BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 1758—1759 (1969)

A Simple Treatment for the Kinetics of Radical Polymerization with Primary Radical Termination

Katsukiyo Ito and Tatsuo Matsuda

Government Industrial Research Institute, Nagoya, Kita-ku, Nagoya

(Received October 2, 1968)

Several workers have reported on the importance of primary radical termination.[1-6] Bamford, Jenkins and Johnston[7] devised a simple treatment for the kinetics of radical polymerization with primary radical termination in the following.

$$\mathrm{C} \rightarrow 2\mathrm{R}\cdot \qquad k_d \qquad \text{(1a)}$$

$$\mathrm{R}\cdot + \mathrm{M} \rightarrow \mathrm{X}_1\cdot \qquad k_i \qquad \text{(1b)}$$

$$\mathrm{X}_r\cdot + \mathrm{M} \rightarrow \mathrm{X}_{r+1}^{\cdot} \qquad k_p \qquad \text{(1c)}$$

$$\mathrm{X}_r\cdot + \mathrm{X}_s\cdot \rightarrow \mathrm{P}_r + \mathrm{P}_s \text{ or } \mathrm{P}_{r+s} \qquad k_t \qquad \text{(1d)}$$

$$\mathrm{X}_r\cdot + \mathrm{R}\cdot \rightarrow \mathrm{P}_r \qquad k_{ti} \qquad \text{(1e)}$$

$$2\mathrm{R}\cdot \rightarrow \text{Products} \qquad k_{tii} \qquad \text{(1f)}$$

Decomposition of the initiator C gives primary radicals R· which react with monomer M to form chain radicals X·. $\mathrm{X}_r\cdot$ and P_r respectively denote radicals and polymer molecules containing r monomer units. In this treatment for the kinetics of radical polymerization with primary radical termination, they derived the cubic Eq. (2)

$$\frac{x^2(1+x)}{(1-x)} = \frac{2fk_d k_{ti}^2[\mathrm{C}]}{k_s k_i^2[\mathrm{M}]^2} = a^2(a \geq 0), \qquad (2)$$

where

$$x = \frac{k_{ti}[\mathrm{X}\cdot]}{k_i[\mathrm{M}]}([\mathrm{X}\cdot] = \sum[\mathrm{X}_r\cdot])$$

and f is initiator efficiency. Because of Eq. (2) being inconvenient for calculating the polymerization rate R_p for given values $2fk_d[\mathrm{C}]$, the reverse procedure of calculating $2fk_d[\mathrm{C}]$ for R_p was mainly used for simple treatment. According to this treatment, polymerizations for styrene and acrylonitrile were analyzed. On the modification of this treatment for very low monomer concentrations, Baldwin[8] analyzed radical polymerization with primary radical termination for methyl methacrylate. But this treatment is very sensitive to experimental errors at very low monomer concentrations. Furthermore, Baldwin's treatment and Bamford, Jenkins and Johnston's treatment are more complex than our treatment in the following.

In this paper, the treatment for the kinetics o radical polymerization with primary radical termination given by Bamford, Jenkins and Johnston was simplified. Using Baldwin's results,[6] Bamford, Jenkins and Johnston's results[7] and Mayo, Gregg and Matheson's results,[9] this simplified treatment was confirmed.

A Simplification for the Kinetics of Radical Polymerization with Primary Radical Termination. From Eq. (2), we obtain

$$a = x\left(\frac{1+x}{1-x}\right)^{1/2} \geq x$$

Accordingly, by the two approximations

$$\frac{1}{1-x} \cong 1 + x$$

and

$$(1 + 4a)^{1/2} \cong 1 + 2a - 2a^2$$

under the condition $x \leq a \ll 1$, Eq. (2) becomes

$$x(1+x) = a \qquad (3)$$

The solution of Eq. (3) is

$$\begin{aligned} x &= \frac{1}{2}[(1+4a)^{1/2} - 1] \\ &\cong a - a^2 \end{aligned} \qquad (4)$$

Under a condition $a \ll 1$, $[\mathrm{X}\cdot]$ is given by

$$[\mathrm{X}\cdot] = \left(\frac{2fk_d}{k_t}\right)^{1/2}[\mathrm{C}]^{1/2}\left[1 - \frac{k_{ti}}{k_i}\left(\frac{2fk_d}{k_t}\right)^{1/2}\frac{[\mathrm{C}]^{1/2}}{[\mathrm{M}]}\right] \qquad (5)$$

Using Eq. (5), R_p is given by

$$\begin{aligned} R_p &= k_i[\mathrm{R}\cdot][\mathrm{M}] + k_p[\mathrm{X}\cdot][\mathrm{M}] \cong k_p[\mathrm{X}\cdot][\mathrm{M}] \\ &= A[\mathrm{M}][\mathrm{C}]^{1/2}\left(1 - B\frac{[\mathrm{C}]^{1/2}}{[\mathrm{M}]}\right) \end{aligned} \qquad (6)$$

where

$$A = k_p\left(\frac{2fk_d}{k_t}\right)^{1/2} \quad \text{and} \quad B = \frac{k_{ti}}{k_i}\left(\frac{2fk_d}{k_t}\right)^{1/2}$$

---

1) A. Chapiro, M. Magat, J. Sebban and P. Whal, *Ric. Sci.*, **25A**, 73 (1955).

2) G. Henrici-Olivé and S. Olivé, *Makromol. Chem.*, **37**, 71 (1960).

3) J. C. Bevington and J. K. Allen, *Trans. Faraday Soc.*, **56**, 1762 (1960).

4) P. Hyden and H. Melville, *J. Polymer Sci.*, **43**, 201 (1960).

5) P. E. M. Allen and C. R. Patrick, *Makromol. Chem.*, **48**, 89 (1961).

6) G. M. Brunett and L. D. Loan, *Trans. Faraday Soc.*, **51**, 219 (1955).

7) C. H. Bamford, A. D. Jenkins and R. Johnston, *Trans. Faraday Soc.*, **55**, 1451 (1959).

8) M. G. Baldwin, *J. Polymer Sci.*, **A1**, 3209 (1963).

9) F. R. Mayo, R. A. Gregg and M. S. Matheson, *J. Am. Chem. Soc.*, **73**, 1691 (1951).

Eq. (6) yield a convenient linear relationship

$$\frac{R_p}{[\mathrm{M}][\mathrm{C}]^{1/2}} = A - AB\frac{[\mathrm{C}]^{1/2}}{[\mathrm{M}]} \qquad (7)$$

Eq. (7) indicates that $R_p/[\mathrm{M}][\mathrm{C}]^{1/2}$ is constant at the low value of $[\mathrm{C}]^{1/2}/[\mathrm{M}]$ (a familiar relationship) and the increase of $[\mathrm{C}]^{1/2}/[\mathrm{M}]$ increases deviation from this familiar relationship. This conclusion is equivalent to Bamford, Jenkins and Johnston's conclusion.⁷⁾ Furthermore, using A and B in Eq. (7), $k_{ti}/k_i k_p$ is directly calculated without the knowledge of the value fk_d or k_t/k_p^2 by Eq. (8)

$$\frac{B}{A} = \frac{k_{ti}}{k_i k_p} \qquad (8)$$

Applications

On the application of Eq. (7) to Baldwin's results⁸⁾ in the polymerization of methyl methacrylate (MMA) initiated by 2,2′-azobisisobutyronitrile (AIBN), a linear relationship between $R_p/[\mathrm{M}][\mathrm{C}]^{1/2}$ and $[\mathrm{C}]^{1/2}/[\mathrm{M}]$ comes into existence in the range 0 to 0.3 $(\mathrm{l/mol})^{1/2}$ (Fig. 1). Using A and B in this linear relationship and Eq. (8), $k_{ti}/k_i k_p$ is

$$\frac{k_{ti}}{k_i k_p} = 3.09\times10^3\ \mathrm{mol\cdot sec}/l$$

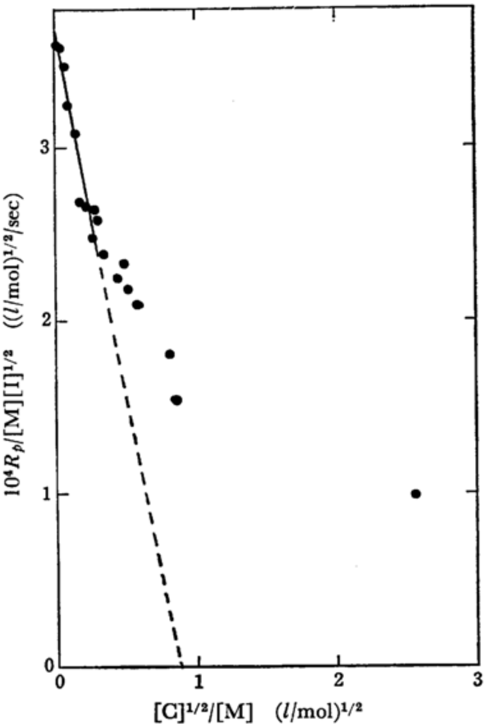

Fig. 1. Relationship between $R_p/[\mathrm{M}][\mathrm{C}]^{1/2}$ and $[\mathrm{C}]^{1/2}/[\mathrm{M}]$ for radical polymerization of MMA initiated by AIBN at 60°C.⁸⁾

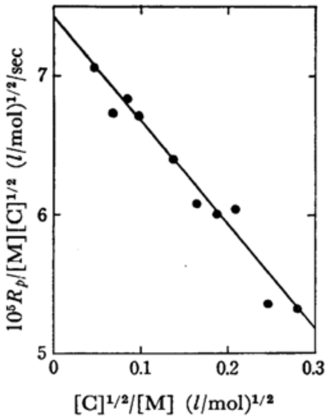

Fig. 2. Relationship between $R_p/[\mathrm{M}][\mathrm{C}]^{1/2}$ and $[\mathrm{C}]^{1/2}/[\mathrm{M}]$ for radical polymerization of styrene initiated by AIBN at 60°C.⁷⁾

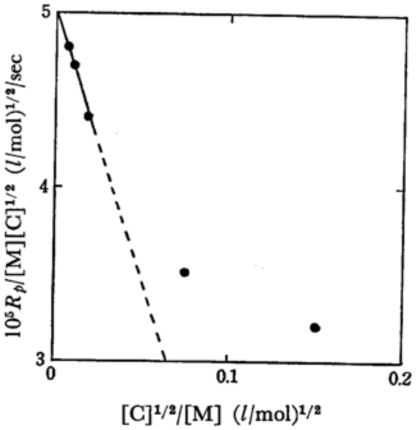

Fig. 3. Relationship between $R_p/[\mathrm{M}][\mathrm{C}]^{1/2}$ and $[\mathrm{C}]^{1/2}/[\mathrm{M}]$ for radical polymerization of styrene initiated by BPO at 60°C.⁹⁾

On the application of Eq. (7) to Bamford, Jenkins and Jonston's results⁷⁾ in the polymerization of styrene initiated by AIBN, a linear relationship between $R_p/[\mathrm{M}][\mathrm{C}]^{1/2}$ and $[\mathrm{C}]^{1/2}/[\mathrm{M}]$ comes into existence in the all experimental range (Fig. 2). $k_{ti}/k_i k_p$ for this polymerization system is

$$\frac{k_{ti}}{k_i k_p} = 1.36\times10^4\ \mathrm{mol\cdot sec}/l$$

On the application of Eq. (7) to Mayo, Gregg and Matheson's results⁹⁾ in the polymerization of styrene initiated by benzoyl peroxide (BPO), a linear relationship between $R_p/[\mathrm{M}][\mathrm{C}]^{1/2}$ and $[\mathrm{C}]^{1/2}/[\mathrm{M}]$ comes into existence in the range 0 to 0.02 $(l/\mathrm{mol})^{1/2}$ (Fig. 3). $k_{ti}/k_i k_p$ for this polymerization system is

$$\frac{k_{ti}}{k_i k_p} = 1.23\times10^5\ \mathrm{mol\cdot sec}/l$$

In conclusion, these applications indicate that a simple treatment based on Eq. (7) is very useful for discussion or calculation of $k_{ti}/k_i k_p$ for the kinetics of radical polymerization with primary radical termination.