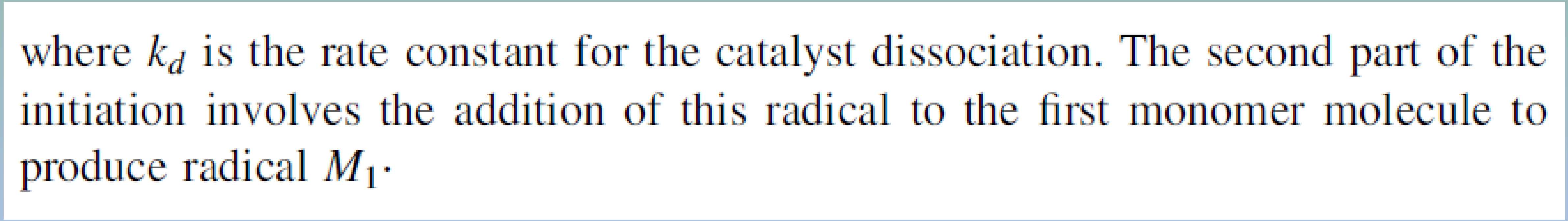
Kinetics of Free Radical Chain Copolymerization

Radical chain polymerization is a chain reaction consisting of a sequence of three steps — initiation, propagation, and, termination. The initiation step involves two reactions. The first is the production of free radicals by homolytic dissociation of an initiator species I to yield a pair of radicals R^*

$$I \xrightarrow{k_d} 2R\cdot$$



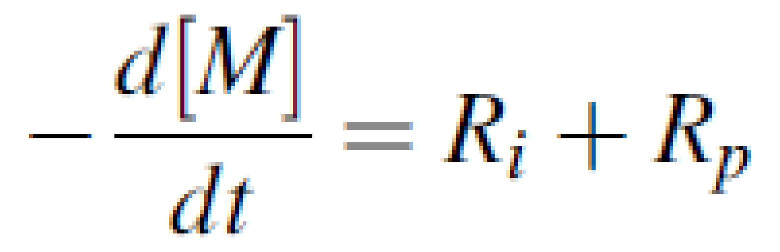
where k_d is the rate constant for the catalyst dissociation. The second part of the initiation involves the addition of this radical to the first monomer molecule to produce radical $M_1\cdot$

$$R\cdot + M \xrightarrow{k_i} M_1\cdot$$

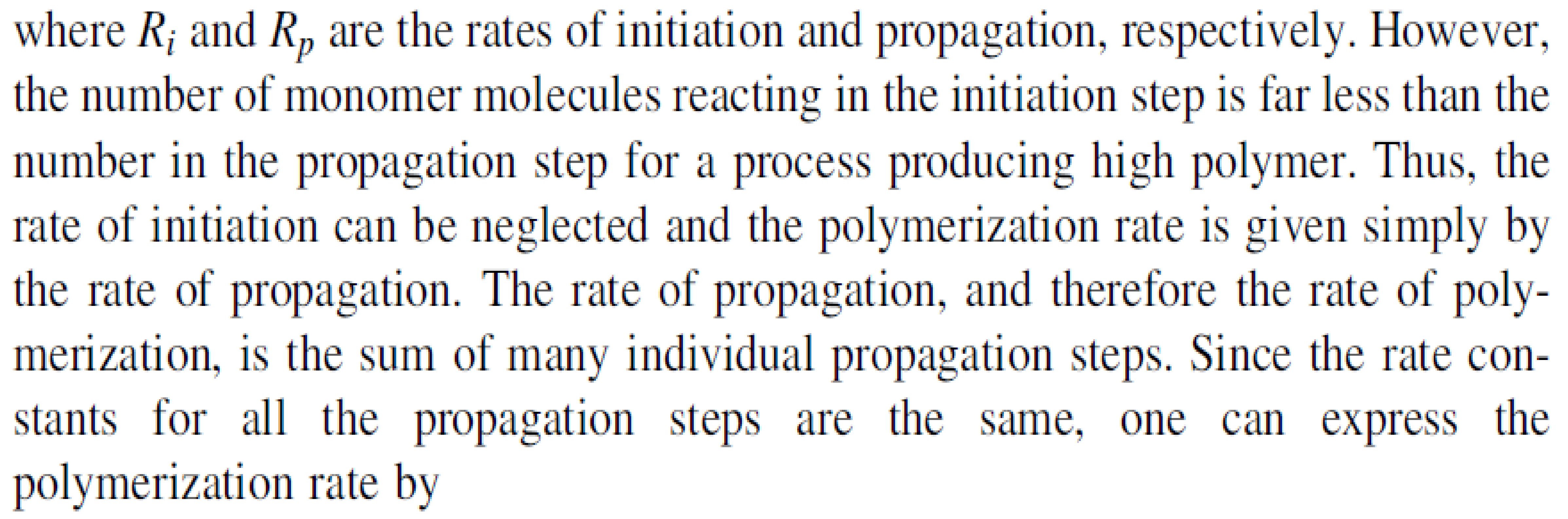
Propagation consists of the growth of $M_n\cdot$ by the successive additions of large numbers (hundreds and perhaps thousands) of monomer molecules. Each addition creates a new radical that has the same identity as the one previously, except that it is larger by one monomer unit. The successive additions may be represented by

$$M_n\cdot + M \xrightarrow{k_p} M_{n+1}\cdot$$

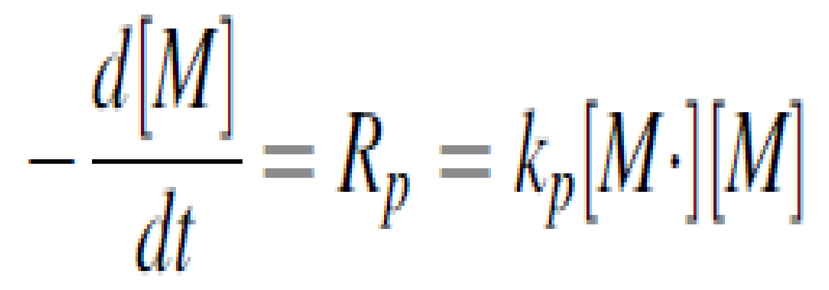
Monomer disappears by the initiation reaction (Eq. 7.45) as well as by the propagation (Eq. 7.46). The *rate of monomer disappearance*, also called the *rate of polymerization*, is given by



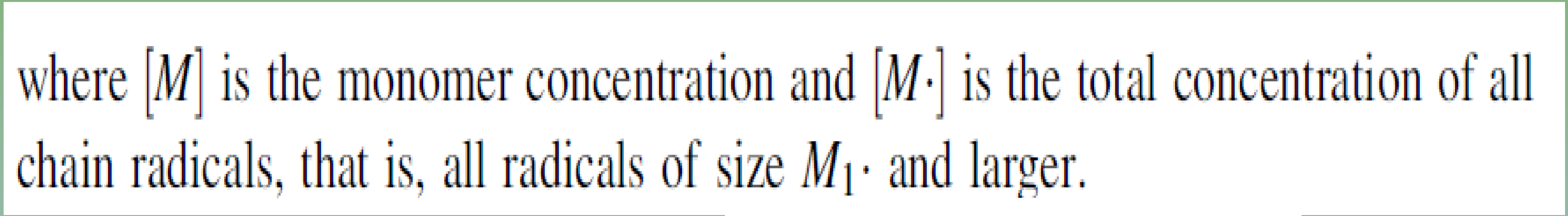
$$-\frac{d[M]}{dt} = R_i + R_p$$



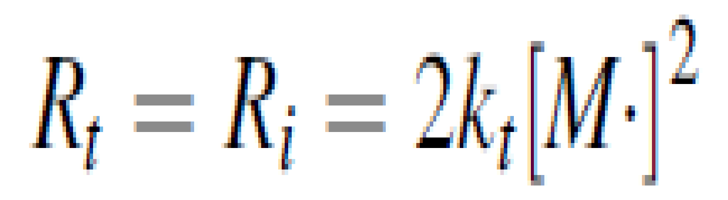
where R_i and R_p are the rates of initiation and propagation, respectively. However, the number of monomer molecules reacting in the initiation step is far less than the number in the propagation step for a process producing high polymer. Thus, the rate of initiation can be neglected and the polymerization rate is given simply by the rate of propagation. The rate of propagation, and therefore the rate of polymerization, is the sum of many individual propagation steps. Since the rate constants for all the propagation steps are the same, one can express the polymerization rate by



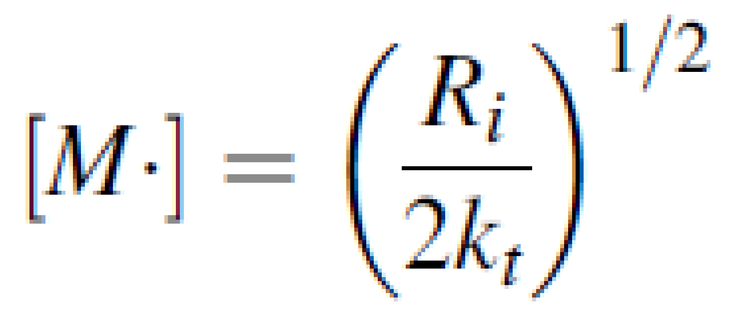
$$-\frac{d[M]}{dt} = R_p = k_p[M\cdot][M]$$



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



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



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

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

$$R_p = k_p[M]\sqrt{\frac{fk_d[I]}{k_t}}$$

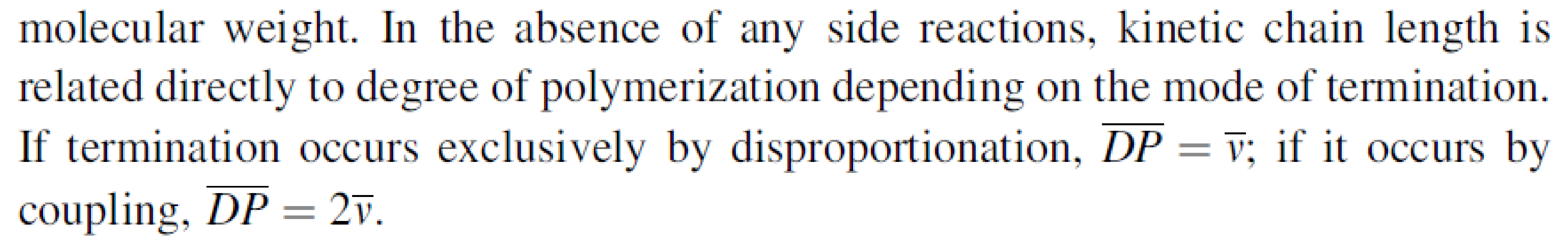
Average Kinetic Chain Length $\overline{v}$

$$\overline{v} = \frac{R_p}{R_i} = \frac{R_p}{R_t}$$

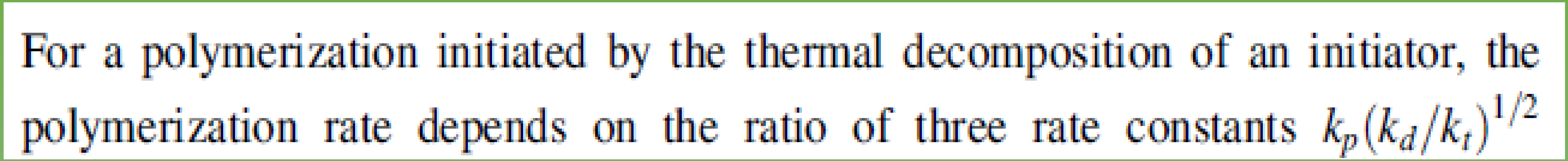
$$\overline{v} = \frac{k_p[M][M\cdot]}{2k_t[M\cdot]^2} = \frac{k_p[M]}{2k_t[M\cdot]}$$

$$\overline{v} = \frac{k_p[M]}{2(fk_t k_d[I])^{1/2}}$$

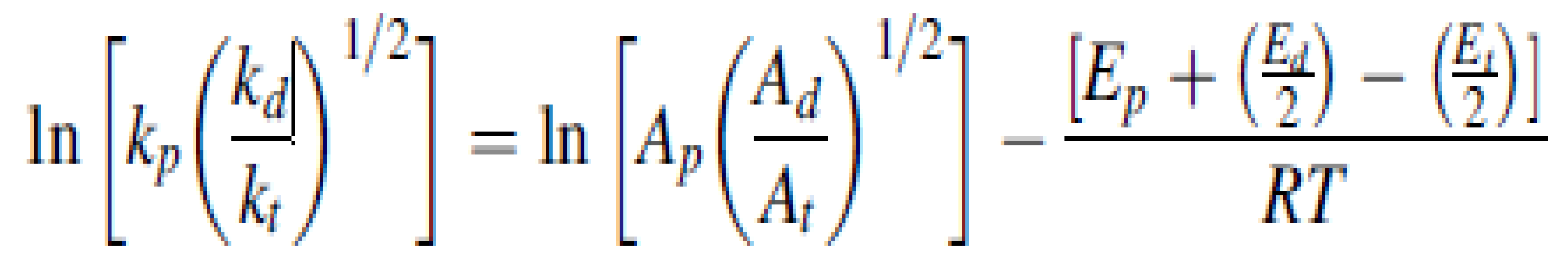
Kinetic chain length is related to a variety of rate and concentration parameters. It will decrease as both of initiator concentration and initiator efficiency increase.



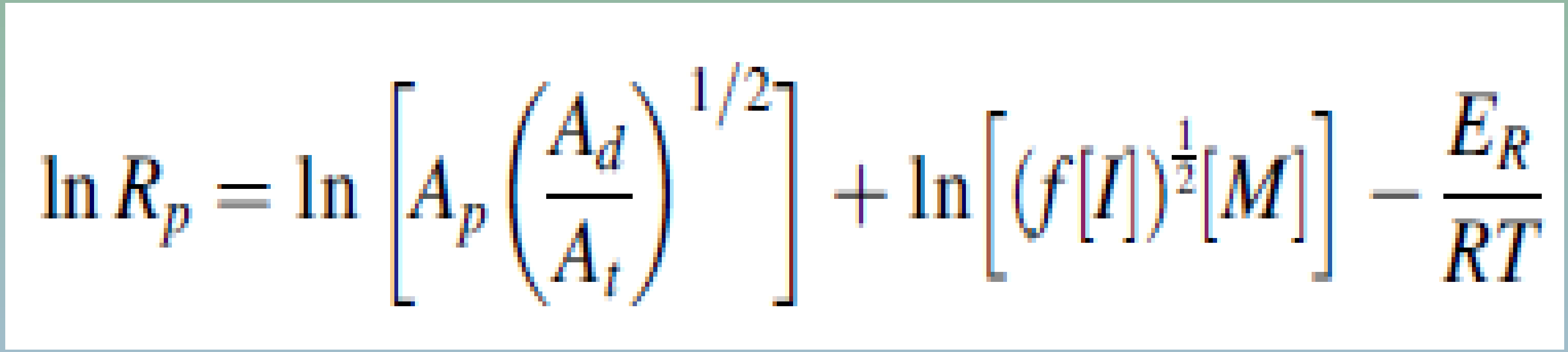
molecular weight. In the absence of any side reactions, kinetic chain length is related directly to degree of polymerization depending on the mode of termination. If termination occurs exclusively by disproportionation, $\overline{DP} = \overline{v}$; if it occurs by coupling, $\overline{DP} = 2\overline{v}$.



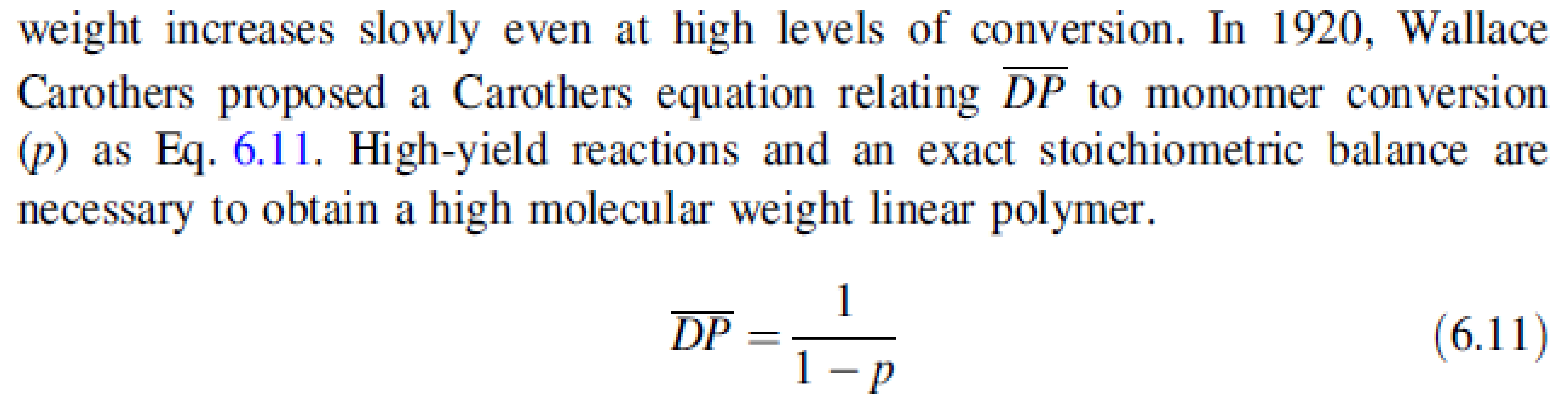
For a polymerization initiated by the thermal decomposition of an initiator, the polymerization rate depends on the ratio of three rate constants $k_p(k_d/k_t)^{1/2}$



$$\ln\left[k_p\left(\frac{k_d}{k_t}\right)^{1/2}\right] = \ln\left[A_p\left(\frac{A_d}{A_t}\right)^{1/2}\right] - \frac{\left[E_p + \left(\frac{E_d}{2}\right) - \left(\frac{E_t}{2}\right)\right]}{RT}$$

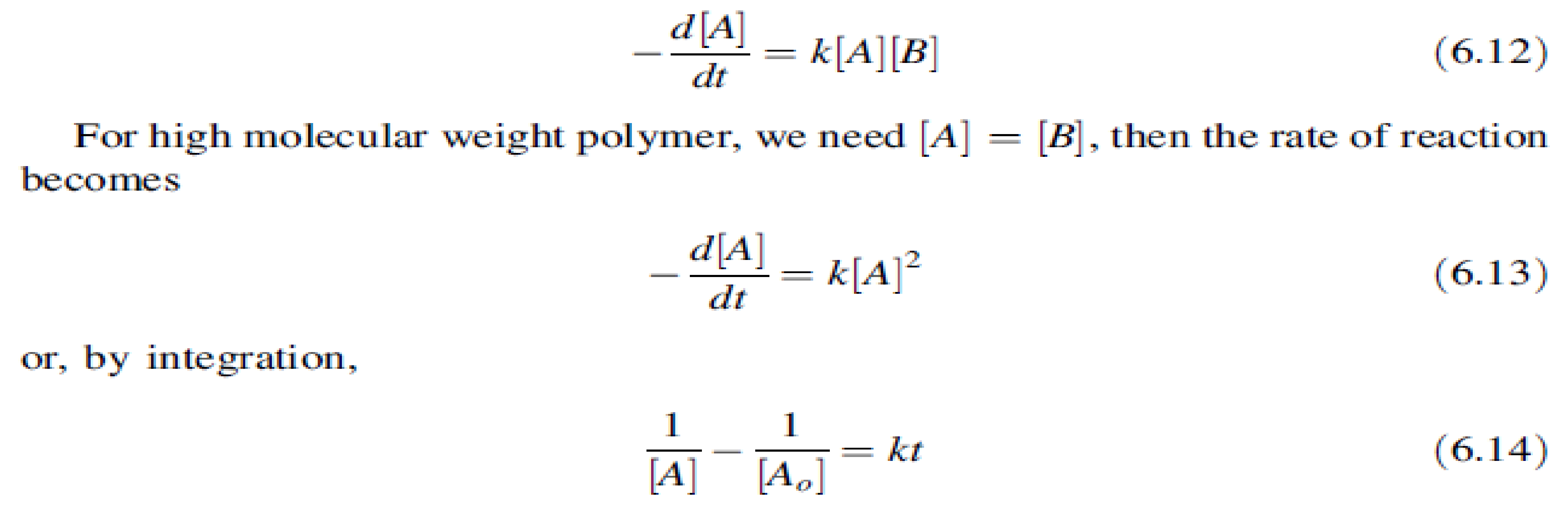


$$\ln R_p = \ln\left[A_p\left(\frac{A_d}{A_t}\right)^{1/2}\right] + \ln\left[(f[I])^{\frac{1}{2}}[M]\right] - \frac{E_R}{RT}$$



weight increases slowly even at high levels of conversion. In 1920, Wallace Carothers proposed a Carothers equation relating $\overline{DP}$ to monomer conversion (p) as Eq. 6.11. High-yield reactions and an exact stoichiometric balance are necessary to obtain a high molecular weight linear polymer.

$$\overline{DP} = \frac{1}{1-p} \tag{6.11}$$



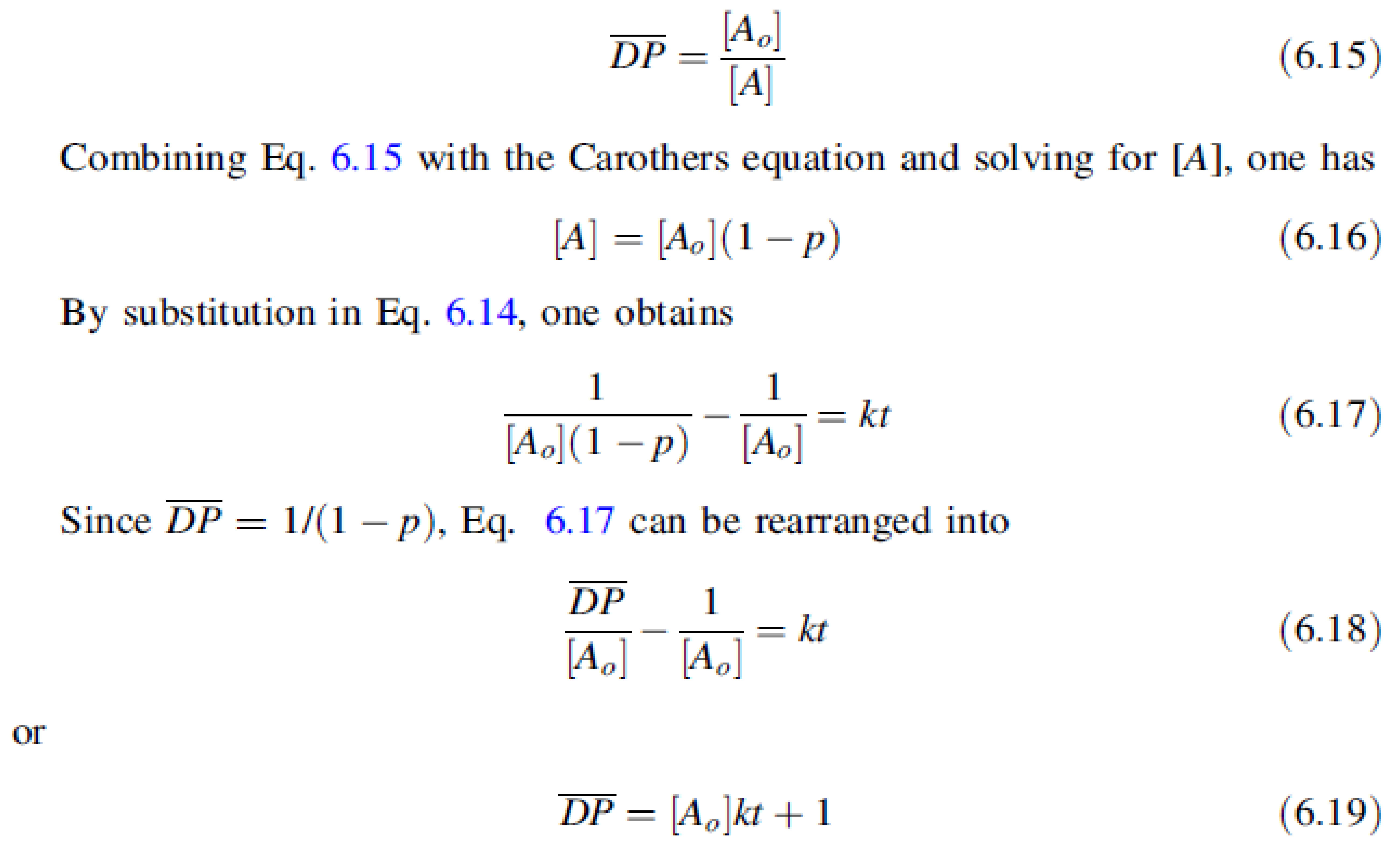
$$-\frac{d[A]}{dt} = k[A][B] \tag{6.12}$$

For high molecular weight polymer, we need $[A] = [B]$, then the rate of reaction becomes

$$-\frac{d[A]}{dt} = k[A]^2 \tag{6.13}$$

or, by integration,

$$\frac{1}{[A]} - \frac{1}{[A_o]} = kt \tag{6.14}$$



$$\overline{DP} = \frac{[A_o]}{[A]} \tag{6.15}$$

Combining Eq. 6.15 with the Carothers equation and solving for $[A]$, one has

$$[A] = [A_o](1 - p) \tag{6.16}$$

By substitution in Eq. 6.14, one obtains

$$\frac{1}{[A_o](1-p)} - \frac{1}{[A_o]} = kt \tag{6.17}$$

Since $\overline{DP} = 1/(1-p)$, Eq. 6.17 can be rearranged into

$$\frac{\overline{DP}}{[A_o]} - \frac{1}{[A_o]} = kt \tag{6.18}$$

or

$$\overline{DP} = [A_o]kt + 1 \tag{6.19}$$