

## Discussion of Treatments for the Kinetics of Radical Polymerization with Primary Radical Termination

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### Synopsis

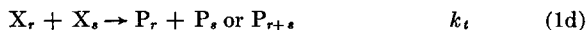
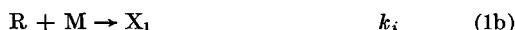
Without knowledge of the familiar geometric mean, the following equation was derived for the radical polymerization with primary radical termination under the condition that reaction between primary radicals is negligible:

$$\frac{[M][C]^{1/2}}{R_p} = \frac{1}{A} + \frac{B}{A} \times \frac{[C]^{1/2}}{[M]}$$

where both  $A$  and  $B$  are constants depending on various rate constants. This equation was mathematically and experimentally dealt with.

### INTRODUCTION

In the past, it has been pointed out that primary radical termination is of importance and several treatments have been derived for radical polymerization with primary radical termination. Bamford et al<sup>1</sup> treated the following polymerization scheme:



Decomposition of initiator  $C$  gives primary radicals  $R$  which react with monomer  $M$  to form chain radicals  $X$ .  $X_r$  and  $P_r$  denote radicals and polymer molecules containing  $r$  monomer units, respectively.

Assuming stationary state and long chain approximation, polymerization rate  $R_p$  is given by

$$\begin{aligned} R_p &= k_i[M][R] + k_p[M][X] \cong k_p[M][X] \\ &= \left(\frac{I}{k_t}\right)^{1/2} \times \frac{k_p k_i [M]^2}{(I k_{ii})^{1/2} + k_i [M]} \quad (2) \end{aligned}$$

where  $I = 2fk_d[C]$  ( $f$  is initiator efficiency) and  $[X] = \Sigma[X_r]$ . In order to obtain this tractable expression, they used the familiar geometric mean

$$k_{tt}^2 = k_{ti} k_t \quad (3)$$

When eq. (3) does not come into existence, the treatment based on eq. (2) is not applicable on this derivation. Conversely, if the same type of equation as eq. (2) is derived without knowledge of eq. (3), though this treatment is applicable to the experimental results, it is not necessary that eq. (3) comes into existence.

Under the condition that reaction (1f) is negligible, Baldwin<sup>2</sup> devised a treatment based on eq. (4):

$$\phi = \frac{k_{tt}[R][X]}{k_{tt}[X][R] + k_t[R][M]} = \frac{1}{1 + k_t k_p [M]^2 / k_{tt} R_p} \quad (4)$$

In this equation,  $\phi$  is the fraction for primary radicals terminating polymeric radicals and cannot be greater than 0.5. The value of  $\phi$  exceeding 0.5 is perhaps an indication that reaction (1f) is significant, or it may reflect a large experimental error.

Without the knowledge of eq. (3), eq. (5) can be derived under the condition that reaction (1f) is negligible<sup>1</sup>:

$$\frac{x^2(1+x)}{1-x} = \frac{Ik_{tt}^2}{k_t k_i^2 [M]^2} = a^2 \quad (a \geq 0) \quad (5)$$

where  $x = (k_{tt}[X]) / (k_t[M])$ .

In this paper, eq. (5) was dealt with by using an inequality. The same type of equation as eq. (3) can be derived. Under the condition that reaction (1f) is negligible, the experimental results were completely analyzed and Baldwin's indication was discussed.

### MATHEMATICAL PROCEDURE

Using the inequality

$$1 + x \leq \frac{1}{1-x} \quad (0 \leq x \leq 1), \quad (6)$$

eq. (5) gives

$$x(1+x) \leq a \leq \frac{x}{1-x} \quad (7)$$

The solution of inequality (7) is

$$\frac{1}{2} \left[ (4a + 1)^{1/2} - 1 \right] \geq x \geq \frac{a}{1+a} \quad (8)$$

Using

$$R_p = k_p [M][X], \quad (9)$$

Inequality (8) becomes

$$\frac{A}{2B} [M]^2 [(4Bu + 1)^{1/2} - 1] \geq R_p \geq \frac{A(M)^2 u}{1 + Bu} \quad (10)$$

or

$$\frac{1}{2A} \gamma [(4Bu + 1)^{1/2} + 1] \leq v \leq \frac{1}{A} + \frac{B}{A} \times u \quad (11)$$

where

$$u = \frac{[C]^{1/2}}{[M]}, \quad v = \frac{[M][C]^{1/2}}{R_p},$$

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

Using eq. (3), the lower boundary of inequality (10) becomes eq. (2). From upper and lower boundaries of inequality (11), one obtains

$$v = \frac{1}{A} + \frac{B}{A} \times u \quad (12)$$

and

$$v = \frac{1}{2A} [(4Bu + 1)^{1/2} + 1]. \quad (13)$$

Equation (12) can be also derived from eq. (2).

Expanding  $(1 + 4a)^{1/2}$  and  $1/(1 + a)$  in a Taylor series eq. (8) becomes

$$a(1 - a + 2a^2 - \dots) \geq x \geq a(1 - a + a^2 - \dots). \quad (14)$$

Retaining terms up to  $a^2$ , inequality (14) gives

$$x = a(1 - a), \quad (15)$$

that is, Ito and Matsuda's equation

$$\frac{1}{v} = A - ABu \quad (16)$$

can be derived.<sup>3</sup>

The above mathematical procedures indicate that, without the familiar geometric mean treatment, an equation of the type of eq. (2) and eq. (12) can be derived under the condition that reaction (1f) is negligible. However, the treatments based on eqs. (12), (13), and (16) are approximate. Complete analysis of the experimental results must be carried out by using the following equation:

$$u = \frac{Av(A^2v^2 - 1)}{B(A^2v^2 + 1)}. \quad (17)$$

This equation can be derived by using eqs. (5) and (9).<sup>1</sup>

## DISCUSSION

Equation (12) is applicable to Baldwin's experimental results<sup>3</sup> in the polymerization of methyl methacrylate (MMA) initiated by 2,2-azobisisobutyronitrile (AIBN) at 60°C at a considerably small value of  $u$  (Fig. 1). A linear relationship between  $u$  and  $v$  becomes

$$v = (2.80 + 3.95u) \times 10^3. \quad (18)$$

$A$  and  $B$  were calculated to be

$$A = 3.57 \times 10^{-4} \text{ sec}(\text{mole/l.})^{1/2},$$

$$B = 1.41 \text{ sec}^2(\text{mole/l.})^{1/2}.$$

Using these values, eqs. (13) and (17) respectively become

$$v = 1.40 \times 10^3 [(5.65u + 1)^{1/2} + 1] \quad (19)$$

and

$$u = \frac{2.53 \times 10^{-4} v (1.27 \times 10^{-7} v^2 - 1)}{1.27 \times 10^{-7} v^2 + 1}. \quad (20)$$

Equations (18), (19), and (20) are shown in Figure 1.

The values of  $v$  at the given values of  $u$  in the experimental results are in the range of the values calculated by using eqs. (18) and (19). That is, the experimental results are completely interpreted by using inequality (11). However,  $v = 10.2 \times 10^3$  at  $u = 2.56$  is not equivalent to the value of  $v$  calculated by eq. (20) at  $u = 2.56$  (Fig. 1). The other experimental results are evaluated by eq. (20). Baldwin<sup>2</sup> calculated  $\phi = 0.62$  for  $v =$

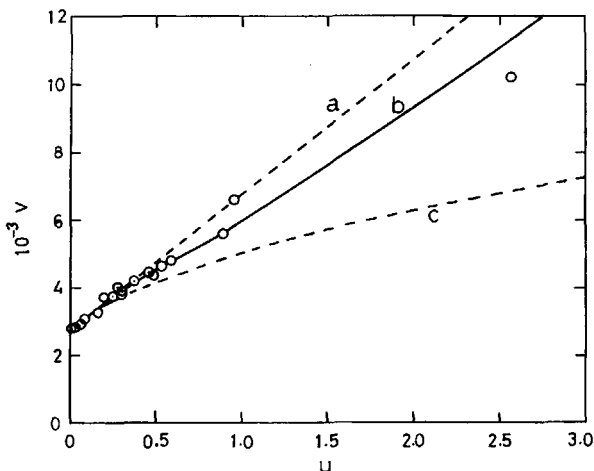


Fig. 1. Relationship between  $v = [M][C]^{1/2}/R_p$  and  $u = [C]^{1/2}/[M]$  for the polymerization of MMA initiated by AIBN<sup>2</sup>: (a) eq. (18); (b) eq. (20); (c) eq. (19).

$10.2 \times 10^3$  at  $u = 2.56$ . Without this experimental result,  $\phi$  does not exceed 0.5. That is, Baldwin's conclusion is equivalent to the conclusion obtained by using eq. (20).

On the application of eq. (12) to Mayo et al.'s experimental results<sup>4</sup> for the polymerization of styrene initiated by benzoyl peroxide (BPO), eq. (21) is obtained for the range  $0.02 \geq u \geq 0$  (Fig. 2):

$$v = (2.0 + 13u) \times 10^4. \quad (21)$$

$A$  and  $B$  were calculated to be  $5.0 \times 10^{-5} \text{ sec}(\text{mole/l.})^{1/2}$  and  $6.5 \text{ sec}(\text{mole/l.})^{1/2}$ , respectively. Using these values, eqs. (13) and (17) become

$$v = [(26u + 1)^{1/2} + 1] \times 10^4 \quad (22)$$

and

$$u = \frac{7.7 \times 10^{-6} v (2.5 \times 10^{-9} v^2 - 1)}{2.5 \times 10^{-9} v^2 + 1}. \quad (23)$$

Equations (21), (22), and (23) are shown in Figure 2.

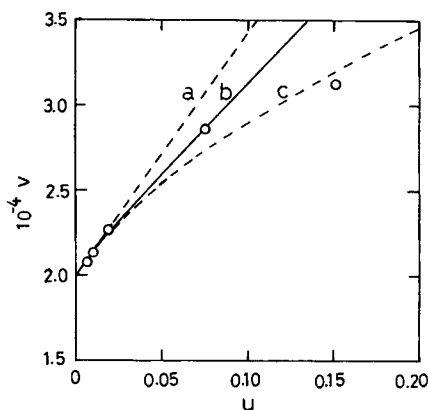


Fig. 2. Relationship between  $v = [M][C]^{1/2}/R_p$  and  $u = [C]^{1/2}/[M]$  for the polymerization of styrene initiated by BPO: (a) eq. (21), (b) eq. (23); (c) eq. (22).

Without the plot of  $v = 3.12 \times 10^{-4}$  at  $u = 1.51$ , the other  $v$  values at  $u$  in the experimental results are in the range between the values calculated by using eqs. (21) and (22) and evaluated by eq. (23).

It was reported that the treatment based on eq. (12) is applicable to the polymerization of styrene under various conditions.<sup>1,5</sup>

In conclusion, the treatment based on inequality (11) is applicable in the wide range of  $[C]^{1/2}/[M]$ . Precisely, this application must be examined by using eq. (17). In the polymerization to which this treatment can be applied, reaction (1f) should be negligible.

### References

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