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CONVERSION-TIME CURVES IN THE DIFFUSION-CONTROLLED FREE RADICAL POLYMERIZATION OF STYRENE

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Abstract—In order to calculate conversion-time curve in radical polymerization, the termination rate constant for interacting polymer radicals with chain lengths n and s is written as: $k_{t,ns} = k(\zeta_n + \zeta_s)$ where $k \propto \exp(-0.40/v_f)$ (v_f: free volume), and $\zeta = 1$ at $n \leqslant n_c$ and $\zeta = (n_c/n)^{1.5}$ at $n \geqslant n_c + 1$ (n_c: a critical chain length of polymer moving by reptation). The curves are applicable to the experimental data obtained from 20°C to 154°C in the thermal polymerization of styrene. Further, it is shown that the curves can be applied to the experimental data for polymerization in the presence of initiator.

NOMENCLATURE

$k_{t,ns}$	rate constant of termination between polymer radicals with chain lengths n and s
k	rate constant between segment radicals
ζ_n	function depending on n
n_c	critical chain length of polymer moving by reptation
n_{co}	n_c in an undiluted polymer solution
b	constants
γ	overlap factor
v^*	critical free volume sufficient to permit a segment to jump
v_f	free volume ($v_f = v_{fg}$ at $x = x_g$)
R	gas constant
T	temperature
T_{gm}	glass-transition temperature of monomer
T_{gp}	glass-transition temperature of polymer
$\bar{p}_w$	instantaneous weight-average degree of polymerization
$\bar{P}_n$	integrated number-average degree of polymerization
$\bar{P}_w$	integrated weight-average degree of polymerization
d_m	density of monomer
d_p	density of polymer
$\bar{k}_t$	average termination rate constant ($\bar{k}_t = \bar{k}_{to}$ at $t = 0$)
k_p	propagation rate constant
k_{th}	thermal initiation rate constant
k_d	decomposition rate constant of initiator
f	initiator efficiency
k_{trM}	rate constant of chain transfer to monomer
C_{tr}	chain transfer constants
$Q(x)$	a function depending on x in terms of chain transfer
t	time
x	conversion
x_g	x at a gel point (an adjustable parameter)
x_{trp}	a critical conversion at which the instantaneous molecular weight abruptly increases with increasing x under the condition of predominant transfer
x_s	x at which all the rates become diffusion-controlled
c	volume fraction of polymer
$\bar{k}_g$	$\bar{k}$ (see Eqn 5) at x_g
[M]	monomer concentration ([M] = [M]$_o$ at $t = 0$)
[N_n]	concentration of polymer radical with n units
[N]	total concentration of polymer radical
[C]	initiator concentration ([C] = [C]$_o$ at $t = 0$)
R_p	polymerization rate

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INTRODUCTION

Since the autoacceleration of polymerization was discovered by Tromsdorff [1], many workers have attempted its theoretical explanation [2–5]. It was considered that termination rate is important to explain the autoacceleration [6]. On the assumption that termination is diffusion-controlled, the author introduced the effect of free volume into a formula for termination, as shown by [7]:

$$k_t \propto k = \text{const}[\exp(-\gamma v^*/v_f)] \tag{1}$$

However, because the analysis using the free volume theory alone is insufficient to model diffusion-controlled termination, it was considered that the termination rate depends also on chain length [8]. Further, it was pointed out that a treatment of such dependence considering chain entanglement is better [9]. To treat quantitatively x–t curves in terms of chain entanglements, Cardenas and O'Driscoll [2] considered a formula for termination rate described by the unit step function. Martin and Hamielec [10] presented a model containing molecular weight-dependence through the cumulative weight-average molecular weight. Soh and Sundberg [3] discussed critically these models and proposed a new model. In view of Eqn (1) and the chain length dependence according to the author's model [4, 11] and the Soh and Sundberg model [3], termination rate is generalized as [7]:

$$k_{t,ns} = k(\zeta_n + \zeta_s) \tag{2}$$

where:

$$\zeta_n \begin{cases} = 1 & \text{at} \quad n \leqslant n_c \\ = (n_c/n)^b & \text{at} \quad n \geqslant n_c + 1 \end{cases} \tag{3}$$

The author [11] used Eqn (3) on the basis of reptation theory to calculate molecular weight. However, in spite of unobserved dependence of specific rate of propagation on conversion below 80% [14], the rate was considered to be dependent on conversion. In view of the diffusion-controlled theory [3, 4], such

slow rates as the propagation rate constant would be independent of conversion, except in very highly viscous media in the final stages of polymerization. The model based on Eqns (1)–(3) was applied to the experimental data reported previously [3] with $b = 2.4$ on the basis of Bueche's theory [12] and $\gamma v^* = 1.0$. However, the x–t curves calculated deviated considerably from the experimental data for the polymerization of styrene.

In the present paper, the value, $\gamma v^* = 0.40$ obtained before [22, 23], is re-examined. This value and $b = 1.5$, based on reptation theory [13], are used to compute x–t curves, which are then compared with the experimental data for the thermal polymerization of styrene and for the bulk polymerization of styrene initiated chemically.

MATHEMATICAL PROCEDURE TO OBTAIN x–t CURVES

On the basis of Eqn (2), an average of termination rate becomes [3, 4, 11]

$$\bar{k}_t = 2k\bar{k} \tag{4}$$

where

$$\bar{k} = \sum_{n=1}^{\infty} \zeta_n X_n \quad (X_n = [\mathrm{N}_n]/[\mathrm{N}]) \tag{5}$$

(1) Predominant chain transfer

In this case, the distribution function is [15]:

$$X_n = C_{tr}/(1 + C_{tr})^n \tag{6}$$

When inequality (7) is satisfied, Eqn (4) is reduced to Eqn (8).

$$n_c C_{tr} \ll 1 \tag{7}$$

$$\ln(\bar{k}_t c^{\delta}) = \text{const} - \gamma v^*/v_f \tag{8}$$

When inequality (7) is not satisfied, the value of $\bar{k}$ must be calculated by:

$$\bar{k} = \sum_{n=1}^{n_c} X_n + \sum_{n=n_c+1}^{\infty} (n_c/n)^b X_n$$

$$= C_{tr}\left[\sum_{n=1}^{n_c} 1/(1+C_{tr})^n + \sum_{n=n_c+1}^{\infty} (n_c/n)^b/(1+C_{tr})^n\right] \tag{9}$$

Here, Eqn (9) is solved numerically. That is, an appropriate guessed value $\bar{k}_1$ is used. The computation based on Eqn (9) yields a better estimate of $\bar{k}_2$. Repeating such computation causes $\bar{k}_j$ to converge to the converged $\bar{k}$. To obtain a valid x–t curve, the calculation is repeated till the following convergence criteria are satisfied.

$$(n_c/n)^b/(1 + C_{tr})^n < 10^{-5} \tag{10}$$

$$|\bar{k}_{j+1}/\bar{k}_j - 1| < 10^{-5} \tag{11}$$

In the past, to treat the kinetics at high conversion for the thermal polymerization of styrene, initiation rates, second-order [16] and third-order [17] in monomer were considered. In a previous paper [18], the author confirmed the validity of the third-order initiation rate. Thus, in the present paper, the x–t curves are calculated on the basis of third-order initiation. The appropriate rate expression follows:

$$\mathrm{d}x/\mathrm{d}t \begin{cases} = A_{1o}(1-x)^{5/2}/(1-\epsilon x)^{1/5} \\ \quad \text{at} \quad x \leqslant x_g & (12a) \\ = A_1[\exp(\gamma v^*/2v_f)](1-x)^{5/2}/[\bar{k}(1-\epsilon x)]^{1/2} \\ \quad \text{at} \quad x \geqslant x_g & (12b) \end{cases}$$

where:

$$A_{1o} = [(k_p^2 k_{th})^{1/2}/\bar{k}_{to}]\{[\mathrm{M}]_o^{3/2}(1-\epsilon)\} \tag{13}$$

$$A_1 = A_{1o}(\bar{k}_g)^{1/2}[\exp(-\gamma v^*/2v_{fg})] \tag{14}$$

$$\epsilon = 1 - d_m/d_p \tag{15}$$

In the above, the calculation of A_1 is automatically carried out setting $(\mathrm{d}x/\mathrm{d}t)$ at $x = x_g$ in Eqn (12a) equal to $(\mathrm{d}x/\mathrm{d}t)$ in Eqn (12b), in the computer program. Here, x_g is a gel point and corresponds to the conversion where termination becomes diffusion-controlled. To obtain a valid x–t curve, a precise value of x_g must be estimated. However, such a precise value could not be calculated by any theories reported previously [19, 20]. Thus, in the present paper, x_g is used as an adjustable parameter, as shown in [3].

(2) Usual polymerization system

In this case, x–t curve is calculated by:

$$\mathrm{d}x/\mathrm{d}t \begin{cases} = A_{2o}[\mathrm{C}]^{1/2}(1-x)(1-\epsilon x) \\ \quad \text{at} \quad x \leqslant x_g & (16a) \\ = A_2([\mathrm{C}]/\bar{k})^{1/2}[\exp(\gamma v^*/2v_f)](1-x)(1-\epsilon x) \\ \quad \text{at} \quad x_g \leqslant x \leqslant x_s & (16b) \end{cases}$$

where:

$$A_{2o} = [2fk_d k_p^2/\bar{k}_{to}(1-\epsilon)]^{1/2} \tag{17}$$

$$A_2 = A_{2o}(\bar{k}_g)^{1/2}[\exp(-\gamma v^*/2\,v_{fg})] \tag{18}$$

The calculation of A_2 is carried out setting $(\mathrm{d}x/\mathrm{d}t)$ at $x = x_g$ in Eqn (16a) equal to that in Eqn (16b). The value of $\bar{k}$ is obtained by solving Eqn (5), where X_n is described as:

$$X_n = F(n) \Big/ \sum_{n=1}^{\infty} F(n) \tag{19}$$

$$F(n) = 1 \Big/ \prod_{n=1}^{n} g(n) \tag{20}$$

$$g(n) = 1 + C_{tr} + h(1 + \zeta_n/\bar{k}) \tag{21}$$

$$h = \{[\mathrm{C}]\bar{k}/(1-\epsilon)\}^{1/2}(fk_d/A_2[\mathrm{M}])$$
$$\exp(-\gamma v^*/2v_f) \tag{22}$$

In the past, the author proposed the method of calculation of the value of $\bar{k}$ when h is given [11]. In Soh and Sundberg's method [3], the resultant master curve for $\bar{k}(=Z$ in their terminology) was made. Essentially, both methods are the same. Here, to obtain the value of $\bar{k}$, the calculation is repeated until inequalitites (11) and (23) are satisfied.

$$(n_c/n)^b F(n) < 10^{-5} \tag{23}$$

In the above, n_c can be calculated by [3, 4, 11]:

$$n_c = n_{co}/c^{\delta} \tag{24}$$

To compute ϵ and c, the values of d_m and d_p in [21] are used.

DISCUSSION

(1) Thermal polymerization

Usually, chain transfer predominates in the thermal polymerization of styrene [15]. Situations when chain transfer predominated at 20°C [22] and 100°C [18] were studied. In the present paper, the data at 60 and 154°C are also shown in Figs 1 and 2, where they were obtained by the procedures as described previously [24]. Below a critical conversion x_{trp}, transfer predominates and its constant is estimated by [4, 18, 22]:

$$2/\bar{p}_w = C_{tr1} + C_{tr2}Q(x) \tag{25}$$

where $\bar{p}_w = \mathrm{d}(\bar{P}_w x)/\mathrm{d}x$ is estimated from the slope of the line in Figs 1 and 2, inequality (26) being satisfied.

$$C_{tr1} \gg C_{tr2}Q(x) \tag{26}$$

At conversions below x_{trp}, instantaneous molecular weight is independent of x (Figs 1 and 2). Beyond x_{trp}, it increases with increasing x, where x_{trp} is higher at higher temperature. The independence below x_{trp} shows that chain transfer to monomer and the Diels–Alder adduct intermediate predominates [25]. Hui and Hamielec [25] carried out thermal polymerization above 100°C, but did not observe increase of molecular weight over the whole range of conversion. The molecular weight of polymer obtained at 100°C was about 6.7×10^5 which is in very good agreement with the value of 6.8×10^5 below $x_{trp} = 0.9$ [18]. The points above may be explained in view of (A) and/or (B). (A) If chain transfer to the Diels–Alder adduct intermediate predominates [25], its concentration in the present system was less than that in the Hui and Hamielec system. Thus, above x_{trp}, the transfer rate to monomer becomes comparable with that to the intermediate. Then, the increase of molecular weight might be detected. (B) The value for C_{tr1} [23] is in good agreement with that obtained previously [24], as transfer constant to monomer. If transfer to monomer predominates when $x < x_{trp}$, the increase of molecular weight with increasing x when $x > x_{trp}$ might show that transfer to polymer is not negligible, that is, the branched polymer may be formed, as estimated in [18, 22]. Relationship between C_{tr1} and T is shown in Fig. 3 and written as:

$$C_{tr1} = 11.9 \exp(-7830/RT) \tag{27}$$

Setting $Q(x_{trp}) = x_{trp}/(1 - x_{trp})$, a linear relationship between $\ln[x_{trp}/(1 - x_{trp})]$ and $1/T$ is obtained (Fig. 3). Thus, x_{trp} is given by:

$$x_{trp} = 1/[1 + 0.000262 \exp(2290/T)] \tag{28}$$

This equation will be discussed for more experimental work in terms of (A) and/or (B). Beyond x_{trp}, the instantaneous molecular weight increases with the increase in conversion. Thus, the present methods should be precise below x_{trp} and are approximate above x_{trp}. The experimental data for conversion at given time are shown in Fig. 4 (60°C), Fig. 5 (100) [18] and Fig. 6 (154). To re-examine the value as $\gamma v^* = 0.40$ [22, 24], Eqn (8) is rewritten as:

$$\ln([\mathrm{M}]^5 c^{1.25}/R_p^2) = \text{const} - \gamma v^*/v_f \tag{29}$$

This equation is applied to the data for 60°C (Fig. 7). Here v_f is calculated [4, 22, 24, 26]:

$$v_f = [25 + 0.48(T - T_{gp})]c + [25 + T - T_{gm}](1 - c)/1000 \tag{30}$$

$$T_{gp} = 100 - 1.8 \times 10^5/(104\,\bar{P}_n) \tag{31}$$

where $T_{gm} = -88.2$°C and $\bar{P}_n = 1/C_{tr1}$ (Table 1). A good linear relationship is obtained for $x > 0.25$,

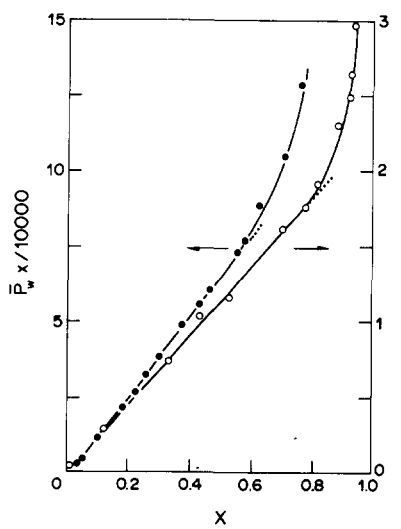

Fig. 1. Relationship between $\bar{P}_w x$ and x at 20°C (●) [23] and 60°C (○) (the present data).

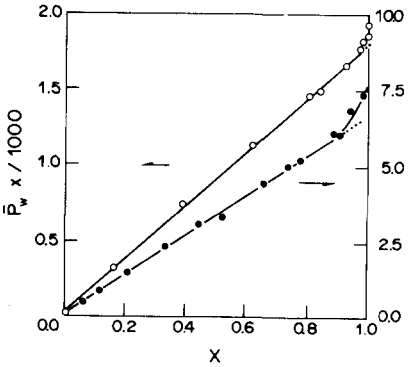

Fig. 2. Relationship between $\bar{P}_w x$ and x at 100°C (●) [18] and 154°C (○) (the present data).

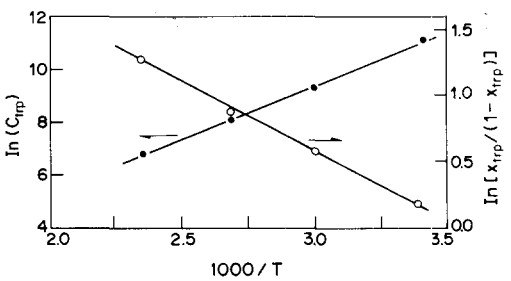

Fig. 3. Relationship between C_{tr} (●) or x_{trP} (○) and T.

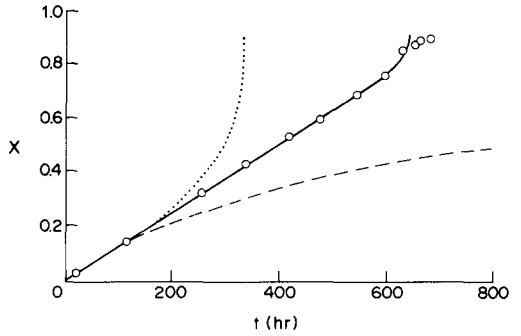

Fig. 4. The x–t curves at 60°C in thermal polymerization of styrene. ○: experimental data obtained by the method reported earlier [4, 22]; ——: $b = 1.5$ and $\gamma v^* = 0.40$; – – –: $b = 0$ and $v^* = 0$; · · · ·: $b = 2.4$ and $\gamma v^* = 1.0$ with v_f given in [3].

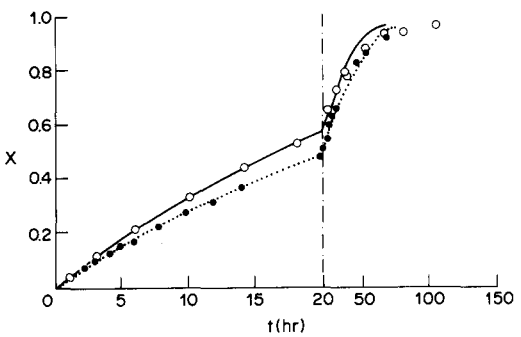

Fig. 5. The x–t curve at 100°C in thermal polymerization of styrene. ○: The experimental data in [8] and ●: those in [25]; ——: the x–t curve calculated using Eqn (12) when $A_{1o} = 0.0444$ and · · · ·: that when $A_{1o} = 0.0376$.

where inequality (7) should be satisfied. The slope of the line is found to be $\gamma v^* = 0.40$ at $\delta = 1.25$. The value of 0.40 is the same as obtained previously [22, 24] and the other value of 1.25 shows that polymer radicals move by reptation [27]. With increasing temperature, the conversion range, in which inequality (7) is satisfied, becomes narrow, because

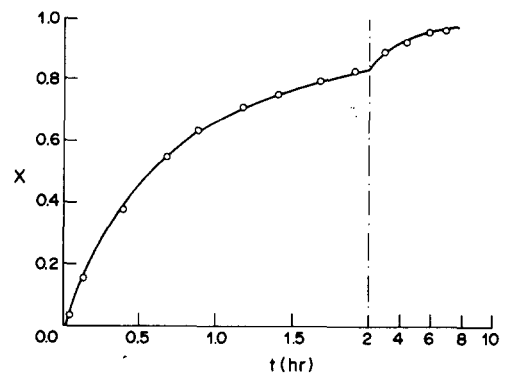

Fig. 6. The x–t curve at 154°C in thermal polymerization of styrene. ○: Experimental data obtained by the method reported previously [4, 22]; ——: $b = 1.5$ and $\gamma v^* = 0.40$.

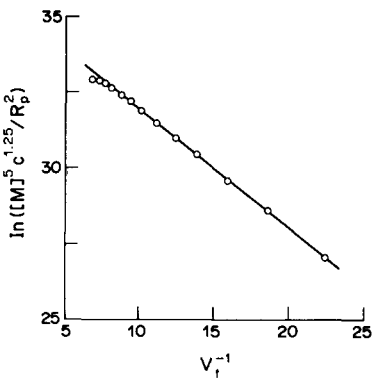

Fig. 7. Estimation of the value of γv^* by Eqn (29) where the experimental data in Fig. 4 are used.

the molecular weight of polymer formed decreases. Thus, the application of Eqn (29) may not be useful and, then, all the experimental data are treated by Eqn (12) with $\gamma v^* = 0.40$, $b = 1.5$ [13], $\delta = 1.25$ and $n_{co} = 300$ [4, 20, 22, 28]. The other values used to compute the x–t curves are shown in Table 1. The curve calculated for 60°C fits all the experimental data (Fig. 4) below 90%. The curves calculated with $\delta v^* = 1.0$ and $b = 2.4$ [3] give poor fits for any chosen x_g. The reason is that the x–t curve with $\gamma v^* = 0$ and $b = 0$ [3] deviates from them above 12% and that with $\gamma v^* = 1$ and $b = 2.4$ also deviates from them above 20% (Fig. 4). The curve calculated by Eqn (12) with $\gamma v^* = 0.40$ and $b = 1.5$ fits the experimental data at 100°C, where the deviation is slight above 90% (Fig. 5). The data obtained at 100°C by Hui and Hamielec are also shown in Fig. 5 and are close to the present data. To fit Eqn (12), A_{1o} is changed from 0.0444 (this work) to 0.0376 for their data, where the other values are held. The fit is quite good. Further, the fit of the curve to the experimental data at 154°C is excellent, as shown in Fig. 6. It is concluded that the x–t curve calculated with $\gamma v^* = 0.40$ and $b = 1.5$ is applicable to the data obtained from 20°C [22] to 154°C.

(2) Polymerization in the presence of initiator

The data obtained for polymerization of styrene initiated by 2,2′-azobisisobutyronitrile (AIBN) at 45°C [8] and 60°C [30] are analyzed by Eqn (16) [8]. The number-average degree of polymerization of polymer formed is above 288, as shown in Tables 2 and 3. Thus, the value of T_{gp} is between 94 and 100°C. The degree of polymerization obtained by integrating the kinetic chain length $\{= k_p[M][N]/(k\bar{k}[N]^2 +$

Table 1. For the calculation of x–t curve in polymerization of styrene

Temp (°C)	A_{1o} (hr^{-1})	$10^5 C_{tr1}$	x_g	x_{trp}
45		5.0		0.74†
60	0.001508	8.67	0.12*	0.80
100	0.0444	29.0	0.125*	0.90
	(0.0376)‡			
154	1.650	110	0.125*	0.95

*For thermal polymerization.
†Calculated by Eqn (21).
‡For the analysis of the data in [25].

Table 2. For the calculation of x–t curve in the polymerization of styrene initiated by AIBN at 45°C [8]

$[C]_o$ (mol l^{-1})	x_g	$\bar{P}_n$ at x_g
0.2	0.34	430
0.1	0.275	636
0.05	0.24	915
0.025	0.22	1296
0.0125	0.20	1813

$k_d = 0.00397\ hr^{-1}$ [32]; $f = 0.545$ [8]; $A_{2o} = 0.937\ l^{1/2}\ mol^{-1/2}\ hr^{-1}$; $x_s = 0.9$.

$k_{trM}[M][N])\}$ is used for $\bar{P}_n$. This may be acceptable because the number-average degree of polymerization would not be affected by the dependence of termination rate on chain length [11, 29]. Even if there is slight error in this calculation of $\bar{P}_n$, the error in v_f should be negligible because of the narrow interval being less than 6°C. The values to compute x–t curve are shown in Tables 1–3. All the calculated curves fit the experimental data well (Figs 8 and 9). The fit is better than that shown before [3]. The adjustable parameter x_g as a gel point increases with increasing molecular weight at given temperature (Tables 2 and 3). The onset of the gel effect occurs at lower conversions with increasing molecular weight. Therefore, the x_g corresponds qualitatively to the onset of the gel effect.

In the final stage of polymerization, the propagation displacement of the radical on the polymer may be important. Further, propagation rate and initiator efficiency may be diffusion-controlled. Here, some modifications of the previous reports [3, 4, 11] are shown as follows. Termination rate may be written by:

$$k_t (\propto k_p[M])\alpha(1-x)\exp(-\gamma v^*/v_f) \qquad (32)$$

Table 3. For the calculation of x–t curve in the polymerization of styrene initiated by AIBN at 60°C [30]

$[C]_o$ (mol $l^{-1/2}$)	x_g	$\bar{P}_n$ at x_g
0.0992	0.40	289
0.0268	0.21	600
0.0164	0.20	768
0.0858	0.18	1060

$k_d = 0.0356\ hr^{-1}$ [32]; $f = 0.60$ [33]; $A_{2o} = 1.382\ l^{1/2}\ mol^{-1/2}\ hr^{-1/2}$; $x_s = 0.9$.

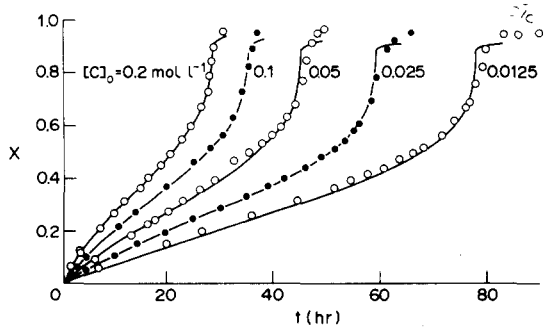

Fig. 8. The x–t curves (——) calculated using Eqns (16) and (34) and the experimental data (○ or ●) in the polymerization of styrene initiated by AIBN at 45°C [8].

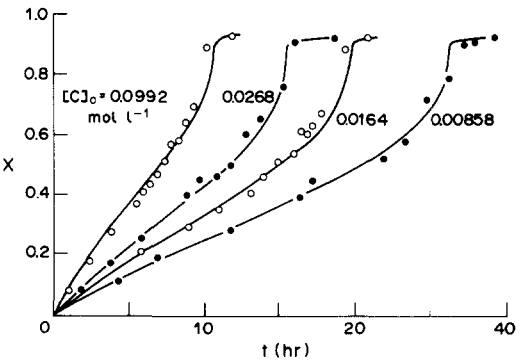

Fig. 9. The x–t curves (——) calculated using Eqns (16) and (34) and the experimental data (○ or ●) in the polymerization of styrene initiated by AIBN at 60°C [31].

If the initiator efficiency is diffusion-controlled [30], it may be also written as [4]:

$$f \propto \exp(-\gamma v^*/v_f) \qquad (33)$$

Then, dx/dt may be written as:

$$dx/dt = A_3(1-x)^2(1-\epsilon x)\exp(-2\gamma v^*/v_f) \quad \text{at} \quad x > x_s \qquad (34)$$

The x–t curves are calculated with the value of A_3 obtained when (dx/dt) at $x = x_s$ in Eqn (16b) is equal to that in Eqn (34) and shown in Figs 8 and 9. It is interesting that $2\gamma v^* = 0.80$ in Eqn (34) is approximated to 0.826 $(= A - B/2$ using the terminology in [10]).

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