidation of the organic component. For example, the oxidation of an alcohol by Ce^{4+} (Mohanty et al., 1980) proceeds according to the reaction



and the rate of initiation is

$$R_i = k_d [Ce^{4+}] [alcohol] \quad (6.48)$$

The termination of the propagating radicals in the alcohol- Ce^{4+} system proceeds according to the reaction (O dian, 1991):



at high ceric ion concentrations and the rate of termination (neglecting the usual bimolecular termination mechanism) is given by

$$R_t = k_t [Ce^{4+}] [M^\bullet] \quad (6.50)$$

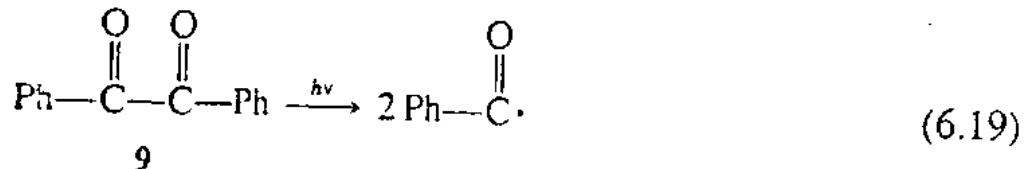
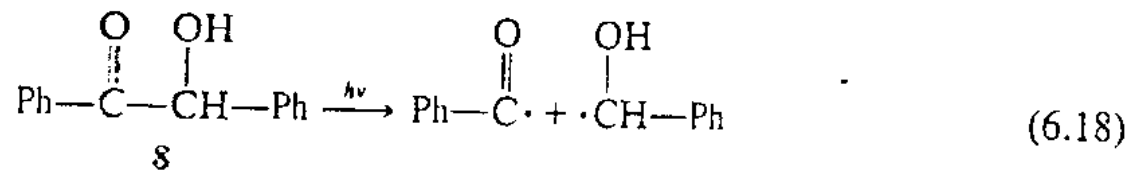
The usual steady-state assumption, $R_i = R_t$, then leads to the polymerization rate as

$$R_p = \left(\frac{k_p k_d}{k_t} \right) [M] [alcohol] \quad (6.51)$$

PHOTOINITIATORS

6.2.4 Photoinitiators

Peroxides and azo compounds dissociate photolytically as well as thermally. The major advantage of photoinitiation¹⁰ is that the reaction is essentially independent of temperature; thus polymerizations may be conducted even at very low temperatures. Furthermore, better control of the polymerization reaction is generally possible because narrow wavelength bands may be used to initiate decomposition, and the reaction can be stopped simply by removing the light source. A wide variety of photolabile compounds are available, including disulfides (6.17), benzoin (8) (6.18), and benzil (9) (6.19).



6.4.3.3 Rate of Photoinitiated Polymerization

In photochemistry, a mole of light quanta is called an *Einstein*. Thus an Einstein of light quanta of frequency ν or wavelength λ has energy $N_{AV}h\nu$ (or $N_{AV}hc/\lambda$), where N_{AV} is Avogadro's number, h is Planck's constant, and c is the speed of light. The rate of photochemical initiation may then be expressed (Ghosh, 1990) as

$$R_i = 2\Phi I_a \quad (6.61)$$

simply by replacing $k_d[I]$ of Eq. (6.11) with I_a , the intensity of absorbed light in moles (*Einsteins*) of light quanta per liter per second, and replacing f with Φ for photochemical polymerization. The factor of 2 in Eq. (6.61) is used only for those photoinitiating systems in which two radicals are produced per molecule undergoing photolysis [cf. Eqs. (6.55)-(6.59)]. Referred to as the *quantum yield for photoinitiation*, Φ may be defined as the ratio of the rate of chain initiation to the rate of light absorption; Φ is thus equivalent to f in thermal initiation [Eq. (6.11)], and both describe the fraction of radicals that are actually used in initiating chain polymerization. As in the case of f , the maximum value of Φ is 1. Substituting for R_i in Eq. (6.23) from Eq. (6.61) gives the expression for the rate of photopolymerization as

$$R_p = k_p [M] (\Phi I_a / k_t)^{1/2} \quad (6.62)$$

Methyl methacrylate is polymerized in 10% w/v solution using a photosensitizer and 3130 Å light from a mercury arc lamp. Direct measurement by actinometry shows that light is absorbed by the system at the rate of 1.2×10^5 ergs/L-s. If Φ for the system is 0.60, calculate (a) the rate of initiation and (b) the rate of polymerization. [$k_p/k_t^{1/2}$ at 60°C = $0.102 \text{ L}^{1/2} \text{ mol}^{-1/2} \text{ s}^{-1/2}$.]

Answer:

$$\begin{aligned} \text{Energy of 1 photon } (hc/\lambda) &= \frac{(6.63 \times 10^{-27} \text{ erg s})(3 \times 10^{10} \text{ cm s}^{-1})}{(3.13 \times 10^{-5} \text{ cm})} \\ &= 6.35 \times 10^{-12} \text{ erg} \end{aligned}$$

Energy of 1 mol of light quanta

$$\begin{aligned} &= (6.02 \times 10^{23} \text{ quanta mol}^{-1})(6.35 \times 10^{-12} \text{ erg quantum}^{-1}) \\ &= 3.82 \times 10^{12} \text{ ergs mol}^{-1} \end{aligned}$$

$$I_a = (1.2 \times 10^5 \text{ ergs L}^{-1} \text{ s}^{-1}) / (3.82 \times 10^{12} \text{ ergs mol}^{-1}) = 3.14 \times 10^{-8} \text{ mol L}^{-1} \text{ s}^{-1}$$

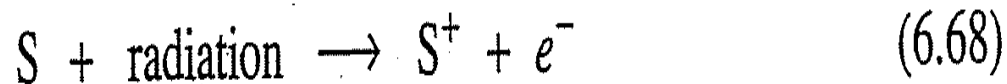
$$[M] = (100 \text{ g L}^{-1}) / (100 \text{ g mol}^{-1}) = 1.0 \text{ mol L}^{-1}$$

$$(a) R_i = 2\Phi I_a = 2 \times 0.6(3.14 \times 10^{-8} \text{ mol L}^{-1} \text{ s}^{-1}) = 3.77 \times 10^{-8} \text{ mol L}^{-1} \text{ s}^{-1}$$

$$\begin{aligned} (b) R_p &= \left(k_p/k_t^{1/2}\right) [M] (R_i/2)^{1/2} \\ &= (0.102 \text{ L}^{1/2} \text{ mol}^{-1/2} \text{ s}^{-1/2})(1.0 \text{ mol L}^{-1})(3.77 \times 10^{-8} \text{ mol L}^{-1} \text{ s}^{-1})^{1/2} / \sqrt{2} \\ &= 1.40 \times 10^{-5} \text{ mol L}^{-1} \text{ s}^{-1} \end{aligned}$$

Initiation by High-Energy Radiations

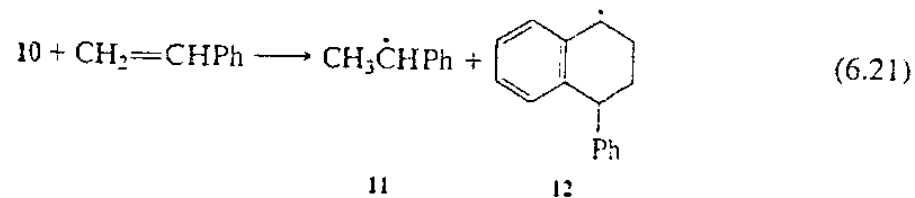
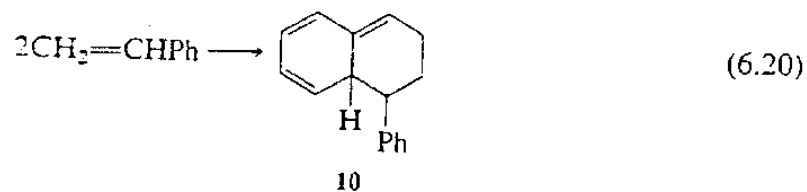
Alpha particles, beta rays (electrons), gamma rays, or high-velocity particles from a particle accelerator have particle or photon energies in the range 10 keV–100 meV, which are much higher than the range of energies (2–6 eV) of visible-ultraviolet photons used in photo-initiated free-radical polymerizations. So practically any monomer that polymerizes by a free-radical mechanism can also be polymerized by these radiations. However, as a consequence of the higher energies of these radiations, the substrate species S, on excitation, may also suffer ionization by ejection of electrons:



THERMAL POLYMERISATION

6.2.5 Thermal Polymerization

Some monomers polymerize slowly on heating in the absence of added initiator.¹¹ In such cases, free radical initiating species are generated in situ by mechanisms that are not, in most cases, well understood. Of the commercially important vinyl monomers, styrene undergoes thermal polymerization most rapidly. The mechanism¹²⁻¹⁴ appears to involve initial formation of a Diels-Alder dimer (**10**) (6.20), which transfers a hydrogen atom to monomer (6.21) to yield an initiator styryl radical (**11**) and a benzylic radical (**12**). This is an example of what is referred to as *molecule-induced homolysis*—the rapid formation of radicals by reaction of nonradical species. Photopolymerization of styrene with no added initiator appears to follow a similar pathway.¹⁵



Apart from some limited applications with styrene, thermal polymerization has been used commercially only with certain polymers or oligomers containing thermally labile end groups (see Chapter 4, Table 4.4).

The higher than second-order rate observed for thermal conversion of monomer indicates that Eq. (6.74) is the slow step. Representing the concentration of Diels-Alder dimer (II) by [D] and that of styrene by [M],

$$R_i = k_i [D][M] = k_i K [M]^3$$

where K is the equilibrium constant for the reaction of Diels-Alder dimer formation [Eq. (6.74)] and k_i is the rate constant for the initiation reaction [Eq. (6.75)].

Using steady-state approximation ($R_i = R_t$),

$$k_t [M^\bullet]^2 = k_i K [M]^3 \Rightarrow [M^\bullet] = \left(\frac{k_i K}{k_t} \right)^{1/2} [M]^{3/2}$$

Substituting this into Eq. (6.22) gives

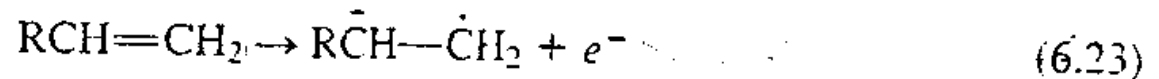
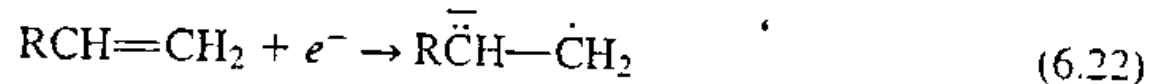
$$R_p = k_p [M]^{5/2} \left(\frac{k_i K}{k_t} \right)^{1/2}$$

showing five-halves order in monomer concentration.

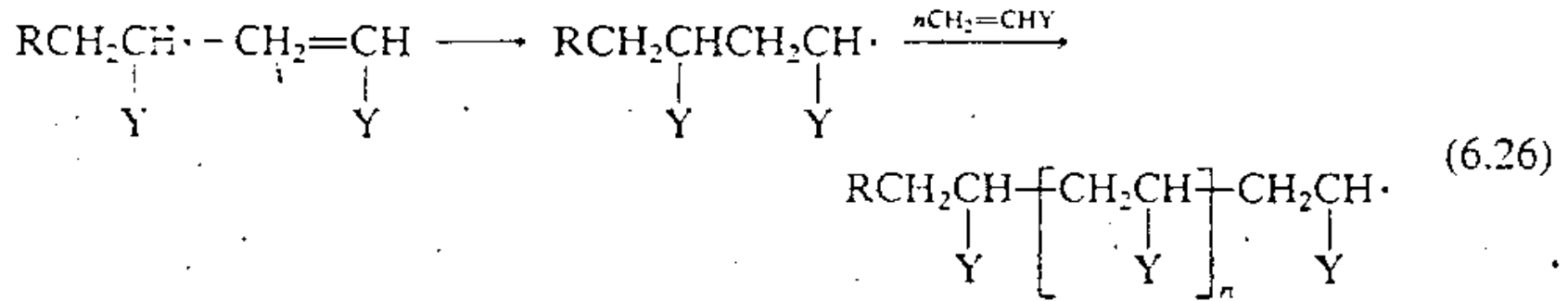
ELECTROCHEMICAL POLYMERISATION

6.2.6 Electrochemical Polymerization

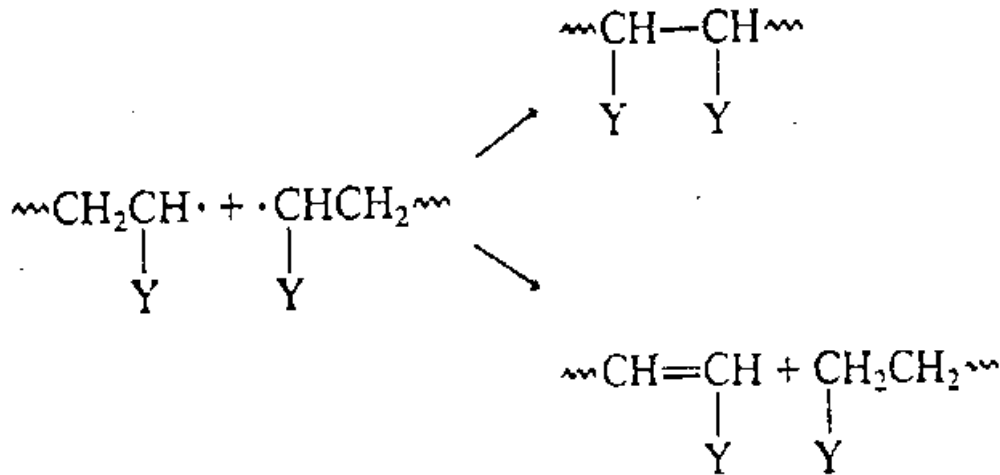
Electrolysis of a solution containing both monomer and electrolyte can be used to initiate polymerization.¹⁶ At the cathode an electron may be transferred to a monomer molecule to form a radical anion (6.22), and at the anode a monomer molecule may give up an electron to form a radical cation (6.23). The radical ions in turn initiate free radical or ionic polymerization or both, depending on electrolysis conditions. Other species present in solution may also undergo electron transfer to generate species that can initiate polymerization. Electrochemical polymerization is particularly useful for coating metal surfaces with polymer films.



STEP2: PROPAGATION



STEP3: TERMINATION



Another possible termination reaction involves combination of initiator radicals with chain end radicals (6.31). Called *primary radical termination*, this process is significant only at relatively high initiator levels or when very high viscosities limit the diffusion of high-molecular-weight chain end radicals.

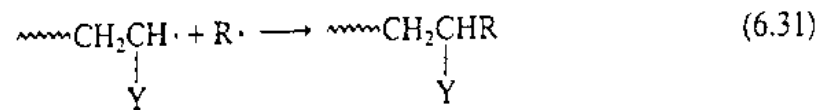


TABLE 6.8. Representative Ceiling Temperatures, T_c , of Pure Liquid Monomers^a

<i>Monomer</i>	T_c (°C)
1,3-Butadiene	585
Ethylene	610
Isobutylene	175
Isoprene	466
Methyl methacrylate	198
α -Methylstyrene	66
Styrene	395
Tetrafluoroethylene	1100

^aData from Allcock and Lampe.⁴⁶