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Estimation of Rate Constants of Bimolecular Decomposition of Redox Initiators in Radical Polymerization

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ABSTRACT

A rigorous statistical method is established to compute the rate constants of the bimolecular decomposition of redox catalysts used to initiate polymer chains. Results obtained for the systems styrene-dimethylaniline-benzoyl peroxide and acrylamide-thioglycollic acid-potassium bromate compare favorably with those reported by other workers. The merits of this error-in-variable technique, which outperforms conventional nonlinear least-square analysis and the dead-end polymerization method, are discussed.

INTRODUCTION

Perhaps the most striking features of redox initiators are their fast decomposition rates and low activation energies [1]. Hence, they have been widely employed in initiating free-radical polymerization of vinyl monomers under mild reaction conditions, particularly

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in emulsion systems. In addition, these polymerizations can be conveniently controlled by selecting the appropriate catalysts from a wide spectrum of redox initiators with known decomposition rate constants. To this end it is desirable to have reliable measurements of these kinetic quantities.

Various techniques for determining the rate constants of both the thermal and redox dissociations of initiators for radical polymerization have been proposed recently [2-5]. Walling and Indictor [4] and O'Driscoll and McArdle [5] studied the polymerization of styrene initiated by dimethylaniline (DMA)-benzoyl peroxide (Bz_2O_2). The former applied a pseudofirst-order differential rate equation, which assumes a large excess of either initiator component for deriving the rate constant of DMA-Bz_2O_2 decomposition. The latter developed a linear expression that requires the polymerization to proceed to completion. Besides, this particular graphical method demands prior information on other related kinetic parameters, thus limiting its applicability. In this study a novel approach is presented to overcome these limitations.

ANALYSIS OF KINETIC DATA BY THE ERROR-IN-VARIABLE METHOD (EVM)

In general, the rate of redox polymerization may be expressed by

$$-d[M]/dt = A(ab)^{\alpha}[M], \qquad (1)$$

where [M], a, and b are, respectively, the instantaneous concentrations of the monomer and the initiator Components 1 and 2 at time t, while A and α are empirical constants. However, the molecular decomposition of redox initiators is a simple second-order kinetic process described by the rate law

$$-da/dt = k_d ab, \qquad (2)$$

where k_d is the associated rate constant. We are particularly concerned with the chain sequences that involve biradical terminations which render $\alpha = \frac{1}{2}$ as well as

$$A = k_p\left(\frac{fk_d}{2k_t}\right)^{\frac{1}{2}}, \qquad (3)$$

where k_p and k_t are, respectively, the rate constants of the propagation and termination steps, and f is the initiator efficiency. Integration of Eqs. (1) and (2) result in

$$-\ln(1 - p) = g_1 A', \tag{4}$$

$$p = 1 - \frac{[M]}{[M]_0}, \tag{4a}$$

$$A' = A/k_d, \tag{4b}$$

$$g_1 = \ln\left[K\left(\frac{y - 1}{y + 1}\right)\right], \tag{4c}$$

$$K = \frac{\sqrt{X_0} + 1}{\sqrt{X_0} - 1}, \tag{4d}$$

$$X = a_0/b_0, \tag{4e}$$

$$y = \sqrt{X_0}\, \exp\left[\frac{(a_0 - b_0)k_d t}{2}\right] \tag{4f}$$

where $[M]_0$, a_0, and b_0 are the initial concentrations of the monomer and Components 1 and 2, respectively, and the experimental constant X_0 is greater than unity.

From the statistical point of view, the conventional nonlinear least-squares method (NLS) is inadequate for the present study, because the variance of $\ln(1 - p)$ in Eq. (4) is not an invariant of p. In view of this, we resort to the error-in-variable method (EVM) which has been outlined by Wentworth [6]. This rigorous statistical algorithm has been successfully applied recently to estimate the viscometric parameters of polymer solutions [7] as well as the kinetic parameters of radical polymerization [8, 9].

In order to facilitate the analysis, Eq. (4) is converted to

$$\ln\ln(1 - p)^{-1} = \ln\left(\frac{g_1}{\sqrt{k_d}}\right) + \ln B, \tag{5}$$

where B is independent of k_d and given by

$$B = A'\sqrt{k_d}. \tag{5a}$$

Basically, the EVM method minimizes the sum of weighted-squares of residual h_i defined by

$$S = \sum_i w_i h_i^2, \tag{6}$$

where h_i is associated with Eq. (5) and written as

$$h_i = \ln \ln (1 - p_i)^{-1} - \ln\left(\frac{g_{1_i}}{\sqrt{k_d}}\right) - \ln B, \tag{6a}$$

and the weight w_i is the reciprocal of the variance of h_i, Var(h_i):

$$w_i = [\mathrm{Var}(h_i)]^{-1}. \tag{6b}$$

Hereafter, the subscript i and summation $\sum$ refer to the i-th data point and a set of n data points, respectively.

If the experimental variables p, t, a_0, and b_0, whose variances are designated as Var(p), Var(t), Var(a_0), and Var(b_0), respectively, are mutually independent, one obtains

$$\mathrm{Var}(h_i) = [(1 - p_i)\ln (1 - p_i)]^{-2}\,\mathrm{Var}(p_i) + (g_{1_i})^{-2}\,\mathrm{Var}(g_{1_i}), \tag{7}$$

where

$$\mathrm{Var}(g_{1_i}) = \left(\frac{\partial g_{1_i}}{\partial a_0}\right)^2 \mathrm{Var}(a_0) + \left(\frac{\partial g_{1_i}}{\partial b_0}\right)^2 \mathrm{Var}(b_0) + \left(\frac{\partial g_1}{\partial t}\right)^2_{t_i} \mathrm{Var}(t_i). \tag{7a}$$

The derivatives are listed as follows:

$$\left(\frac{\partial g_{1_i}}{\partial a_0}\right) = \frac{-\sqrt{X_0}}{a_0(X_0 - 1)} + \frac{y_i(a_0^{-1} + k_d t_i)}{(y_i^2 - 1)}, \tag{8}$$

$$\left(\frac{\partial g_{1_i}}{\partial b_0}\right) = \frac{\sqrt{X_0}}{b_0(X_0 - 1)} - \frac{y_i(b_0^{-1} + k_d t_i)}{(y_i^2 - 1)}, \tag{9}$$

$$\left(\frac{\partial g_1}{\partial t}\right)_{t_i} = \frac{(a_0 - b_0)k_d y_i}{(y_i^2 - 1)}. \tag{10}$$

The function h_i (Eq. 6a) may be expanded by means of a Taylor series to the first power terms of k_d and B, whose first approximations are designated as k_d' and B', respectively. Equation (6) is then differentiated twice with respect to the above parameters, yielding two normal equations that may be solved to acquire the second approximation of k_d designated as

$$k_d'' = \frac{\sum E_i F_i \sum F_i G_i - \sum F_i^2 \sum E_i G_i}{\sum E_i^2 \sum F_i^2 - (\sum E_i F_i)^2}, \tag{11}$$

where

$$E_i = \sqrt{w_i}\left(\frac{\partial h}{\partial k_d}\right)_i', \tag{11a}$$

$$F_i = \sqrt{w_i'}\left(\frac{\partial h}{\partial B}\right)_i', \tag{11b}$$

$$G_i = \sqrt{w_i'}\left[h_i' - k_d'\left(\frac{\partial h}{\partial k_d}\right)_i' - B'\left(\frac{\partial h}{\partial B}\right)_i'\right], \tag{11c}$$

and, hereafter, the prime superscript refers to the respective value based on k_d' and B'. Here, we have

$$\left(\frac{\partial h}{\partial k_d}\right)_i' = \frac{-1}{g'_{1_i}} \frac{y_i'(a_0 - b_0)t_i}{(y_i'^2 - 1)} + \frac{1}{2k_d'}, \tag{12}$$

$$\left(\frac{\partial h}{\partial B}\right)_i' = -\frac{1}{B'}. \tag{13}$$

Iteration involving Eqs. (11)-(13) would lead to the estimate of k_d, denoted by $\hat{k}_d$. The variance of $\hat{k}_d$ is

$$\mathrm{Var}(\hat{k}_d) = \frac{\sum F_{i0}^2}{\sum E_{i0}^2 \sum F_{i0}^2 - (\sum E_{i0}F_{i0})^2}, \tag{14}$$

where E_{i0}, F_{i0}, and G_{i0} are, respectively, the values of E_i, F_i, and G_i computed at $k_d = \hat{k}_d$. The foregoing procedure may be readily adapted to yield the NLS estimate of k_d merely by setting $w_i' = 1$.

The first approximation of k_d for the above algorithms may be acquired by a simple method as follows. The initial rate of polymerization R_{p0} is first determined and utilized to evaluate

$$A = \frac{R_{p0}}{(a_0 b_0)^{\frac{1}{2}}}, \tag{15}$$

where

$$R_{p0} = -\frac{1}{[M]_0}\left(\frac{d[M]}{dt}\right)_{t=0} = \left(\frac{dp}{dt}\right)_{t=0}. \tag{15a}$$

At infinite time, Eq. (4) becomes

$$A' = \frac{-\ln(1 - p_\infty)}{\ln\left[\dfrac{\sqrt{X_0} + 1}{\sqrt{X_0} - 1}\right]}, \tag{16}$$

where p_∞ is the limiting conversion. Combining Eqs. (15) and (16) yields the first approximation

$$k_d' = A/A'. \tag{17}$$

In fact, Eq. (17) can be applied as a novel dead-end polymerization method (DEP) for obtaining k_d if R_{p0} and p_∞ are precisely known. However, if p_∞ is not accessible, then it may be estimated by an approximate formula empirically proposed as

$$p_\infty = (1.0 + \beta N)p_l \tag{18}$$

where

$$N = 0, 1, 2, 3, \ldots, \tag{18a}$$

p_l is the highest measured p, and β is an adjustable parameter which may be equal to 0.1. When p_l is close to p_∞ (presumably with $p_l/p_\infty \geq 3/4$), one may take $N = 0$, making the iterative process converge rapidly to a root of k_d. In contrast, if p_l is sufficiently high, but still small in comparison with p_∞ (presumably in the range of $1/4 < p_l/p_\infty < 3/4$), then different values of p_∞ should be generated by Eq. (18) in order to compute the corresponding S values (Eq. 6) via Eqs. (16) and (17), and search for the minimum S that finally offers the first approximation of k_d. In this work, the DEP, NLS, and EVM analyses will be pursued to compute k_d.

RESULTS AND DISCUSSION

Acrylamide has been polymerized by thioglycolic acid (TGA)-potassium bromate ($KBrO_3$) at various temperatures in aqueous media [10]. Since the original data are rather scattered, the values of p at various t were interpolated from the smooth curves constructed by plotting p versus t at 25 and 30°C, and listed as System B in Table 1. The observed degrees of conversion for System A (Table 1) were faithfully reproduced from Ref. 5. The factor α for the two systems has been verified to be 1/2. In the present investigation the errors in p, a_0, b_0, and t are assumed to be normally distributed and have

TABLE 1. Kinetic Data

A: $CH_2CH(C_6H_5)$-DMA[a]-Bz_2O_2 with $\alpha = 1/2$

Temperature, °C	$a_0 \times 10^2$, M	$b_0 \times 10^2$, M	$R_{p0} \times 10^6$, s^{-1}	Experimental p at t, h							
				4	18	25	33	45	55	66	∞[b]
0	7.50	3.76	1.25	0.021	0.051	0.073	0.083	0.089	0.104	0.122	0.140

B: $CH_2CHCONH_2$-TGA[a]-$KBrO_3$ with $\alpha = 1/2$

Temperature, °C	$a_0 \times 10^3$, M	$b_0 \times 10^3$, M	$R_{p0} \times 10^4$, s^{-1}	Interpolated p at t, min							
				2.5	5.0	10	15	20	25	30	∞[c]
25	5.00	3.00	3.33	0.050	0.093	0.163	0.218	0.260	0.290	0.310	0.355
30	6.46	3.00	2.87	0.043	0.075	0.130	0.168	0.193	0.211	0.224	0.238

[a] Used as Component 1.

[b] Time required is about 140 h.

[c] Time required is slightly above 60 min.

zero mean. The variances of these measurable quantities, Var(p), Var(a_0), Var(b_0), and Var(t), are constants with estimated values, respectively, equal to 9.0×10^{-6}, 1.6×10^{-5} M^2, 4.0×10^{-6} M^2, and 9.0×10^4 s^2 for System A, and 2.5×10^{-5}, 9.0×10^{-8} M^2, 4.0×10^{-8} M^2, and 1.0×10^2 s^2 for System B. All the calculations were performed on a Univac 1100/60 computer system. By setting $N \leq 13$, we obtained the NLS and EVM results displayed in Table 2 with less than 5 iterations in any case. The standard deviation of $\hat{k}_d$ is equal to the square root of Var($\hat{k}_d$) computed by Eq. (14).

Table 2 compares the values of k_d resulting from the three distinct calculations for Systems A and B. Differences between the EVM and the other results are indeed noticeable. The application of the NLS algorithm to the present situation is statistically unjustifiable in the sense that it would produce biased results [7]. Basically, the DEP calculations rely upon just two measurements, viz., p_∞ and R_{p0}. Hence, the ensuing discussion refers exclusively to the most reliable k_d values listed under the EVM procedure.

The literature values of k_d for the system styrene-DMA-Bz_2O_2 at 0°C vary from 1.1 to 3.1×10^{-4} $[M{\cdot}s]^{-1}$ [4, 5]. Our result happens to fall within this range and thus is acceptable. Unfortunately, to the best of our knowledge, no k_d values have been reported for the System B so far. However, by using the Arrhenius equation, we have estimated the activation energy for the TGA-$KBrO_3$ decomposition to be 11 kcal/mol, which is a reasonable value for a redox catalyst reaction [11].

The EVM method uses the actual values of p. It is superior to classical means based on the instantaneous polymerization rates, which are obtained indirectly from the gradients of p-t curves [4]. Unlike the linear least-squares treatment advanced by O'Driscoll and McArdle [5], the present method does not depend on the exact value of p_∞. This means that it reduces the experimental time significantly since the polymerization rate usually drops considerably toward the end of the reaction, as illustrated by the data contained in Table 1. This technique may be readily exploited to evaluate the initiator efficiency if the ratio $k_p/\sqrt{k_t}$ is predetermined.

One of the distinct merits of the EVM method is that it also indicates the precision of each estimate. None of the standard deviations of k_d for the systems included in Table 2 are more than 20% of their resprive k_d estimates, based on the above error structures assigned to the various independent and dependent variables. However, these uncertainties may be greatly reduced by improving the experimental technique to minimize the errors.

TABLE 2. Estimates of k_d Obtained by Various Methods

No.	System	Temperature, °C	k_d, $(M \cdot s)^{-1}$ DEP	k_d, $(M \cdot s)^{-1}$ NLS	k_d, $(M \cdot s)^{-1}$ EVM	S_{k_d},[a] $(M \cdot s)^{-1}$
1	A	0	2.76×10^{-4}	3.87×10^{-4}	2.54×10^{-4}	0.44×10^{-4}
2	B	25	0.405	0.239	0.268	0.054
3	B	30	0.399	0.338	0.364	0.060

[a] Standard deviations of k_d obtained by EVM.

Equations (6)-(14) provide the facility for depicting the course of any polymerizations initiated by the bimolecular redox reactions that follow Eq. (2). Hence, our method will be useful for determining the second-order decomposition rate constant of a redox system by monitoring the polymerization rate to a relatively high degree of conversion with respect to p_∞.

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