

THE OVERALL KINETICS OF FREE RADICAL (CO)POLYMERIZATION WITH HIGHLY DIFFUSION CONTROLLED TERMINATION

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ABSTRACT

The overall reaction rate kinetics of polymerization of diethyleneglycol dimethacrylate and copolymerization of it with styrene in bulk and in the presence of inert diluents were investigated. The results indicated that these reactions can be treated as free radical polymerization with highly diffusion controlled termination reaction in which the termination rate constant is an empirically derived function of monomer conversion: $K_t = K_{t_0} (1 - c \ln[M]/[M_0])^{-1}$ in which K_{t_0} is the initial termination rate constant and c is a factor related to the magnitude of diffusion control. The following equation of monomer conversion as a function of time could then be derived: $U = 1 - \exp \{1/c [1 - (1 + ckt/2)^2]\}$ in which $k = K_p (R_i/2K_{t_0})^{1/2}$ and t is the time of reaction. Excellent agreement between the theoretical and experimental overall reaction kinetic curves was obtained. The equation is valid for crosslinking and noncrosslinking free radical polymerizations in which the self-acceleration effect is effective from the very beginning of the reaction. The equation can be expressed in a more generally applicable form: $U = 1 - \exp\{1/c[1 - (1 + c^*t/n)^n]\}$ in which $n \geq 0$.

INTRODUCTION

The kinetics of free radical (co)polymerization has been the subject of numerous interesting investigations and the classical kinetic equation has been an important contribution in interpreting the kinetic behavior and characteristics of the initial stage of the reaction. However, the overall kinetics of free radical polymerization remains a subject of significance that is still to be explored.

From a kinetical point of view, one of the most important reasons which accounts for the deviations between the classical treatment and the actual overall kinetics is the highly diffusion controlled nature of the termination reaction. The termination rate constant tends to decrease with increasing viscosity of the reaction medium whereas the reaction rate is relatively increased. Although many investigations have been accomplished, but from a practical point of view some problems are still to be solved. The acceleration of the rate of polymerization^[1] and the decrease of the termination rate constant^[2] with the increase of viscosity of the reaction medium were investigated. The dependence of the termination rate constant on the flexibility of the polymer chains was reported^[3], and, the relationships between termination rate constant and chain radical length^[4, 5], or, and molecular weight^[6] were derived. These

results were important contributions to solution of the overall rate expression but are rather laborious in practice. Moreover, several other exponential equations^[7] of the rate of polymerization have been suggested which are but the extended versions of the classical rate equation.

For convenience, the monomer conversion-time curves of free radical polymerizations can be considered to be divided into three categories (Fig. 1).

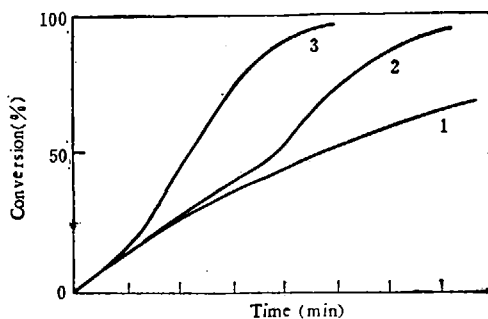


Fig. 1 Common conversion-time curves of radical polymerization

1. Faint autoacceleration in overall reaction;
2. Marked autoacceleration from the middle of reaction;
3. Obvious autoacceleration from the beginning of reaction.

Curves 1 and 2 related to polymerizations in which the termination rates are not or only a little affected by diffusion controlled effects, while obvious diffusion controlled terminations take place from the very beginning of polymerizations represented by curve 3. Bulk polymerizations forming rigid polymer chains^[8,9], precipitation polymerizations^[10], emulsion polymerizations^[11] and crosslinking polymerizations^[12, 13] are in some cases likely to belong to the last category and the crosslinking polymerizations are most typical examples thereof.

EXPERIMENTAL

Diethyleneglycol dimethacrylate (DEGDM) is purified by column chromatography (silica gel column). The purified divinyl monomer is polymerized and copolymerized with styrene using AIBN as the initiator. The copolymerizations are carried out with different styrene/DEGDM ratios. The reactions are conducted in bulk or in the presence of equal amounts of inert solvents (toluene or iso-octanol) at $60 \pm 0.5^\circ\text{C}$. All the reactions are carried out in sealed ampoules. Prior to polymerization, the reaction mixtures are degassed under vacuum by several freeze-thaw cycles with liquid nitrogen.

The reaction samples are stopped at different times of reaction with rapid quench in liquid nitrogen. Residual monomer is extracted with carbon disulfide and quantitated by gas chromatography on an OV-1 column.

RESULTS AND DISCUSSION

1. Crosslinking polymerizations of DEGDM

The retarded termination effect in highly diffusion controlled polymerizations should be

taken in consideration from the beginning of the reaction. Obviously, the retardation of the terminations is mainly determined by the increase of the viscosity of the reaction medium. Under present experimental conditions the viscosity is in turn determined by the monomer conversion. The termination rate constant can therefore be expressed as a function of the latter.

$$K_t = K_{t_0} f([M] / [M_0]) \quad (1)$$

in which K_{t_0} is the initial termination rate constant. $[M] / [M_0]$ is the ratio of the instantaneous and initial monomer concentrations.

The motion of the mobile monomer molecules are less affected by the increase of the viscosity of the reaction medium and it can be assumed that the propagation rate constant K_p is not affected by the diffusion effects of the reaction medium. The classical rate equation can therefore be written as the following overall rate equation:

$$-\frac{d[M]}{dt} = K_p \left(\frac{R_i}{2K_{t_0}} \right)^{\frac{1}{2}} \left[f \left(\frac{[M]}{[M_0]} \right) \right]^{-\frac{1}{2}} [M] \quad (2)$$

where R_i is the rate of initiation and under general conditions is considered to be constant.

The diffusion control function $f([M] / [M_0])$ must satisfy the following conditions:

1. $f \left(\frac{[M]}{[M_0]} \right) = 1$ when $\frac{[M]}{[M_0]} = 1$
2. $f \left(\frac{[M]}{[M_0]} \right)$ decreases with decreasing values of $\frac{[M]}{[M_0]}$
3. The integral form of eq. (2) should be consistent with conditions:

$$\left. \frac{[M]}{[M_0]} \right|_{t=0} = 1 \quad \text{and} \quad \left. \frac{[M]}{[M_0]} \right|_{t=\infty} = 0$$

According to the shape of the experimental conversion curves the authors obtained an empirical but simple relationship for the function $f \left(\frac{[M]}{[M_0]} \right)$ which satisfies the above-mentioned conditions:

$$f \left(\frac{[M]}{[M_0]} \right) = \left(1 - c \ln \frac{[M]}{[M_0]} \right)^{-1} \quad (3)$$

c is the diffusion control factor; its magnitude implies to the degree of the diffusion effect.

When $k = K_p \left(\frac{R_i}{2K_{t_0}} \right)^{\frac{1}{2}}$ and substituting eq. (3) into eq. (2):

$$-\frac{d[M]}{dt} = k \left(1 - c \ln \frac{[M]}{[M_0]} \right)^{\frac{1}{2}} [M] \quad (4)$$

is obtained.

Integrating eq. (4) and let the monomer conversion $u = 1 - \frac{[M]}{[M_0]}$, then

$$u = 1 - \exp \left\{ \frac{1}{c} \left[1 - \left(1 + \frac{1}{2} c k t \right)^2 \right] \right\} \quad (5)$$

Substitution of the appropriate values of k and c in eq. (5) will yield monomer conversion curves which are very close to the experimental curves. The experimental and calculated curves of DEGDM polymerization in bulk and in the presence of inert solvents are shown in

Figs. 2, 3, 4. k can be measured from the initial slope of the experimental curve and c is further simulated from the experimental curve.

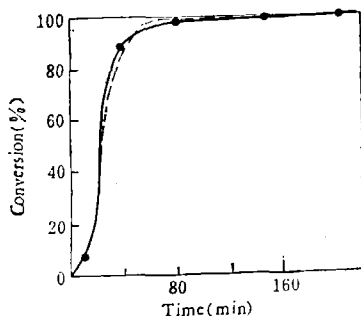


Fig. 2 Bulk polymerization of DEGDM

— Exp.; --- Cal.
 $k = 0.0041$; $c = 250$.

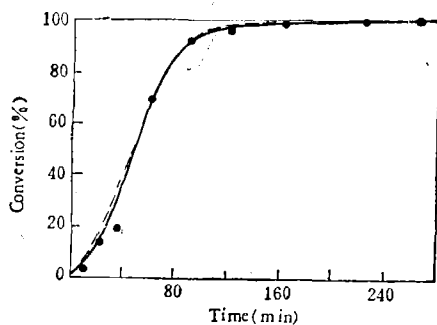


Fig. 3 Solution polymerization of DEGDM in toluene

— Exp.; --- Cal.
 $k = 0.0024$; $c = 180$.

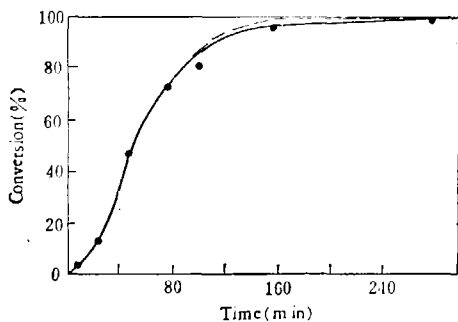


Fig. 4 Solution polymerization of DEGDM in iso-octanol

— Exp.; --- Cal.
 $k = 0.0024$; $c = 150$.

2. Crosslinking copolymerization

Considering the diffusion effects on the termination rates of copolymerizations, the copoly-

merization of vinyl and divinyl monomers can be approached by the classical rate equation by allowing the necessary modifications of K_t in eqs. (1) and (3). The reaction rate equation for each monomer can then be derived as follows:

$$-d[S]/dt = K_{ss}[S][S\cdot] + K_{ds}[D\cdot][S] \quad (6)$$

$$-d[D]/dt = 2K_{sd}[S\cdot][D] + 2K_{dd}[D\cdot][D] \quad (7)$$

Under steady state conditions the following equations should hold:

$$K_{ds}[D\cdot][S] = 2K_{sd}[S\cdot][D] \quad (8)$$

$$R_i = 2K_{tss}[S\cdot]^2 + 2K_{tsd}[S\cdot][D\cdot] + 2K_{tdd}[D\cdot]^2 \quad (9)$$

$K_{t_{ij}}$ is the termination rate constant between an i and j terminated radical. By eliminating the radical concentrations, the following equation is obtained.

$$-\frac{d[S]}{dt} = K_{ss} \left(\frac{R_i}{2K_{tss}} \right)^{\frac{1}{2}} [S] \left\{ \frac{1 + \frac{2}{r_s} \frac{[D]}{[S]}}{\left[1 + \frac{K_{tsd}}{2K_{tss}} \frac{K_{ss}}{K_{dd}} \frac{r_d}{r_s} \frac{[D]}{[S]} + \frac{K_{tdd}}{4K_{tss}} \left(\frac{K_{ss}}{K_{dd}} \frac{r_d}{r_s} \frac{[D]}{[S]} \right)^2 \right]^{\frac{1}{2}}} \right\} \quad (10)$$

From which it can be seen that the rate of styrene in copolymerization is equal to its homopolymerization rate multiplied by the factor in braces denoted as P_s . Substitution of eqs. (1) and (3) into (10) and let

$$k_s = K_{ss} \left(\frac{R_i}{2K_{tss}} \right)^{\frac{1}{2}}$$

$$\text{then} \quad -\frac{d[S]}{dt} = k_s \left[1 - c_s \ln \frac{[S]}{[S_0]} \right]^{\frac{1}{2}} [S] P_s \quad (11)$$

is obtained.

Similarly, a rate equation for DEGDM can be obtained from eqs. (7)–(9).

$$-\frac{d[D]}{dt} = 2K_{dd} \left(\frac{R_i}{2K_{tdd}} \right)^{\frac{1}{2}} [D] \left\{ \frac{1 + \frac{1}{2r_d} \frac{[S]}{[D]}}{\left[1 + \frac{1}{2} \frac{K_{tsd}}{K_{tdd}} \frac{K_{dd}}{K_{ss}} \frac{r_s}{r_d} \frac{[S]}{[D]} + \frac{1}{4} \frac{K_{tss}}{K_{tdd}} \left(\frac{K_{dd}}{K_{ss}} \frac{r_s}{r_d} \frac{[S]}{[D]} \right)^2 \right]^{\frac{1}{2}}} \right\} \quad (12)$$

Substitution of eqs. (1) and (3) into (12) and let

$$k_d = 2K_{dd} \left(\frac{R_i}{2K_{tdd}} \right)^{\frac{1}{2}}$$

$$\text{then} \quad -\frac{d[D]}{dt} = k_d \left[1 - c_d \ln \frac{[D]}{[D_0]} \right]^{\frac{1}{2}} [D] P_d \quad (13)$$

is obtained in which P_d stands for the factor in braces in eq. (12)

P_s and P_d are both functions of the monomer ratio and are therefore functions of the monomer conversion. In our previous paper^[14] the reactivity ratios of styrene and DEGDM were determined to be $r_s \approx 0.54$ and $r_d = 1.85$. K_{ss} and K_{dd} are calculated from the initial slopes of the homopolymerizations of styrene and DEGDM from which $\frac{K_{ss}}{K_{dd}} \approx 0.8$ is obtained (assuming that under the same experimental conditions the R_i and K_t values of both the reactions are equal). In addition, in the case of highly diffusion controlled termina-

tions, K_t depends mainly on the diffusion coefficient of the macromolecule as a whole and is not dependent on the chemical nature of the two radicals^[4, 5]. It can therefore be assumed that the three termination rate constants are nearly equal. This is shown in Fig. 5 in which P_S and P_D are given as a function of the monomer ratio, and of monomer conversion. It can be seen that P_S and P_D change only to a small extent with $[S]/[D]$ and with monomer conversion. In fact, even within K_{SS}/K_{DD} values of 0–1.5, P_S and P_D are only within a narrow range close to unity. The variation tendencies of P_S and P_D are consistent with that of $(1 - c \ln [M]/[M_0])^{1/2}$ (Fig. 6).

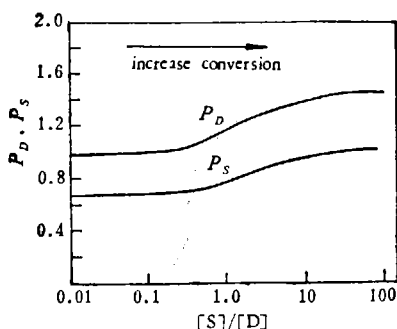


Fig. 5 P_S and P_D versus $[S]/[D]$ when $K_{SS}/K_{DD}=0.8$

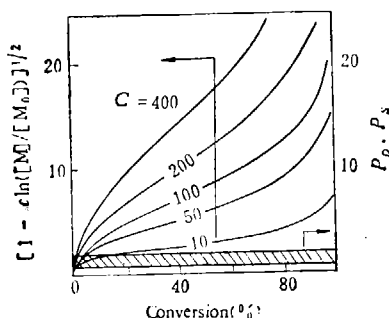


Fig. 6 Comparison of variations of the diffusion control function and P_S or P_D

This implies that multiplication of the monomer function with either P_S or P_D will not alter the $1 - c \ln \frac{[M]}{[M_0]}$ function but will more or less alter the k and c values of the kinetic rate equation. Therefore eqs. (11) and (13) can be written as:

$$-\frac{d[S]}{dt} = K_S \left(1 - C_S \ln \frac{[S]}{[S_0]} \right)^{1/2} [S] \quad (14)$$

$$-\frac{d[D]}{dt} = K_D \left(1 - C_D \ln \frac{[D]}{[D_0]} \right)^{1/2} [D] \quad (15)$$

where K_S , C_S , K_D and C_D are constants which come from k_S , c_S , k_D and c_D of eqs. (11) and (13) affected by P_S and P_D . This indicates that the kinetic behavior of the two monomers in copolymerization is similar to that of DEGDM homopolymerization. Similar results

have been reported by Hubca^[15].

Eqs. (14) and (15) are in fact the same as eq. (4). In their integral form, K and C can be determined to define the overall kinetic behavior of the copolymerization of divinyl and vinyl monomers (Fig. 7—15).

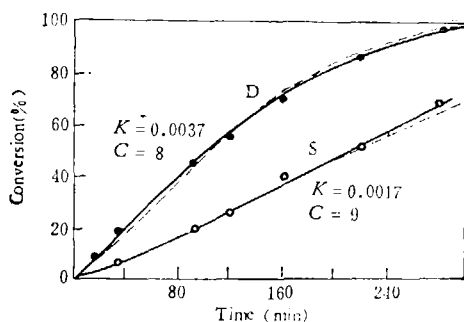


Fig. 7 Bulk copolymerization of styrene and DEGDM (5% wt).

— Exp.; ---- Cal.

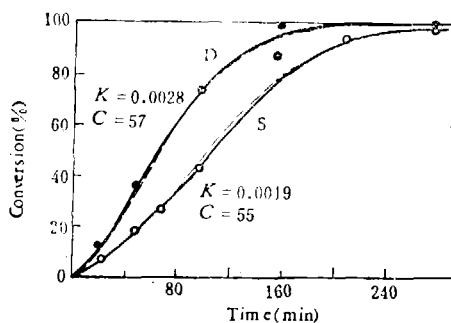


Fig. 8 Bulk copolymerization of styrene and DEGDM (20% wt)

— Exp.; ---- Cal.

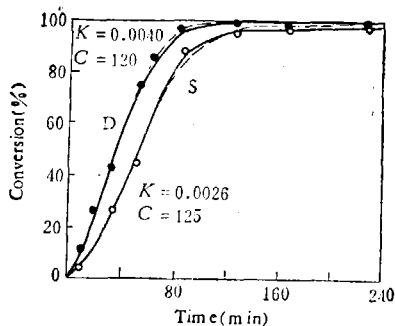


Fig. 9 Bulk copolymerization of styrene and DEGDM (50% wt)

— Exp.; ---- Cal.

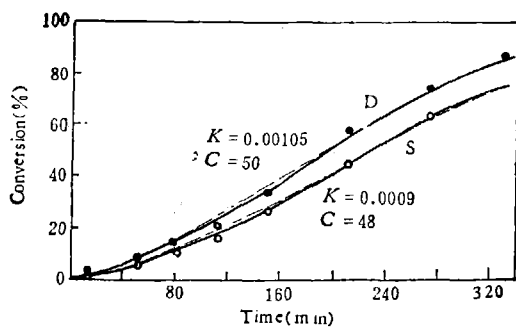


Fig. 10 Solution copolymerization of styrene and DEGDM (35% wt) in toluene
— Exp.; ---- Cal.

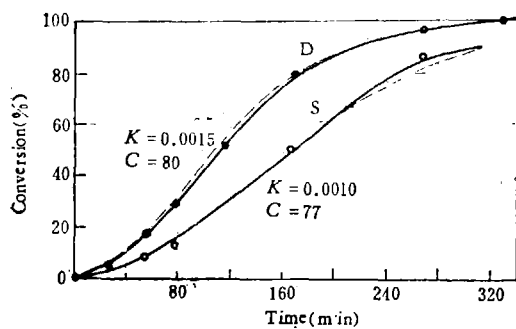


Fig. 11 Solution copolymerization of styrene and DEGDM (50% wt) in toluene.
— Exp.; ---- Cal.

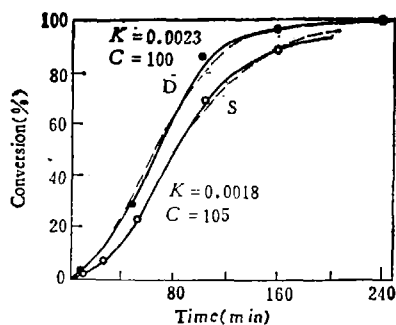


Fig. 12 Solution copolymerization of styrene and DEGDM (80% wt) in toluene
— Exp.; ---- Cal.

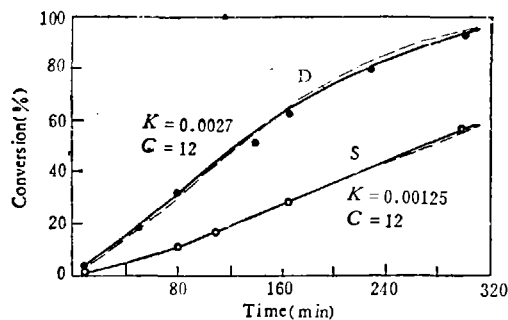


Fig. 13 Solution copolymerization of styrene and DEGDM (10% wt) in iso-octanol
— Exp.; ---- Cal.

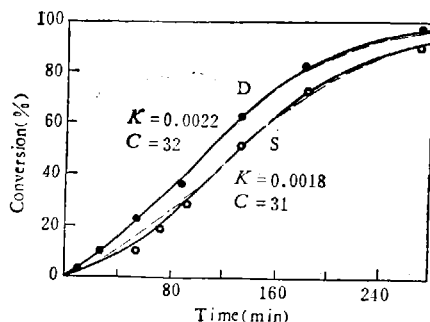


Fig. 14 Solution copolymerization of styrene and DEGDM (20% wt) in iso-octanol
— Exp.; ---- Cal.

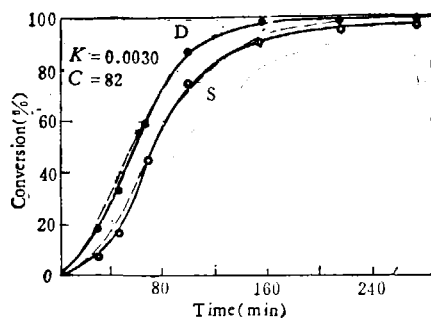


Fig. 15 Solution copolymerization of styrene and DEGDM (50% wt) in iso-octanol
— Exp.; ---- Cal.
 $K = 0.0022$; $C = 85$.

3. The copolymerization kinetic equation

Within certain limits, the values of k and c (or K and C) are mutually matched for the appropriate values. Experimental deviations during the evaluation of the k (K) value from an initial slope are compensated by adequate c (C) value from the monomer conversion curve. For instance, too large or too small value of k (K) will be compensated by comparatively

smaller or larger c (C) value. The experimental curves are therefore in fair agreement with the calculated ones. However, the parameter c (C) has its own characteristic behavior, c (C) increases with increasing divinyl monomer concentration and decreases upon the addition of solvent.

As C expresses the degree of diffusion control on the termination, it can be assumed that within the same copolymerization system C_s and C_D are approximately equal. This has been experimentally verified (Figs. 7–15).

Therefore, in the copolymerization of DEGDM and styrene, the following equation should hold for equal conversion values of styrene and DEGDM respectively:

$$\frac{1}{C_s} \left[1 - \left(1 + \frac{C_s K_s}{2} t_s \right)^2 \right] = \frac{1}{C_D} \left[1 - \left(1 + \frac{C_D K_D}{2} t_D \right)^2 \right] \quad (16)$$

where t_s and t_D are the reaction time of the respective monomers at which equal conversion is arrived. It follows then that:

$$\frac{K_s}{K_D} = \frac{t_D}{t_s} \quad (17)$$

This indicates that at equal conversion of the respective monomers, the ratio of the reaction time is a constant which is approximately the ratio of the initial slopes of the individual conversion curves (Table 1).

Table 1 Comparison between t_s/t_D at different conversion levels and K_D/K_s

Conversion (%)	10	20	30	40	50	60	70	80	90	$\frac{K_D}{K_s}$
System*	t_s/t_D									
5B	2.50	2.40	2.15	2.18	2.20	2.05	1.88			2.18
20B	1.50	1.49	1.48	1.61	1.62	1.55	1.56	1.48	1.51	1.47
50B	1.61	1.50	1.54	1.52	1.54	1.47	1.41	1.42	1.44	1.54
35T	1.23	1.19	1.18	1.13	1.17	1.18	1.17	1.14		1.17
50T	1.50	1.58	1.56	1.51	1.49	1.47	1.45	1.41		1.50
80T	1.29	1.26	1.20	1.21	1.19	1.18	1.26			1.28
10I	2.33	2.18	2.21	2.29	2.12	2.12	2.08			2.16
20I	1.57	1.43	1.26	1.33	1.35	1.29	1.24	1.25	1.23	1.22
50I	1.75	1.56	1.43	1.38	1.31	1.28	1.31	1.29	1.35	1.36

* The numbers are concentration of DEGDM (% wt); B, polymerizations in bulk; T, in toluene; I, in iso-octanol.

CONCLUSION

The obtained rate equation (eq. (4)) is not only in good agreement with almost all polymerizations with highly diffusion controlled termination such as in the copolymerizations of styrene with divinylbenzene^[13], but it is also useful to describe the kinetic behaviour of reactions where

autoacceleration is observed from the very beginning of the reaction^[8, 9, 16-18]. Eq. (3) can be written in a more generalized form:

$$f\left(\frac{[M]}{[M_0]}\right) = \left(1 - c \ln \frac{[M]}{[M_0]}\right)^{-x} \quad (x \geq 0) \quad (18)$$

then

$$-\frac{d[M]}{dt} = k \left(1 - c \ln \frac{[M]}{[M_0]}\right)^{x/2} [M] \quad (19)$$

$$u = 1 - \exp\left\{\frac{1}{c} \left[1 - \left(1 + \frac{1}{n} ckt\right)^n\right]\right\} \quad \left(n = \frac{2}{2-x} \text{ and } x < 2\right) \quad (20)$$

Eq. (20) has a wider scope of application than eq. (4).

For polymerizations with a glass effect in the last stage of reaction, the monomer conversions cannot be carried out through the end. For such reactions, the residual monomer content should be subtracted and the equation should then be written as:

$$u = u_{\max} - \exp\left\{\frac{1}{c} \left[1 - \left(1 + \frac{1}{n} ckt\right)^n\right]\right\} \quad (21)$$

For reactions with an induction period the time of induction should be subtracted from the actual time of reaction.

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