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The Estimation of Primary Radical Termination from Rate Data in Free Radical Polymerization

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Recently an article has been published by Ito and Matsuda[1] in which a simple treatment of primary radical termination in free radical polymerization was proposed. Starting from the kinetic scheme for primary radical termination as it had been developed by Bamford and Jenkins,[2] however, omitting an eventual recombination of primary radicals outside the solvent cage, *viz.*,

$R_0=2(1-h)R_d$	rate of formation of primary radicals ($R_d=k_d[\mathrm{I}]$=rate of initiator decomposition)
$R_i=k_i[\mathrm{R}][\mathrm{M}]$	rate of initiation (polymer radical formation)
$R_p=k_p[\mathrm{P}][\mathrm{M}]$	rate of chain propagation
$R_t=k_t[\mathrm{P}]^2$	rate of mutual termination between polymer radicals
$R_{ti}=k_{ti}[\mathrm{R}][\mathrm{P}]$	rate of termination of polymer radicals by primary radicals

[I], [M], [R], and [P] denoting the concentrations of initiator, monomer, primary radicals, and polymer radicals, respectively, $(1-h)$ being the fraction of primary radicals escaping the solvent cage, Ito and Matsuda simplified the cubic equation,

$$R_p^3+(k_ik_p/k_{ti})[\mathrm{M}]^2R_p^2+R_0(k_p^2/k_t)[\mathrm{M}]^2R_p-(k_ik_p/k_{ti})(k_p^2/k_t)R_0[\mathrm{M}]^4=0 \tag{1}$$

which is obtained after the usual stationary state treatment for primary and polymer radicals, by introducing several approximations finally arriving at an equation of the form

$$R_p/[\mathrm{M}][\mathrm{I}]^{0.5}=A-A^2B([\mathrm{I}]^{0.5}/[\mathrm{M}]) \tag{2}$$

where

$$A=k_p\{2(1-h)k_d/k_t\}^{0.5} \text{ and } B=k_{ti}/k_ik_p$$

which should allow an evaluation of the ratio $k_{ti}/k_ik_p(\equiv B)$ characteristic for the termination of the growing polymer radicals by the specific primary radicals by plotting $R_p/[\mathrm{M}][\mathrm{I}]^{0.5}$ *vs.* $[\mathrm{I}]^{0.5}/[\mathrm{M}]$ and dividing the (absolute value of the) slope by the squared intercept.

However, as had apparently escaped the notice of Ito and Matsuda, in 1965 an article had already appeared[3] in which the cubic equation (1) had been simplified on similar lines to yield another linear relationship

$$R_p/[\mathrm{M}][\mathrm{I}]^{0.5}=A-AB(R_p/[\mathrm{M}]^2) \tag{3}$$

A and B being defined identically as before. In this case which also does not require the knowledge of either k_p^2/k_t or $2(1-h)k_d$, the characteristic ratio $k_{ti}/k_ik_p(\equiv B)$ is easily calculated by dividing the absolute slope by the intercept after a plot of $R_p/[\mathrm{M}][\mathrm{I}]^{0.5}$ *vs.* $R_p/[\mathrm{M}]^2$ has been made. This method has been successfully applied to the polymerization of styrene initiated by 2,2′-azobisisobutyronitrile (AIBN) using results of Henrici-Olivé and Olivé[4] and Olaj[3] and later on also to the polymerization of styrene initiated by 1,1′-azobis-1-phenylethane and 1,1′-azobis-1-cyanocyclohexane[5] and the superiority of estimating k_{ti}/k_ik_p from rate measurements over all other methods existing at that time thoroughly discussed.[3] Although the rate of polymerization had been varied over a wide range, perfectly linear plots have been obtained within experimental accuracy.[3,5] This is in marked contrast to two of the three examples given by Ito and Matsuda[1] where strong deviations from linearity occur when experimental data are plotted according to their equation (Eq. (2)). The reason for this is that Eq. (3), which in the meantime also has been acknowledged and accepted by other workers,[6] is a clearly better approximation to the

TABLE 1

$10^5\cdot R_p$ mol/$l\cdot$sec	$10^4\cdot R_0^{0.5}$ (mol/$l\cdot$sec)$^{1/2}$	$10^2(R_p/[\mathrm{M}]R_0^{0.5})$ (l/mol·sec)$^{1/2}$			
		Eq. (1)	Eq. (2)	Eq. (3)	Eq. (4)
1	0.594	1.980_3	1.980_0	1.980_2	1.980_3
5	3.090	1.903	1.896	1.901	1.902
10	6.496	1.811	1.782	1.803	1.808
15	10.245	1.723	1.656	1.706	1.716
20	14.375	1.637	1.517	1.611	1.626
25	18.928	1.554	1.364	1.517	1.540
30	23.952	1.474	1.195	1.426	1.457

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1) K. Ito and T. Matsuda, This Bulletin, **42**, 1758 (1969).

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

3) O. F. Olaj, *Ber. Bunsenges. Phys. Chem.*, **69**, 238 (1959).

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

5) O.F. Olaj, *ibid.*, **114**, 1 (1968).

6) M. Munzer, *Angew. Makromol. Chem.*, **11**, 1 (1970).

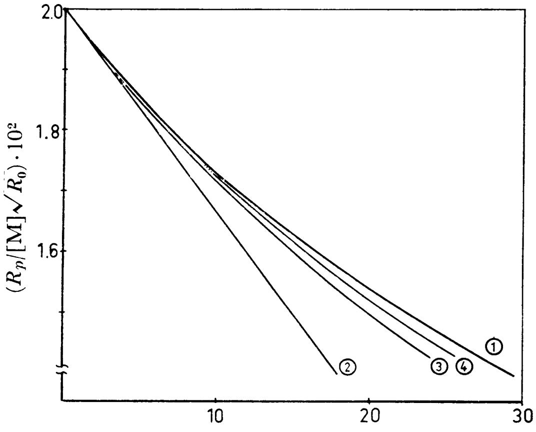

Fig. 1. $R_p/[M]R_0^{0.5}$ (mol$^{-1/2}$ $l^{1/2}$ sec$^{-1/2}$) calculated from given $R_0^{0.5}$ (mol$^{1/2}$ $l^{-1/2}$ sec$^{-1/2}$) values according to the (exact) Eq. (1) (curve 1, plot 1), Eq. (2) (curve 2), Eq. (3) (curve 3), and Eq. (4) (curve 4), plotted *vs.* $R_0^{0.5}$.
$k_ik_p/k_{ti}=1.4\times10^{-4}$ l mol$^{-1}\cdot$sec^{-1}
$k_p^2/k_t=4.10^{-4}$ l mol$^{-1}\cdot$sec^{-1}, $[M]=8.5$ mol l^{-1}

exact Eq. (1) than the Ito-Matsuda equation, Eq. (2). This will be shown in the following discussion.

In order to avoid ambiguity from experimental uncertainties let us assume a theoretical system with $k_p^2/k_t=4.10^{-4}$ l mol$^{-1}\cdot$sec^{-1}, $k_ik_p/k_{ti}=1.4\times10^{-5}$$l\cdot$mol$^{-1}\cdot$sec^{-1}, and $[M]=8.5$ mol l^{-1} (for convenience a constant monomer concentration independent of the initiator concentration is used) which approximately corresponds to the system styrene - AIBN at 50°C. Let us further take a set of $R_p/[M]R_0^{0.5}-R_0^{0.5}$ pairs from the exact Eq. (1). On the other hand we use the same $R_0^{0.5}$ values and calculate the approximate $R_p/[M]R_0^{0.5}$ values according to Eqs. (2) and (3) (Table 1, columns 4 and 5). It can be easily seen from Fig. 1 that the latter (curve 3) deviate by far less from the exact values (curve 1) than Ito and Matsuda's values (curve 2). At a rate of initiation where $R_p/[M]R_0^{0.5}$ is reduced by 10% compared to its value at zero rate of initiation the deviation from the true values is *ca.* 0.45% for Olaj's equation while it amounts to *ca.* 1.65% for Eq. (2), at a 25% reduction of $R_p/[M]R_0^{0.5}$ the deviations are 3.2 and 18%, respectively.

The superiority of Eq. (3) over Eq. (2) can be demonstrated even more clearly in another way. Let us again take the true values from Table 1 and plot them according to the Eqs. (2) *vs.* $R_0^{0.5}$ (Fig. 1, curve 1) and (3) *vs.* R_p (Fig. 2). It appears from first sight that the latter plot (plot 2) is nearly linear, while Ito and Matsuda's plot (plot 1) shows a considerable curvature. Due to the small variation of $R_p/[M]R_0^{0.5}$ with R_p or $R_0^{0.5}$, respectively, the slope as the critical quantity will be comparatively sensitive to experimental error, and a least square treatment of the experimental data is often necessary. Such a treatment, however, will lead to erroneous results even from the theoretical point of view if the (theoretical) linearity of the plot is not warranted to a satisfying degree. On the other hand this difficulty is only partially circumvented if in the awareness of the limited theoretical linearity of the plot data only from low polymerization or initiation rates are used as the slope and therefore the value for k_{ti}/k_ik_p obtained in this way will be subject to considerable error due to the inevitable scatter of the experimental results. The difference between plot 1 and plot 2 becomes evident when the least square treatment is applied to the first six points in Table 1 to obtain the best slope and intercept: while plot 1 (Ito and Matsuda) gives a value of 5.04×10^4 (mol sec l^{-1}) for k_{ti}/k_ik_p which deviates by nearly 30% from the theoretical value (7.143×10^4) the value obtained from plot 2 (Olaj) is correct within 10% (6.44×10^4) which in most cases is less than the experimental uncertainty.

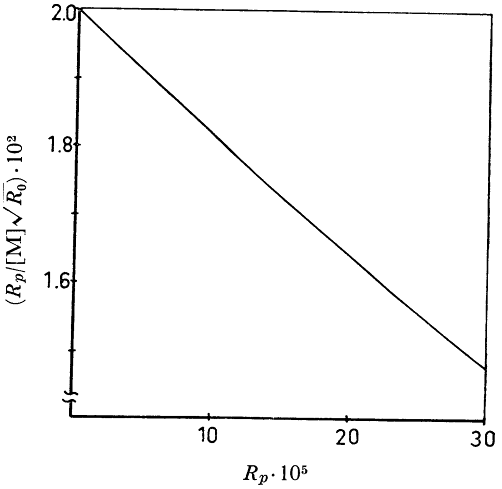

Fig. 2. $R_p/[M]R_0^{0.5}$ (mol$^{-1/2}$ $l^{1/2}$ sec$^{-1/2}$) calculated according to Eq. (1) and plotted *vs.* R_p (mol$\cdot l^{-1}$ sec^{-1}) (plot 2).
(k_ik_t/k_{ti}, k_p^2/k_t, and [M] as in Fig. 1)

Mathematically the superiority of Eq. (3) over Eq. (2) can be explained as follows: When $R_p/A[M][I]^{0.5}(\equiv y)$ is expanded into a series of powers of $R_p\cdot B/[M]^2(\equiv x)$ the exact Eq. (1) will be written as

$$y=1-x+\frac{1}{2}x^2-\frac{1}{2}x^3\cdots \qquad (1a)$$

Ito and Matsuda's Eq. (2) will take the form

$$y=1-x-x^2-\frac{1}{2}x^3\cdots \qquad (2a)$$

while Eq. (3) will give the simple expression

$$y=1-x$$

Whereas the second term is represented correctly by both equations, the deviation from Eq. (1a) in the quadratic term is by far less in Eq. (3a) $(-\frac{1}{2}x^2)$ than in Eq. (2a) $(-\frac{3}{2}x^2)$. Furthermore Eq. (3a) profits from a partial compensation of the deviations in the quadratic and the cubic term.

Following these considerations even further improvements in deriving a linear relationship as an approximation for Eq. (1) are possible,[*1] *e. g.* adding $\frac{1}{4}x^2$ to the right hand side of Eq. (3a) and extracting the square root yields

$$y^{1/2} = 1 - \frac{1}{2}x$$

or as a full expression

$$(R_p/[\mathrm{M}][\mathrm{I}]^{0.5})^{0.5} = A^{0.5} - \frac{1}{2}A^{0.5}B(R_p/[\mathrm{M}]^2) \quad (4)$$

Therefore a plot of $(R_p/[\mathrm{M}][\mathrm{I}]^{0.5})^{0.5}$ *vs.* $R_p[\mathrm{M}]^2$ will give a nearly optimal linear representation of the experimental data provided they obey the kinetic scheme outlined above. From this plot B ($\equiv k_{ti}/k_ik_p$) will be available from a division of double the absolute value of the slope by the intercept, again the knowledge of k_p^2/k_t and $2(1-h)k_d$ being not necessary. $R_p/[\mathrm{M}][\mathrm{I}]^{0.5}$ values calculated according to Eq. (4) using the same kinetic parameters as before are summarized for comparison to the true values in the last column of Table 1 and plotted *vs.* $R_0^{0.5}$ (Fig. 1, curve 4). It can be seen that the deviations are reduced to 0.22 and 1.5% at a rate corresponding to an approximately 10 and 25% reduction of $R_p[\mathrm{M}][\mathrm{I}]^{0.5}$ compared to its value extrapolated to zero polymerization rate, respectively. From these examples it will appear that the fit to the theoretical curve is improved by one order of magnitude compared to the equation derived by Ito and Matsuda.[1] Using the same six $R_p-[\mathrm{I}]^{0.5}$ pairs as before the least square treatment yields a k_{ti}/k_ik_p value which differs from the theoretical one by only 4.2%. This is better by a factor of 7 compared to the result obtained by application of Eq. (2) (plot 1).

After all, there will be no need to analyze primary radical termination using the method proposed by Ito and Matsuda[1] as there exist more accurate procedures which are at least as easily performed.

[*1] A comprehensive survey on these improvements will be given in a separate paper.[7]

7) O. F. Olaj, to be published in *Angew. Makromol. Chem.*