Overall Extent of Polymerization

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

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

$$[\text{I}] = [\text{I}]_0 \, e^{-k_d t}$$

$$-\frac{d[\text{M}]}{[\text{M}]} = \left(\frac{k_p}{k_t^{1/2}} \right) (f k_d [\text{I}]_0)^{1/2} \left(e^{-k_d} \right) dt$$

Integration between $[\text{M}]_0$ at $t = 0$ and $[\text{M}]$ at t gives

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

Since the extent of monomer conversion, p, is usually defined as

$$p = \frac{[\text{M}]_0 - [\text{M}]}{[\text{M}]_0} \quad \text{or} \quad (1 - p) = [\text{M}]/[\text{M}]_0$$

The decomposition of benzoyl peroxide is characterized by a half-life of 7.3 h at 70°C and an activation energy of 29.7 kcal/mol. What concentration (mol/L) of this peroxide is needed to convert 50% of the original charge of a vinyl monomer to polymer in 6 hours at 60°C? (Data: $f = 0.4$; $k_p^2/k_t = 1.04\times10^{-2}$ L/mol-s at 60°C.)

Answer:

From Eq. (6.27) at 70°C, $k_d = \dfrac{\ln 2}{t_{1/2}} = \dfrac{\ln 2}{(7.3\times 3600 \text{ s})} = 2.638\times 10^{-5} \text{ s}^{-1}$

Using Arrhenius-type relationship, $k_d = A_d e^{-E_d/RT}$ at 60°C and 70°C:

$$\ln\left[\frac{(k_d)_{60°}}{(2.638\times 10^{-5} \text{ s}^{-1})}\right] = \frac{-E_d}{R}\left(\frac{1}{333} - \frac{1}{343}\right)$$

From the given value of E_d, $E_d/R = (29.7\times 10^3 \text{ cal mol}^{-1})/(1.987 \text{ cal mol}^{-1}\,°K^{-1}) = 1.495\times 10^4 \,°K$.

Substituting the value of E_d/R in Eq. (P6.2.1), $(k_d)_{60°} = 7.128\times 10^{-6} \text{ s}^{-1}$.

Using Eq. (6.31) for 50% conversion at 60°C,

$$- \ln 0.5 = \frac{2(1.04\times 10^{-2} \text{ L mol}^{-1}\text{s}^{-1})^{1/2}}{(7.128\times 10^{-6} \text{ s}^{-1})^{1/2}} (0.4\,[I]_0)^{1/2} \times$$
$$\left[1 - e^{-(7.128\times 10^{-6} \text{ s}^{-1})(6\times 3600 \text{ s})/2}\right]$$

Solving, $[I]_0 = 3.75\times 10^{-2} \text{ mol L}^{-1}$.

$$\nu = \frac{R_p}{R_i} = \frac{R_p}{R_t}$$

$$R_p = k_p[\text{M·}][\text{M}]$$

$$R_t = 2k_t[\text{M·}]^2$$

$$\nu = \frac{k_p[\text{M}]}{2k_t[\text{M·}]}$$

$$\nu = \frac{k_p[\text{M}]}{2(fk_d k_t[\text{I}])^{1/2}}$$

The *number-average degree of polymerization* $\overline{X}_n$, defined as the average number of mono-mer molecules contained in a polymer molecule, is related to the kinetic chain length. If the propagating radicals terminate by coupling (Eq. 3-16a), a dead polymer molecule is composed of two kinetic chain lengths and

$$\overline{X}_n = 2\nu \tag{3-99a}$$

For termination by disproportionation (Eq. 3-16b) the kinetic chain length is synonymous with the number-average degree of polymerization

$$\overline{X}_n = \nu \tag{3-99b}$$

The number-average molecular weight of a polymer is given by

$$\overline{M}_n = M_o\overline{X}_n \tag{3-100}$$

where M_o is the molecular weight of the monomer.

Average Lifetime of Kinetic Chains

The average lifetime (τ) of the kinetic chain is given by the ratio of the steady-state radical concentration to the steady-state rate of radical disappearance:

$$\tau = \frac{\nu}{k_p\,[\text{M}]}$$

$$\tau = \overline{DP}_n / k_p\,[\text{M}]$$

For termination by disproportionation

$$\tau = \overline{DP}_n / 2k_p\,[\text{M}]$$

and for termination by coupling or combination

In an experiment, styrene polymerization in bulk at 60°C is initiated by 1×10^{-3} M benzoyl peroxide. The density of liquid styrene is 0.909 g/cm³ at the reaction temperature. What is the average radical lifetime and what is the steady-state radical concentration? [Data at 60°C: k_t (styrene) $= 6.0 \times 10^7$ L mol^{-1} s^{-1}; k_d (benzoyl peroxide) $= 7.1 \times 10^{-6}$ s^{-1}; $f = 0.5$.]

Answer:

$$1/\tau = 2(f k_d k_t [I])^{1/2}.$$

$$= 2\left[(0.5)(7.1 \times 10^{-6} \text{ s}^{-1})(6.0 \times 10^7 \text{ L mol}^{-1} \text{ s}^{-1})(1 \times 10^{-3} \text{ mol L}^{-1})\right]^{1/2}$$

$$= 0.923 \text{ s}^{-1} \implies \tau = 1.1 \text{ s}$$

$$[M\cdot] = \left(\frac{f k_d [I]}{k_t}\right)^{1/2} = \left[\frac{(0.5)(7.1 \times 10^{-6} \text{ s}^{-1})(1 \times 10^{-3} \text{ mol L}^{-1})}{(6.0 \times 10^7 \text{ L mol}^{-1} \text{ s}^{-1})}\right]^{1/2}$$

$$= 7.7 \times 10^{-9} \text{ mol L}^{-1}$$

Chain Transfer

It is often observed that the measured molecular weight of a polymer product made by free-radical chain polymerization is lower than the molecular weights predicted from Eq. (6.102) for termination by either coupling [Eq. (6.103)] or disproportionation [Eq. (6.104)]. Such an effect, when the mode of termination is known to be disproportionation, can be due to a growing polymer chain terminating prematurely by transfer of its radical center to other species, present in the reaction mixture. These are referred to as *chain transfer reactions* and may be generally written as

$$M_n{}^\bullet + TA \xrightarrow{k_{tr}} M_nA + T^\bullet \tag{6.111}$$
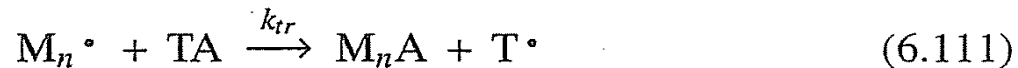
where the chain transfer agent TA may be monomer, initiator, solvent, polymer, or any other substance present in the reaction mixture, and A is the atom or species transferred; k_{tr} is the chain transfer rate constant.

The new radical $T^\bullet$, which results from chain transfer, can reinitiate polymerization by the reaction

$$T^\bullet + M \xrightarrow{k_r} TM^\bullet \text{ (or } M_1{}^\bullet) \tag{6.112}$$
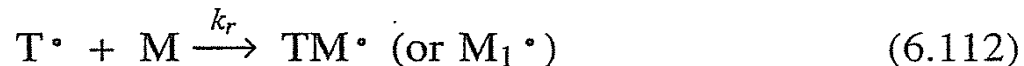
where k_r is the rate constant for addition of monomer to $T^\bullet$, leading to chain reinitiation by the process,

$$T^\bullet + M \xrightarrow{k_r} M_1{}^\bullet \xrightarrow{k_p} M_2{}^\bullet \xrightarrow{k_p} \cdots \xrightarrow{k_p} M_n{}^\bullet \tag{6.113}$$
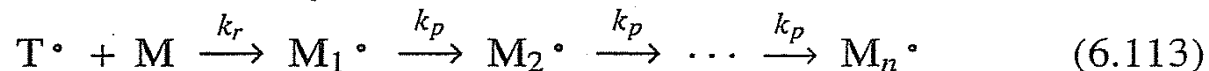
where k_p is the normal propagation rate constant.

While chain transfer to monomer is negligible for most monomers, it may, however, be significant for some monomers, such as vinyl acetate, vinyl chloride, and α-methyl substituted vinyl monomers, e.g., propylene and methyl methacrylate (MMA). For MMA the chain transfer proceeds by the reaction :

$$\text{wwwCH}_2\text{-}\underset{\underset{\text{COOCH}_3}{|}}{\overset{\overset{\text{CH}_3}{|}}{C}}\text{•} \ + \ \text{H}_2\text{C}\text{=}\underset{\underset{\text{COOCH}_3}{|}}{\overset{\overset{\text{CH}_3}{|}}{C}} \ \xrightarrow{k_{tr,\,M}} \ \text{wwwCH}_2\text{-}\underset{\underset{\text{COOCH}_3}{|}}{\overset{\overset{\text{CH}_3}{|}}{CH}} \ + \ \text{H}_2\text{C}\text{=}\underset{\underset{\text{COOCH}_3}{|}}{\overset{\overset{\overset{\bullet}{\text{CH}_2}}{|}}{C}} \qquad (6.114)$$
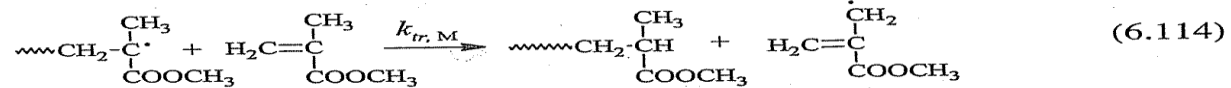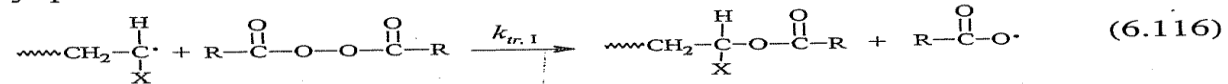
where $k_{tr,M}$ is the rate constant for chain transfer to monomer. In general, the rate of transfer to monomer is given by

$$R_{tr,M} \ = \ k_{tr,M}\,[\text{M}]\,[\text{M}^{\bullet}] \qquad (6.115)$$

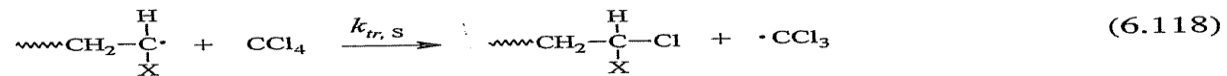where $[\text{M}^{\bullet}]$ represents growing chain radicals of all sizes.

Many peroxide initiators have significant chain transfer reactions. Dialkyl and diacyl peroxides undergo chain transfer due to breakage of the O—O bond, e.g.,

$$\text{wwwCH}_2\text{-}\underset{\underset{X}{|}}{\overset{\overset{H}{|}}{C}}\text{•} + \text{R}\text{—}\overset{\overset{O}{\|}}{C}\text{—O—O—}\overset{\overset{O}{\|}}{C}\text{—R} \ \xrightarrow{k_{tr,\,I}} \ \text{wwwCH}_2\text{—}\underset{\underset{X}{|}}{\overset{\overset{H}{|}}{C}}\text{—O—}\overset{\overset{O}{\|}}{C}\text{—R} \ + \ \text{R—}\overset{\overset{O}{\|}}{C}\text{—O•} \qquad (6.116)$$

where $k_{tr,I}$ is the rate constant for chain transfer to initiator. Usually the strongest transfer agents among the initiators are the hydroperoxides. In general, the rate of chain transfer to initiator is given by

$$R_{tr,I} \ = \ k_{tr,I}\,[\text{I}]\,[\text{M}^{\bullet}] \qquad (6.117)$$

In some polymerizations, the solvent itself may act as the chain transfer agent. For example, during vinyl polymerization in solvent CCl_4 chain transfer takes place by the reaction

$$\text{wwwCH}_2\text{—}\underset{\underset{X}{|}}{\overset{\overset{H}{|}}{C}}\text{•} \ + \ \text{CCl}_4 \ \xrightarrow{k_{tr,\,S}} \ \text{wwwCH}_2\text{—}\underset{\underset{X}{|}}{\overset{\overset{H}{|}}{C}}\text{—Cl} \ + \ \text{•CCl}_3 \qquad (6.118)$$

where $k_{tr,S}$ is the rate constant for chain transfer to solvent. However, in industrial free-radical polymerizations the use of solvent is usually avoided for economic reasons, while some ingredients may be deliberately added as chain transfer agents to limit the molecular weight of the polymer. In general, the rate of chain transfer to solvents and/or added chain transfer agents is given by

$$R_{tr,S} \ = \ k_{tr,S}\,[\text{S}]\,[\text{M}^{\bullet}] \qquad (6.119)$$
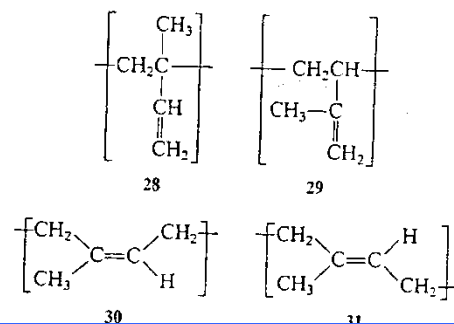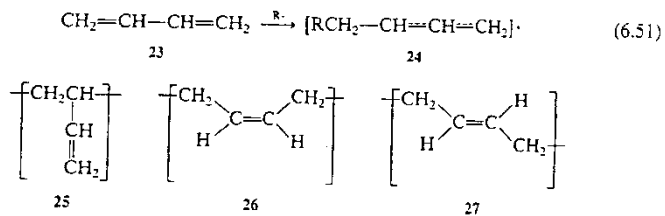
Since chain transfer terminates a growing chain, its effect is a lower molecular weight than would result in its absence. The effect of any chain transfer on the rate of polymerization will, however, vary depending on the relative rates of the transfer [Eq. (6.111)] and reinitiation [Eq. (6.112)], as compared to the rate of normal propagation reaction [Eq. (6.6)].

INHIBITION AND RETARDATION
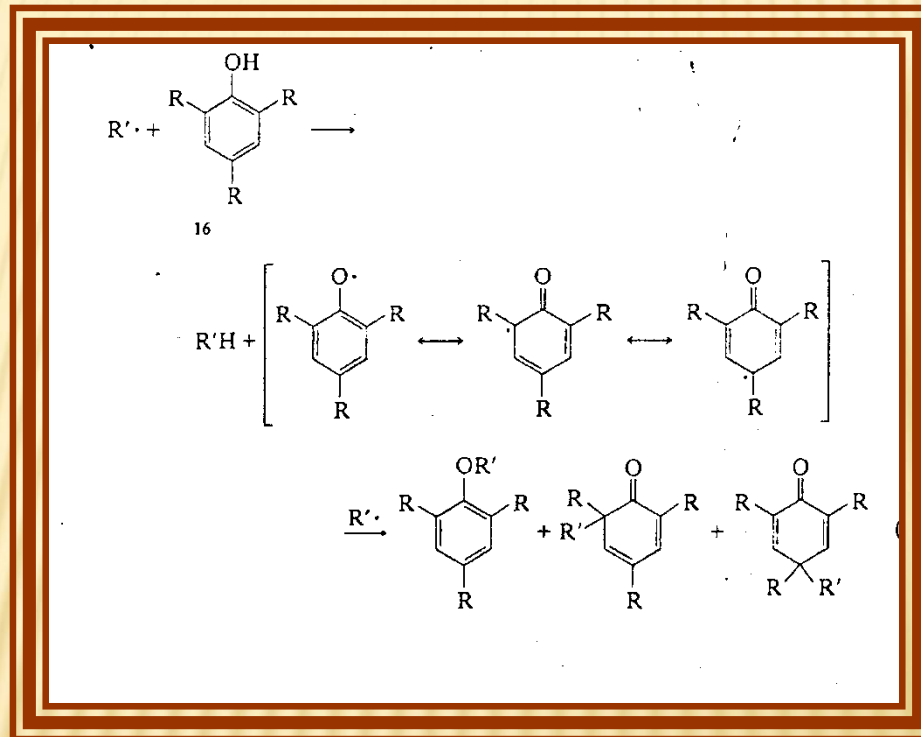
CONJUGATED DIENES

Conjugated dienes such as 1,3-butadiene (23) undergo both 1,2- and 1,4-addition. Addition polymerization thus leads by analogy to 1,2- and 1,4-addition polymers via the delocalized radical intermediate 24 (6.51). Thus, 1,2-addition gives polymer (25) with pendant vinyl groups, while 1,4-addition leads to polymer with unsaturation in the chain. In the latter case, both cis (26) and trans (27) configurations are possible.

$$CH_2=CH-CH=CH_2 \xrightarrow{R\cdot} [RCH_2-CH \cdots CH \cdots CH_2]\cdot \qquad (6.51)$$

23   24

25   26   27

28   29

30   31

STRUCTURE OF FREE RADICAL DIENE POLYMERS

TABLE 6.6. Structure of Free Radical–Initiated Diene Polymers[a]

Monomer	Polymerization Temperature (°C)	Percent			
		cis-1,4	trans-1,4	1,2	3,4
Butadiene	−20	6	77	17	—
	20	22	58	20	—
	100	28	51	21	—
	233	43	39	18	—
Isoprene	−20	1	90	5	4
	−5	7	82	5	5
	50	18	72	5	5
	100	23	66	5	6
	257	12	77	2	9
Chloroprene	−46	5	94	1	0.3
	46	10	81–86	2	1
	100	13	71	2.4	2.4

[a]Data from Cooper[34] p. 275.

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CEILING TEMPERATURE (TC)

* The ceiling temperature (Tc) is reached at which the propagation and de propagation rate are equal

$$\Delta G_p = \Delta H_p - T\Delta S_p$$

$$T_c = \frac{\Delta H}{\Delta S}$$