RATE OF TERMINATION IN BULK POLYMERIZATION OF MMA INITIATED BY AIBN AND BPO*

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Introduction

Satisfactory treatments have never been made quantitatively on the acceleration of polymerization rate by radical mechanism. Some people have tried to relate the termination rate constant with viscosity of the reaction system. Though both viscosity and rate constant might be the function of both conversion and initiator concentration, it was difficult to correlate with each other directly.

In this paper, the apparent termination rate constant of the bulk polymerization of methylmethacrylate was measured. Then the rate constant was correlated with conversion and initiator concentration by an empirical equation. Further, a new dispersion model is proposed to extend the conversion range where the polymerization rate can be explained as the radicals are formed and destroyed at identical rates.

1. Correlation of Apparent Termination Rate Constant with Experimental Data

1.1 Apparent rate constant, k_t^*

Under the following assumptions, a set of well known equations have been derived. 1) Rate of radical formation by the thermal decomposition of initiator, v_i , and rate of radical disappearance, v_t , are in a state of balance. 2) Termination rate constant, k_{t0} , initiator efficiency, f , decomposition rate constant, k_d , and propagation rate constant, k_p , are held constant. 3) Chain transfer reaction is neglected. 4) Termination occurs only by second order reaction of radical.

$$\left. \begin{aligned} v_i &= 2fk_d c, & v_p &= k_p (fk_d c/k_{t0})^{1/2} (M) \\ v_t &= 2k_{t0} (R^*)^2, & v_i &= v_t, & k_{t0} &= \text{const} \end{aligned} \right\} \quad (1)$$

$$-c_0^{-1/2} \ln(1-x_i) = 2k_p (2f/k_{t0}k_d)^{1/2} [1 - \exp(-k_d t/2)] \quad (2)$$

$$\begin{aligned} \bar{P}_{nt} &= \int k_p (R^*) (M) dt / \int k_{t0} (R^*)^2 dt \\ &= M_0 x_i / 2f(c_0 - c) \end{aligned} \quad (3)$$

If the assumption, $v_i = v_t$ is valid over the range where the acceleration results from the decrease of reaction rate in the termination step alone, Eq. (4) is given corresponding to Eq. (2).

$$\left. \begin{aligned} v_i &= 2fk_d c, & v_t &= 2k_t^* (R^*)^2 \\ v_p &= k_p (fk_d c/k_{t0})^{1/2} (M) (k_{t0}/k_t^*)^{1/2} \end{aligned} \right\} \quad (4)$$

Eq. (5) is obtained corresponding to Eq. (3), where, x is the observed conversion at reaction time t .

$$\bar{P}_{nt} = M_0 x / 2f(c_0 - c), \quad x = 1 - M/M_0 \quad (5)$$

Combination of Eqs. (2) and (4) gives Eq. (6)

$$dx/dx_i = (1-x)/(1-x_i) \cdot (k_{t0}/k_t^*)^{1/2} \quad (6)$$

where, x_i is the calculated conversion by Eq. (2) at the same reaction time. k_t^* could be calculated, if x and dx/dx_i are observed and x_i is calculated through known values of f , c_0 , k_p and k_{t0} .

Here, k_t^* is defined as an apparent termination rate constant.

1.2 Measurement of conversion and correlation of rate constant with c_0 and x

i) Contraction factor, α Bulk polymerization of MMA was carried out in a sealed glass tube using azo-bis-isobutyronitrile (AIBN) as an initiator. Experimental condition and constituents of monomer are shown in Table 1.

The volume of the tube was about 5cc and the shape of the tube was like a spheroidal so that heat could be removed easily. The temperature was regulated within $\pm 0.1^\circ\text{C}$ around the desired value. The temperature rise at the center of the tube was found to be 3°C from the regulated temperature of the thermostat even at the conversion where acceleration occurs conspicuously.

Dilatometry method was used to measure the conversion. In preparing the calibration curve, the conversion was determined by both gravimetric and double bond analysis.

The relation between x and the volume contraction is shown in Fig. 1. Temperature dependence of α (total volume contraction equivalent to 100% conversion) is shown in Table 2.

Though few reports which cover such wide range of x have been presented, our result is in good agreement with that of Mackay et al.²⁾ in the range of lower conversion.

ii) Determination of f As commercial monomer was used without further purification, induction period was determined first of all. Then the value of f was deter-

Table 1 Experimental condition and constituents of monomer used

Experimental condition			Constituents of monomer	
c :	10^{-3}	10^{-2} (mol/l)	water:	0.002%
T :	50	70 ($^\circ\text{C}$)	free acid:	0.007%
x :	0	0.6 (—)	inhibitor:	0.1 ppm
			purity:	99.6%

Table 2 Dependence of α on temperature

$T(^\circ\text{C})$	50	60	70
α	0.315	0.32	0.33

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Fig. 1 Relation between the observed conversion and the volume contraction at 60°C.

Fig. 3 Comparison between Schulz's data and the conversion calculated by Eq. (11-1)

Fig. 2 Comparison between the observed conversion and the calculated one by Eq. (10-1)

mined by trial and error method by using the following established rate constants for each elemental reaction, under the assumption that the value of f depends only on the kind of initiator.

$$k_a = 1.18(10)^{14} \exp(-30(10)^3/RT), \quad \text{BPO} \quad (7-1)$$

$$k_a = 1.0(10)^{15} \exp(-30.7(10)^3/RT), \quad \text{AIBN} \quad (7-2)$$

$$k_p = 6.6(10)^5 \exp(-4.7(10)^3/RT), \quad \text{MMA} \quad (7-3)$$

$$k_{t0} = 4.9(10)^9 \exp(-0.4(10)^3/RT), \quad \text{MMA} \quad (7-4)$$

The value of f was chosen to be 0.6 and 1.0 for AIBN and BPO respectively.

Dashed lines in **Fig. 2** and **Fig. 3** show the calculated conversion through Eq. (2) using rate constants of Eqs. (7) with the above determined values of f .

iii) **Correlation of k_t^*** Assuming that k_p , k_a and f are independent of c_0 , x and t , and further that over-all resistance of termination reaction is a sum of chemical resistance and diffusional resistance, the following relation is provided.

$$1/k_t^* = 1/k_{t0} + 1/k_{tD} \quad (8)$$

k_t^* was calculated from Eq. (6) using the observed conversion, x , and the value of x_i calculated by Eq. (2) and Eq. (7). $k_{t0}/k_{tD} = k_{t0}/k_t^* - 1$, is supposed to be a function of polymer concentration (that is a function of x), average degree of polymerization, $\bar{P}_{nt}$, initiator concentration, c , temperature, T , and reaction time, t . In the case of constant temperature reaction, x , c and $\bar{P}_{nt}$ depends only on c_0 and t , therefore k_{t0}/k_{tD} becomes a function of c_0 and x . Thus we can write,

$$k_{t0}/k_{tD} = F(c_0, x) \quad (9-1)$$

Plotting k_{t0}/k_{tD} so calculated vs. x , a group of straight lines is obtained with c_0 as a parameter as shown in **Fig. 4**. This suggests that function F in Eq. (9-1) can be written down in the form of $F(c_0, x) = F_1(c_0)x^n$, where dependence of F on c_0 and x is separated. Although the form of F_1 is not entirely clear, it is presumed to be directly proportional to c_0^m from the reason that the value of k_{t0}/k_{tD} at

constant x roughly fell on the straight line when it is plotted vs. c_0 on log-log paper. So that Eq.(9-1) can be converted to Eq.(9-2)

$$k_{t0}/k_{tD} = K_1(c_0)^m(10x)^n \quad (9-2)$$

or, $k_t^*/k_{t0} = 1/[1 + K_1(c_0)^m(10x)^n] \quad (9-3)$

For bulk polymerization of MMA using AIBN ($f=0.6$) as an initiator, the following empirical equations were found to be appropriate.

$$k_{t0}/k_{tD} = 2.3(10)^{-3}(c_0)^{-0.5}(10x)^{6.8}, \text{ at } 60^\circ\text{C} \quad (10-1)$$

$$k_{t0}/k_{tD} = 2.0(10)^{-3}(c_0)^{-0.5}(10x)^{5.0}, \text{ at } 50^\circ\text{C} \quad (10-2)$$

Calculation of Eq. (10-1) are in good agreement with observation as shown in Fig.(2) for example.

The same procedure was applied to Schulz's data⁵⁾ carried out with BPO as the initiator and the similar cor-

relations were obtained as follows.

$$k_{t0}/k_{tD} = 1.27(10)^{-4}c_0^{-0.74}(10x)^{6.8}, \quad 70^\circ\text{C} \quad (11-1)$$

$$k_{t0}/k_{tD} = 8.69(10)^{-3}c_0^{-0.74}(10x)^5, \quad 50^\circ\text{C} \quad (11-2)$$

In Fig. 3 are shown comparison between his observed data and calculation by Eq.(11-1).

Above discussion leads to the conclusion that Eq.(9-2) is a good approximation to apparent termination rate constant, where m (signifies the contribution of c_0) is held almost constant regardless of temperature, but n (signifies the contribution of x) is found to be effected by temperature.

Data reported by Robertson⁴⁾ and Trommsdorff⁵⁾ are correlated by the same procedure.

2. Extension of Stationary State Equation by New Dispersion Model

2-1 Dispersion model

i) A concept Under the usual experimental condition, $\bar{P}_{nt}$ is in the order of 10^3 , which means polymers are much larger in size than a monomer molecule. If the propagating radicals are nearly the same in size with dead polymer, the reaction system is considered as a dispersed one. Propagating polymer radicals and formed polymers bind or adsorb monomers of certain volume per unit chain length. A mixture of polymer and bound monomer is defined as "a swollen polymer" and denoted **SP** herein-after.

Authors suppose four stages of mechanism for diffusion of polymer radicals.

1st stage : $x < x_1$. When the polymer concentration is low, the polymer fluctuates rather unrestrictedly through monomers as a **SP**. So that Eq. (2) may hold good.

2nd stage : $x_1 < x < x_2$. As the reaction proceeds, volume fraction of **SP** reaches high enough to cause **SPs** to be bound one another and the polymer diffuses under the effect of entanglement. Concentration of segment in **SP** may be kept constant and the over all reaction proceeds according as unbound monomers decrease. Diffusivity of **SP** steeply decreases and accelerated reaction begins.

3rd stage : $x_2 < x < x_3$. If the reaction proceeds further, unbound monomer disappears and the whole reaction system apparently becomes a big swollen polymer. In this stage polymers or polymer radicals diffuse through **SP**. The concentration of segment in **SP** increases and bound monomers decrease with the increase in the extent of polymerization reaction.

4th stage : Perhaps the propagation constant varies sharply.

ii) Estimation of the presence of SP Precise data on

Fig. 4 Correlation of k_{t0}/k_{tD} with the observed conversion

Fig. 5 Conceptual diagram for dispersion model

the diffusion of MMA is not available. Fig. 6 shows the variation of diffusivity of benzene with polymer fraction where the diffusivity was calculated from the observed mutual diffusivity of rubber in benzene¹¹. Solid line shows calculated value by applying Bruggeman and Rayleigh equation of electrical diffusivity³³ of benzene, where the diffusion in segment was neglected.

Above polymer concentration of 65%, calculation by Bruggeman's is in good agreement with observed data but apparent diffusivity of benzene in benzene is less than that of benzene in pure liquid benzene. In the range of below 65%, observed diffusivity of benzene is in good agreement with calculation by Rayleigh's assuming that linear SP containing 35% of benzene is dispersed in pure liquid benzene.

From the above consideration, it seems reasonable to estimate that polymer exists as a **SP** in the polymer concentration range below 65% and that the whole system becomes apparently a big SP mass in the concentration range of over 65%. The same situation may be true to PMMA-MMA system.

2.2 Rate equation for 2nd and 3rd stage

i) φ_p , φ_s and α , and their dependence on conversion and temperature From basic balances, the following equations are obtained;

$$\left. \begin{aligned} n_0 - n_t &= n_0 x, & V_0 &= n_0 v_M, & N_t v_s &= k(n_0 - n_t), \\ \varphi_s &= N_t v_s / V_t, & \alpha &= (V_0 - V_t) / V_0 x \end{aligned} \right\} \quad (12)$$

where, V is the volume of reaction system, n the number of monomers, N , the number of segments in the system, v_M , the volume of unit monomer, v_s , the volume of unit segment and subscripts o and t refer to the condition at

Fig. 6 The diffusivity of benzene in a gum-benzene mixture¹¹

$t=0$ and $t=t$, respectively, and then φ_p , φ_s and α are the volume fraction of swollen polymer, that of segment and contraction factor in reaction system, respectively, and the following relation is derived.

$$\begin{aligned} \varphi_s &= k(n_0 - n_t) / v_M n_t + k(n_0 - n_t) \\ &= (1 - \alpha)x / (1 - \alpha x) \end{aligned} \quad (13-1)$$

Denoting the volume fraction of segment in SP to be φ_{sp} , the volume fraction of SP, φ_p , becomes

$$\varphi_p = \varphi_s / \varphi_{sp} = (1 - \alpha / \varphi_{sp})x / (1 - \alpha x) \quad (13-2)$$

ii) Resistance against the diffusion of polymer radicals,

R_D Generally speaking, diffusional resistance of particles suspended in the dispersed system is a function of the shape and the concentration of the particles concerned.

In the 2nd stage, both polymers and radicals exist as a form of SP and fluctuate under the influence of other swollen polymers. The effect of interaction among SP is expected to be approximately proportional to φ_p^2 and the resistance between entangled SPs at the constant concentration may be proportional to the square of intrinsic viscosity of SP which is proportional to $\bar{P}_{nt}^{0.5} \sim \bar{P}_{nt}^{0.6}$ according to Flory's theorem.

In the 3rd stage, un-bound monomers disappear and the whole reaction system apparently becomes a big swollen polymer where segments are dispersed in bound monomers. Therefore the diffusion of polymers or polymer radicals is supposed to be controlled by the size of segment and the mutual hindering among segments. If the size of segments are constant, the resistance to the diffusion of segments will be proportional to the square of their concentration.

Thus, the following relations are provided.

$$\begin{aligned} R_D &\propto \bar{P}_{nt}^{1-1.2} \cdot \varphi_p^2 \\ \therefore R_D &\propto \bar{P}_{nt} \cdot \varphi_p^2, & \text{for 2nd stage} & \quad (14-1) \\ R_D &\propto \varphi_s^2, & \text{for 3rd stage} & \quad (14-2) \end{aligned}$$

φ_{sp} is considered constant in 2nd stage.

ii) Rate equation

$$v_p = k_p(R^*) (M) = k_p(R^*) (M_0) (1 - x) / (1 - \alpha x)$$

if, $k_{td} \ll k_{t0}$,

$$dx/dt = k_p(fk_d/k_{td})^{1/2} (1 - x) / (1 - \alpha x) \quad (15-1)$$

k_{td} in Eq. (8) may be inversely proportional to R_D . Substituting Eq. (14-1) into Eq. (15-1), we have Eq. (15-2) as the rate equation for 2nd stage. Similarly substituting Eq. (14-2) into Eq. (15-1) we have Eq. (15-3) for 3rd stage.

$$dx/dt = K_0 (c/c_0)^{1/2} (1 - c/c_0)^{-1/2} (1 - x) x^{3/2} / (1 - \alpha x)^2 \quad (15-2)$$

$$dx/dt = K_1 c_0^{1/2} (c/c_0)^{1/2} x (1 - x) / (1 - \alpha x)^2 \quad (15-3)$$

where, K_0 , K_1 , are constants determined by k_p , k_d , φ_{sp} , α and other proportional coefficients, and $c/c_0 = e^{-k_d t}$ is the function of t .

2.3 Verification of rate equation by experimental measurements

i) Dependence of x on t and c_0 From Eq. (4), we have

$$dx_i/dt = k_p(fk_d/k_{td})^{1/2} c_0^{1/2} (c/c_0)^{1/2} (1 - x_i) \quad (16)$$

Combining this equation with (15-2), the following expression is obtained for the same c_0 and t ,

$$\frac{(1 - \alpha x)^2}{(1 - x) x^{3/2}} dx \propto c_0^{-1/2} (1 - c/c_0)^{-1/2} \cdot d(-\ln(1 - x)) \quad (17-1)$$

on the other hand, from Eq. (2) we have,

$$c_0^{1/2} (1 - (c/c_0)^{1/2}) \propto -\ln(1 - x_i)$$

therefore, c/c_0 becomes a function of $\ln(1-x_i)$ and the relation between x and $\ln(1-x_i)$ can be obtained.

In the range of, $1 > c/c_0 > 0.8$, $1 - (c/c_0)^{1/2}$ is directly proportional to $1 - c/c_0$. This approximation is nearly true for the reaction range reported by Schulz where BPO was used as an initiator. Thus,

$$\int \frac{(1-\alpha x)^2}{(1-x)x^{3/2}} dx \propto c_0^{-1/4} \int (-\ln(1-x_i))^{-1/2} d(-\ln(1-x_i)) \quad 1 > c/c_0 > 0.8 \quad (17-2)$$

As the function, $(1-\alpha x)/x^{3/2}$, is almost proportional to x^{-2} , the indefinite integral of the left hand side of Eq. (17-2) may be approximated by the following expression.

$$\int \frac{(1-\alpha x)^2}{(1-x)x^{3/2}} dx \doteq I_0 - \left(\frac{1}{(1-\alpha)x} - \ln \frac{x}{1-x} \right) \quad (17-3)$$

where, I_0 is an integral constant.

Fig. 7 shows the correlation of Schulz's data according to Eq. (17-3). It is obvious that in 2nd stage, the linear relation is realized between them and that the critical conversions equivalent to x_1 , x_2 , and x_3 are distinctly recognized.

In the range of $x_1 < x < x_2$, the slope of each straight line varies proportionally to $c_0^{-1/4}$, which precisely agrees with theoretical value, but in the range of $x_2 < x < x_3$, they become nearly equal.

x_1 decreases with the decrease of c_0 . This is considered

reasonably by the fact that $\bar{P}_{nt}$ increases with decrease of c_0 at constant conversion. It is natural that x_2 is constant, because x_2 corresponds to the conversion where unbound monomers just disappear. Furthermore, it is interesting that x_3 is about 0.83, which is equivalent to $\varphi_s = 0.74$ in the case of $\alpha = 0.32$. 0.74 is very close to the value of the solid fraction in the closest packing of uniform spheres.

ii) Apparent termination constant, k_t^* Apparent termination constant is represented by Eq. (6). Combination of Eq. (15-1) with Eq. (15-2) and that of Eq. (15-1) with Eq. (15-3) give the following relations for 2nd and 3rd stages.

$$k_{t0}/k_t^* \propto c_0^{-1} (1 - c/c_0)^{-1} x^3 / (1 - \alpha x)^4 \quad (18-1)$$

$$k_{t0}/k_t^* \propto x^2 / (1 - \alpha x)^4, \quad \text{for 2nd stage} \quad (18-2)$$

and from the rate equations, are derived

$$(1 - c/c_0) \doteq \left(\int \frac{(1-\alpha x)^2}{(1-x)x^{3/2}} dx + I_0 \right)^2, \quad 1 > c/c_0 > 0.8, \quad \text{for 2nd stage} \quad (18-3)$$

$$c_0^{1/2} (1 - c/c_0) \doteq \left(\int \frac{(1-\alpha x)^2}{x(1-x)} dx + I_1 \right), \quad 1 > c/c_0 > 0.8, \quad \text{for 3rd stage} \quad (18-4)$$

where I_0, I_1 , are integral constants.

The right hand side of both equations are the only function of x which means that the dependence of k_{t0}/k_t^* on c_0 in 2nd stage apparently varies from c_0^{-1} to $c_0^{-1/2}$. Though the right hand side of Eq. (18-3) is affected by

Fig. 7 Correlation of Schulz's data according to Eq. (17)

the value of x_1 and x_2 , its numerical calculation decrease roughly with $x^{1.4} \sim x^{2.0}$.

Namely k_{t0}/k_t^* varies with $x^6 \sim x^{7.2}$. The results of these qualitative discussions agree with the empirical equation (11-1).

Summary

Under the assumption that $v_i = v_t$ is valid over the conversion range where the accelerated reaction occurs and that all the rate constants are kept constant except termination rate constant, the apparent termination rate constant, k_t^* , was correlated empirically with conversion, x , and initial concentration of initiator, c_0 , by Eqs. (9-2) and (9-3). Such direct correlation of k_t^* with c_0 and x was found to be better than that with viscosity of the reaction system.

Besides, authors proposed new dispersion model to explain the contribution of diffusion to polymerization reaction, where the mechanism of diffusion of polymer radicals in reaction system was divided into four stages. The rate equations, (15-2) and (15-3) were derived based on Eqs. (14) for 2nd and 3rd stages respectively.

Schulz's data were correlated and the empirical correlations obtained in Section 1 were also explained through the theoretical analysis.

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Nomenclature

c, c_0 = initiator concentration at $t=t$ and $t=0$, respectively [mol/l]

f = initiator efficiency [—]
 I_0, I_1 = integral constants
 K_0, K_1 = proportional coefficients
 k_d = thermo decomposition rate constant of initiator [1/sec]
 k_p, k_{t0} = propagation and termination rate constant, respectively [l/mol·sec]
 k_t^* = apparent termination rate constant defined by Eq.(2) [l/mol·sec]
 k_{tD} = defined by Eq.(8) [l/mol·sec]
 M, M_0 = monomer concentration at $t=t$ and $t=0$ [mol/l] or [g/100ml]
 $\bar{P}_{nt}$ = number average degree of polymerization at $t=t$ [—]
 R = gas constant
 R^* = Concentration of radicals [mol/l]
 R_D = diffusional resistance of propagating radicals
 SP = "Swollen Polymer" defined in 2-1
 T = temperature [°C]
 t = reaction time [sec] or [min]
 v_i, v_p, v_t = radical initiation, polymer propagation and radical disappearance rate, respectively [mol/l·sec]
 x, x_i = observed conversion and conversion calculated by Eq.(2) [—]
 α = contraction factor defined in 1-2, i) [—]
 $\varphi_p, \varphi_s, \varphi_{sp}$ = concentration of swollen polymer, of segment and of segment in swollen polymer, respectively [—]
 others = $k, N_t, n_0, n_t, V_0, V_t, v_M$ and v_s are mentioned under Eqs.(12) and (13-1)

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FLUID AND PARTICLE DISPERSION IN FLUID-BED REACTORS*

—Experimental Investigations by Steady Heat-transfer and Steady Back-mixing of Adsorptive Gases—

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1. Introduction

The phenomenon of fluid mixing in fluid-bed reactors is related closely to the behaviour of the beds, particularly when such rate processes as heat- and mass-transfer and adsorption are superposed on catalytic reaction between

reactant fluid and catalyst particles, and has been investigated by several workers^{2-5, 9, 12-17, 20}.

As for the mixing processes of bed particles, the works performed so far are rather confined to the topics on making clear the mechanisms of particle mixing or its fluid dynamic influence on fluid mixing, and little has been known about the influence of particle movement on the rate processes taking place in the beds. This means that the rate equations developed to describe the rate processes such as catalytic reaction or mass transfer usually do not include the influence of diffusive and convective

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