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Polymer 43 (2002) 4859–4867

polymer

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Modeling of the bulk free radical polymerization up to high conversion—three stage polymerization model. II. Number-average molecular weight and apparent initiator efficiency

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Received 9 November 2001; received in revised form 26 March 2002; accepted 27 March 2002

Abstract

The equations for predicting the number-average molecular weight are derived on the basis of the three stage polymerization model (TSPM) in this paper. By applying the equations, a plotting approach is proposed to determine the apparent initiator efficiency defined as $f[(\alpha_{td} + 1)/2]$ and the constant of chain transfer to monomer, where f is the initiator efficiency and α_{td} denotes the fraction of the termination rate constants by disproportionation. Using the approach to plot the experimental data in the literature, it is found that the chain transfer to monomer can be neglected for both methylmethacrylate (MMA) and styrene (St) polymerizations, but it can exert a significant effect on ethylmethacrylate (EMA) polymerization. In addition, the apparent initiator efficiency is found to be independent of reaction temperature and initiator concentration at each stage. The values of $f[(\alpha_{td} + 1)/2]$ at gel effect stage are slightly reduced as compared with that at low conversion stage for MMA and EMA polymerizations. However, it decreases significantly at gel effect stage for St polymerization. Using the equations derived and the apparent initiator efficiencies obtained from TSPM plots, the number-average molecular weights at different conversions can be predicted. Comparisons show that the agreement between predictions and experimental data is satisfactory.

Keywords: Apparent initiator efficiency; Chain transfer to monomer; Number-average molecular weight

1. Introduction

In order to predict the number-average molecular weight, it is necessary to know the constants of chain transfer to monomer and to initiator, the initiator efficiency and the reaction rate constants. Unfortunately, there were only some data available in the literature for low conversion and almost no such data for high conversion. Some investigators [1,2] considered the initiator efficiency to be a constant throughout the polymerization. However, a theoretical study of Russell et al. [3] on initiator efficiency showed that the initiator efficiency at intermediate conversion was slightly reduced compared to that at low conversion and it was decreased drastically in many orders of magnitude when the conversion was beyond a certain conversion. Since the conclusion of Russell et al. [3] was examined only by methylmethacrylate (MMA) bulk polymerization at 50 °C, it is very important to know whether the conclusion is applicable for different reaction temperatures and other monomer systems. Again, a recent study by Tefera et al. [4] also showed that it was necessary to consider the rapid decrease of initiator efficiency at high conversion. Relatively, the viewpoints on chain transfer to monomer and to initiator were consistent with each other in the literature. It was found that the chain transfer to initiator could be neglected when azobisisobutyronitrile (AIBN) was used as initiator [5]. The chain transfer to MMA and styrene (St) could also be neglected [5], but the chain transfer to ethylmethacrylate (EMA) might exert a significant effect on EMA polymerization [6]. However, it is still unknown whether the constants of chain transfer to monomer are about the same at different polymerization stages since there are no such experimental data available in the literature.

In order to study the variation of the number-average molecular weight with conversions and the questions mentioned earlier, the equations to predict the number-average molecular weight will be derived in this paper based on the three stage polymerization model (TSPM) [7]. In addition, an approach is proposed to determine the

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PII: S0032-3861(02)00243-4

Nomenclature

C_m	constant of chain transfer to monomer
f	initiator efficiency
f'	apparent initiator efficiency
$[I]$	initiator concentration (mol/l)
$[I]_0$	initial initiator concentration (mol/l)
k_d	initiator decomposition rate constant (min^{-1})
k_p	chain propagation rate constant (l/mol min)
k_{tc}	chain termination rate constant by combination (l/mol min)
k_{td}	chain termination rate constant by disproportionation (l/mol min)
$k_{tr,m}$	rate constant of chain transfer to monomer (l/mol min)
K	overall reaction rate constant
$[M]$	monomer concentration (mol/l)
$[M]_0$	initial monomer concentration (mol/l)
$[M^*]$	free radical concentration (mol/l)
$\bar{M}_{n1,x=x1}$	cumulative number-average molecular weight at $x = x_1$
$\bar{M}_{n2,x=x2}$	cumulative number-average molecular weight at $x = x_2$
r_m	monomer density (g/l)
R_i	chain initiation reaction rate (mol/l min)
R_p	chain propagation reaction rate (mol/l min)
R_{tc}	chain termination reaction rate by combination (mol/l min)
R_{td}	chain termination reaction rate by disproportionation (mol/l min)
$R_{tr,m}$	reaction rate of chain transfer to monomer (mol/l min)
t	temperature (°C)
x	conversion
x_1	critical conversion transferred from low conversion stage to gel effect stage
x_2	critical conversion transferred from gel effect stage to glass effect stage
w	molecular weight of monomer
α_{td}	fraction of chain termination rate constant by disproportionation
θ	time (min)
θ_1	time transferred from low conversion stage to gel effect stage (min)
θ_2	time transferred from gel effect stage to glass effect stage (min)

Subscripts

1	low conversion stage
2	gel effect stage
3	glass effect stage

apparent initiator efficiency and the constant of chain transfer to monomer at different polymerization stages.

2. Equations for predicting number-average molecular weight

According to the TSPM [7], the equations for predicting the number-average molecular weight can be derived based on the kinetic mechanism of classical free radical polymerization. The following is an example to illustrate the derivations of such equation for free radical bulk polymerization using AIBN as initiator.

Based on the theory of classical free radical polymerization, the cumulative number-average molecular weight, $\bar{M}_n$, is given by

$$\bar{M}_n = \bar{P}_n w \tag{1}$$

where w is the molecular weight of the monomer and $\bar{P}_n$ is the cumulative number-average polymerization degree which can be expressed as

$$\frac{1}{\bar{P}_n} = \frac{\int_{[M]_0}^{[M]} \frac{1}{p_n}\mathrm{d}[M]}{-\{[M]_0 - [M]\}} \tag{2}$$

Since the chain transfer to initiator can be neglected for the case of the initiator AIBN [5], the instantaneous number-average polymerization degree, p_n, can be given by

$$\begin{aligned}\frac{1}{p_n} &= \frac{(R_{tc}/2) + R_{td} + R_{tr,m}}{R_p}\\ &= \frac{(k_{tc} + 2k_{td})[M^*]^2 + k_{tr,m}[M^*][M]}{k_p[M^*][M]}\\ &= \frac{(k_{tc} + 2k_{td})[M^*]}{k_p[M]} + \frac{k_{tr,m}}{k_p}\end{aligned} \tag{3}$$

where R_{tc} and R_{td} are the chain termination rates by combination and disproportionation, respectively, $R_{tr,m}$ is the chain transfer rate to monomer and R_p is the chain propagation rate.

According to the quasi-steady-state approximation for free radical concentrations, the chain initiation rate, R_i, should be equal to chain termination rate, R_t, therefore

$$R_i = 2fk_d[I] = R_t = R_{tc} + R_{td} = 2(k_{tc} + k_{td})[M^*]^2 \tag{4}$$

By using Eq. (4) to eliminate $[M^*]$, Eq. (3) turns to

$$\frac{1}{p_n} = \frac{(k_{tc} + 2k_{td})}{k_p}\left(\frac{fk_d}{k_{tc} + k_{td}}\right)^{1/2}[I]^{1/2}\frac{1}{[M]} + \frac{k_{tr,m}}{k_p} \tag{5}$$

The equations for predicting the cumulative number-average molecular weight $\bar{M}_n$ at three stages of polymerization can be derived on the basis of the TSPM [7] as in the following sections.

2.1. Low conversion stage ($x \leq x_1$)

For the low conversion stage, the following equations were obtained in Part (1) of this study [7]

$$-\ln(1-x) = -K_1[\exp(-k_d\theta/2) - 1] \tag{6}$$

and

$$[I] = [I]_0 \exp(k_d\theta) \tag{7}$$

According to the definition of K_1 in Part (1) of this study [7] and by considering that the chain termination consisted of two parts, combination and disproportionation, K_1 can be rewritten as

$$K_1 = k_{p1}\left(\frac{f_1 k_d}{k_{tc1} + k_{td1}}\right)^{1/2}[I]_0^{1/2}\left(\frac{2}{k_d}\right) \tag{8}$$

Rearranging Eq. (8) yields

$$\left(\frac{f_1 k_d}{k_{tc1} + k_{td1}}\right)^{1/2}[I]_0^{1/2} = \frac{K_1 k_d}{2k_{p1}} \tag{9}$$

Substituting Eqs. (6), (7) and (9) into Eq. (5) gives

$$\frac{1}{p_{n1}} = \frac{k_d(k_{tc1} + 2k_{td1})}{2k_{p1}^2[M]}\left(K_1 + \ln\frac{[M]}{[M]_0}\right) + C_{m1} \tag{10}$$

where $C_{m1} = k_{tr,m1}/k_{p1}$.

After being squared and rearranged, Eq. (8) can be rewritten as

$$\frac{k_{p1}^2}{k_d} = \frac{K_1^2}{4f_1[I]_0}(k_{tc1} + k_{td1}) \tag{11}$$

By defining that $\alpha_{td1} = k_{td1}/(k_{tc1} + k_{td1})$ and considering that $\alpha_{tc1} = 1 - \alpha_{td1}$, the following equation is obtained.

$$k_{tc1} + 2k_{td1} = (k_{tc1} + k_{td1})(\alpha_{td1} + 1) \tag{12}$$

Substituting Eqs. (11) and (12) into Eq. (10) yields

$$\frac{1}{p_{n1}} = \frac{2f_1(\alpha_{td1} + 1)[I]_0}{K_1^2[M]}\left(K_1 + \ln\frac{[M]}{[M]_0}\right) + C_{m1} \tag{13}$$

Based on Eqs. (1), (2) and (13), and defining an apparent initiator efficiency at low conversion stage, $f'_1 = f_1[(\alpha_{td1} + 1)/2]$, an equation for calculating the cumulative number-average molecular weight $\bar{M}_{n1}$ can be obtained

$$\frac{1}{\bar{M}_{n1}} = \frac{1}{\bar{P}_{n1}w} = \frac{\int_{[M]_0}^{[M]}\frac{1}{p_{n1}}\,\mathrm{d}[M]}{-([M]_0 - [M])} = f'\phi_1 + \frac{C_{m1}}{w} \tag{14}$$

where ϕ_1 is defined as

$$\phi_1 = \frac{4[I]_0}{K_1[M]_0 w}\frac{-\ln(1-x)}{x} + \frac{2[I]_0}{K_1^2[M]_0 w}\frac{-\ln^2(1-x)}{x} \tag{15}$$

It is observed from Eq. (14) that the plot of $1/\bar{M}_{n1}$ vs. ϕ_1 should be a straight line. The slope of the straight line is f'_1 and the intercept is C_{m1}/w.

2.2. Gel effect stage ($x_1 \leq x \leq x_2$)

For the gel effect stage, Eq. (2) can be rewritten as

$$\frac{1}{\bar{P}_{n2}} = \frac{\int_{[M]_0}^{[M]_1}\frac{1}{p_{n1}}\,\mathrm{d}[M] + \int_{[M]_1}^{[M]}\frac{1}{p_{n2}}\,\mathrm{d}[M]}{-([M]_0 - [M])} \tag{16}$$

Similarly, the following equation was obtained at gel effect stage in Part (1) of this study [7].

$$-\ln(1-x) = -\ln(1-x_1) - K_2[\exp(-k_d\theta/2) - \exp(-k_d\theta_1/2)] \tag{17}$$

Using Eq. (6), the following equation can be obtained

$$\exp(-k_d\theta_1/2) = 1 + \frac{\ln\frac{[M]_1}{[M]_0}}{K_1} = 1 + \frac{\ln(1-x_1)}{K_1} \tag{18}$$

By applying Eq. (17) and a similar way as for the low conversion stage, the instantaneous number-average polymerization degree at this stage, p_{n2}, may be given by

$$\frac{1}{p_{n2}} = \frac{(R_{tc2}/2) + R_{td2} + R_{tr,m2}}{R_{p2}} = \frac{2f_2(\alpha_{td2} + 1)[I]_0}{K_2[M]}\left(1 + \frac{\ln(1-x_1)}{K_1} + \frac{\ln\frac{[M]}{[M]_1}}{K_2}\right) + C_{m2} \tag{19}$$

where $\alpha_{td2} = k_{td2}/(k_{tc2} + k_{d2})$ and $C_{m2} = k_{tr,m2}/k_{p2}$.

As it has been done for the low conversion stage, by combining Eqs. (1), (13), (16) and (19), and defining an apparent initiator efficiency, $f'_2 = f_2[(\alpha_{td2} + 1)/2]$, an equation for calculating the cumulative number-average molecular weight at gel stage, $\bar{M}_{n2}$, can be obtained as follows

$$\begin{aligned}\frac{1}{\bar{M}_{n2}} = \frac{1}{\bar{P}_{n2}w} = &\left[\frac{4f'_1[I]_0}{K_1[M]_0 w}\frac{-\ln(1-x_1)}{x} + \frac{2f'_1[I]_0}{K_1^2[M]_0 w}\frac{-\ln^2(1-x_1)}{x} + \frac{C_{m1}}{w}\frac{x_1}{x}\right] \\ &+ \left\{\frac{4f'_2[I]_0}{K_2[M]_0 w}\left[1 + \frac{\ln(1-x_1)}{K_1}\right]\frac{-\ln\left(\frac{1-x}{1-x_1}\right)}{x} + \frac{2f'_2[I]_0}{K_2^2[M]_0 w}\frac{-\ln^2\left(\frac{1-x}{1-x_1}\right)}{x} + \frac{C_{m2}}{w}\frac{x-x_1}{x}\right\}\end{aligned} \tag{20}$$

By applying Eq. (14), the cumulative number-average molecular weight at the transit point from low conversion stage to gel effect stage, $\bar{M}_{\mathrm{n}1,x=x1}$, can be expressed as

$$\frac{1}{\bar{M}_{\mathrm{n}1,x=x1}} = \frac{4f'_1[I]_0}{K_1[M]_0 w}\,\frac{-\ln(1-x_1)}{x_1} + \frac{2f'_1[I]_0}{K_1^2[M]_0 w}\,\frac{-\ln^2(1-x_1)}{x_1} + \frac{C_{\mathrm{m}1}}{w} \qquad (21)$$

Substituting Eq. (19) into Eq. (18) yields

$$\frac{1}{\bar{M}_{\mathrm{n}2}}\,\frac{x}{x-x_1} - \frac{1}{\bar{M}_{\mathrm{n}1,x=x1}}\,\frac{x_1}{x-x_1} = f'_2\phi_2 + \frac{C_{\mathrm{m}2}}{w} \qquad (22)$$

where ϕ_2 is defined as

$$\phi_2 = \frac{4[I]_0}{K_2[M]_0 w}\left[1 + \frac{\ln(1-x)}{K_1}\right]\frac{-\ln\left(\dfrac{1-x}{1-x_1}\right)}{x-x_1} + \frac{2[I]_0}{K_2^2[M]_0 w}\,\frac{-\ln^2\left(\dfrac{1-x}{1-x_1}\right)}{x-x_1} \qquad (23)$$

As expected by Eq. (22), the experimental data at gel effect stage should also be dropped on a straight line in a plot of $(1/\bar{M}_{\mathrm{n}2})(x/(x-x_1)) - (1/\bar{M}_{\mathrm{n}1,x=x1})(x_1/(x-x_1))$ vs. ϕ_2, in which the slope of the straight line is f'_2 and the intercept is $C_{\mathrm{m}2}/w$. For the case of $C_{\mathrm{m}2} = 0$, Eq. (22) can be reduced as

$$\frac{x}{\bar{M}_{\mathrm{n}2}} - \frac{x_1}{\bar{M}_{\mathrm{n}1,x=x1}} = f'_2\phi_{\mathrm{A}2} \qquad (24)$$

where $\phi_{\mathrm{A}2}$ is defined as $\phi_{\mathrm{A}2} = \phi_2(x-x_1)$. Under this condition, the experimental data for the molecular weight at gel effect stage should be again dropped on a straight line, but it is through the origin with a slope of f'_2 in a plot of $(x/\bar{M}_{\mathrm{n}2}) - (x_1/\bar{M}_{\mathrm{n}1,x=x1})$ vs. $\phi_{\mathrm{A}2}$.

2.3. Glass effect stage ($x \geq x_2$)

Similarly, for glass effect stage, Eq. (2) can be rewritten as

$$\frac{1}{\bar{P}_{\mathrm{n}3}} = \frac{\int_{[M]_0}^{[M]_1} \mathrm{d}[M] + \int_{[M]_1}^{[M]_2} \mathrm{d}[M] + \int_{[M]_2}^{[M]} \mathrm{d}[M]}{-([M]_0 - [M])} \qquad (25)$$

and

$$\frac{1}{\bar{M}_{\mathrm{n}3}}\,\frac{x}{x-x_2} - \frac{1}{\bar{M}_{\mathrm{n}2,x=x2}}\,\frac{x_2}{x-x_2} = f'_3\phi_3 + \frac{C_{\mathrm{m}3}}{w} \qquad (26)$$

where $f'_3 = f_3[(\alpha_{\mathrm{td}3}+1)/2]$, $C_{\mathrm{m}3} = k_{\mathrm{tr,m}3}/k_{\mathrm{p}3}$, $\alpha_{\mathrm{td}3} = k_{\mathrm{td}3}/(k_{\mathrm{tc}3} + k_{\mathrm{d}3})$ and ϕ_3 is defined as

$$\phi_3 = \frac{4[I]_0}{K_3[M]_0 w} \times \left[1 + \frac{\ln(1-x_1)}{K_1} + \frac{\ln\left(\dfrac{1-x_2}{1-x_1}\right)}{K_2}\right]\frac{-\ln\left(\dfrac{1-x}{1-x_2}\right)}{x-x_2} + \frac{2[I]_0}{K_3^2[M]_0 w}\,\frac{-\ln^2\left(\dfrac{1-x}{1-x_2}\right)}{x-x_2} \qquad (27)$$

Similarly, the experimental data at glass effect stage should be also dropped on a straight line in a plot of $(1/\bar{M}_{\mathrm{n}3})(x/(x-x_2)) - (1/\bar{M}_{\mathrm{n}2,x=x2})(x_2/(x-x_2))$ vs. ϕ_3, in which the slope of the straight line is f'_3 and the intercept is $C_{\mathrm{m}3}/w$.

In the case of $C_{\mathrm{m}3} = 0$, Eq. (26) can be reduced as

$$\frac{x}{\bar{M}_{\mathrm{n}3}} - \frac{x_2}{\bar{M}_{\mathrm{n}2,x=x2}} = f'_3\phi_{\mathrm{A}3} \qquad (28)$$

where $\phi_{\mathrm{A}3} = \phi_3(x-x_2)$. Again, for such case, the experimental data should be dropped on a straight line through the origin with a slope of f'_3. It is clear that the cumulative number-average molecular weight $\bar{M}_{\mathrm{n}}$ for three different stages of the polymerization can be predicted from Eqs. (14), (22) or (24) and Eq. (26) or (28), respectively.

3. Determination of the apparent initiator efficiency and comparison between experimental data and model prediction

In order to process the experimental data, the density equations for MMA, St and EMA related to temperature are given in Table 1.

3.1. MMA bulk free radical polymerization

In order to determine the apparent initiator efficiency, it is preferable to plot together the experimental data presented by different investigators with the plotting approach proposed in this paper. Unfortunately, the experimental data of the molecular weight varying with conversions in the literature are few and not consistent with each other. Fig. 1 shows the experimental data measured by Balke

Table 1
The density expressions of monomer

Monomer	Density r_{m} (g/l)	Reference
MMA	$973 - 1.164t$ (°C)	[8,9]
St	$923.6 - 0.887t$ (°C)	[8,9]
EMA	$1081 - 3.36t$ (°C)	[8]

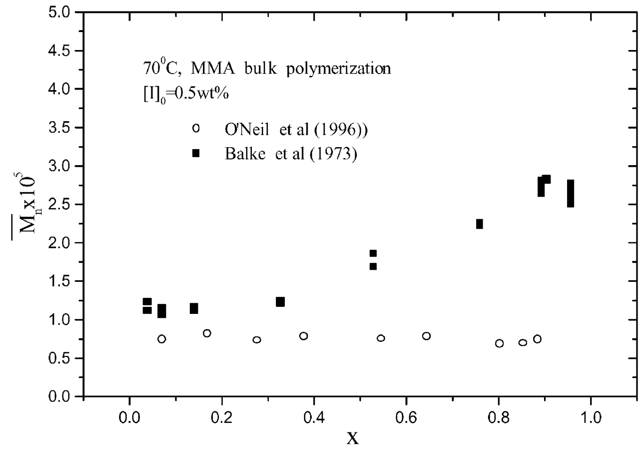

Fig. 1. Comparison of experimental data from different researchers.

and Hamielec [10] and O'Neil et al. [11] at same polymerization condition. It is observed from the figure that the difference between two sets of the data is not only in their values, but also for the varying trend. Therefore, the data presented by different investigators are unable to be used together in the plot for determining the apparent initiator efficiency.

Since the work of Balke and Hamielec [10] has been used as a source of kinetic and molecular weight data in a number of modeling and simulation exercises, their data are chosen for determining the apparent initiator efficiency and the constant of chain transfer to monomer in this paper. By using Eqs. (14), (24) and (28) to plot the experimental data presented by Balke and Hamielec [10], the values of the apparent initiator efficiencies and the constants of chain transfer to monomer can be obtained as shown in Figs. 2–4. The values of K_1, K_2, K_3, x_1 and x_2 employed in the plots are taken from Part (1) of this study [7].

It is observed from the figures that the apparent initiator efficiency in each polymerization stage is independent of the reaction temperature and initiator concentration, which is slightly reduced from a value of 0.54 at low conversion stage to 0.4 at gel effect stage. At glass effect stage, it reduces drastically in several orders of magnitude and only equals to 0.004.

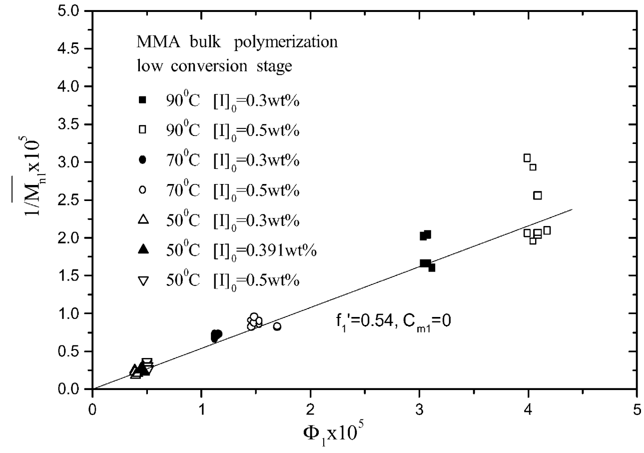

Fig. 2. Plot of data presented by Balke and Hamielec at low conversion stage.

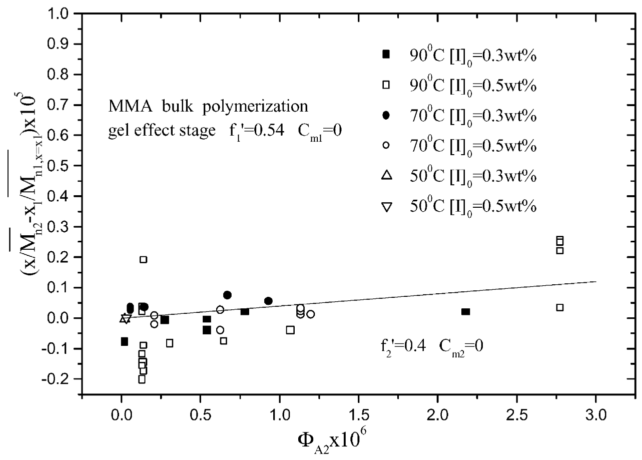

Fig. 3. Plot of data presented by Balke and Hamielec at gel effect stage.

Pan [5] reviewed the studies on the fraction of the terminations by disproportionation or combination in his book and concluded that the chain termination by disproportionation played a major role for MMA polymerization when the reaction temperature was over 60 °C. In fact, the chain termination by combination at low conservation was usually omitted in the literature as shown in Refs. [3,12,13]. It means that the initiator efficiency in the literature is equivalent to the apparent initiator efficiency at low conversion stage. Therefore, the value of the apparent initiator efficiency at low conversion stage obtained in this paper should be close to the value of the initiator efficiency reported in the literature. Stickler [12] reported that the value of the initiator efficiency at low conversion was 0.72; Achilias and Kiparissides [13] recommended it be 0.58 and Russell et al. [3] suggested that $f_1 \geq 0.47$. Our value of the apparent initiator efficiency at low

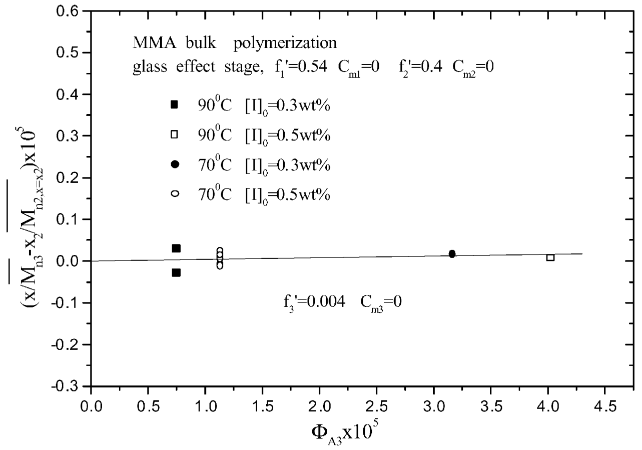

Fig. 4. Plot of data presented by Balke and Hamielec at glass effect stage.

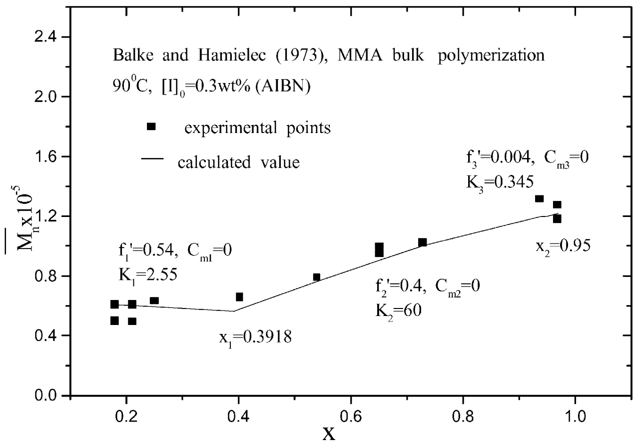

Fig. 5. Effect of conversion on number-average molecular weight.

conversion stage, 0.54, is in the middle of three. Moreover, the varying trend of the apparent initiator efficiency from low conversion to high conversion is consistent with the theoretical study of Russell et al. [3] as mentioned in Section 1.

In addition, it is observed from Figs. 2–4 that all of the straight lines pass through the origin, which means that the chain transfer to monomer can be neglected and the constant of chain transfer to monomer equals to zero for MMA bulk polymerization. This is consistent with the results in Refs. [5,6].

On the basis of the apparent initiator efficiencies obtained above, the number-average molecular weights throughout the polymerization can be calculated by the model proposed in this paper. The calculated results and the experimental data given by Balke and Hamielec [10] are compared in Figs. 5–10, which shows that the agreement is satisfactory.

3.2. St bulk free radical polymerization

Similarly, the experimental data of number-average molecular weight for St bulk polymerization are also few in the literature. Marten and Hamielec [14] referred the data of Braks in their paper, the only data for this purpose we found in the literature. Since the experiments of Braks are limited to low conversion and gel effect stages, the plots can only be performed for these two stages as shown in Figs. 11 and 12. It is observed from the figures that the apparent initiator efficiencies reduce obviously from 0.45 at low conversion stage to 0.06 at gel effect stage.

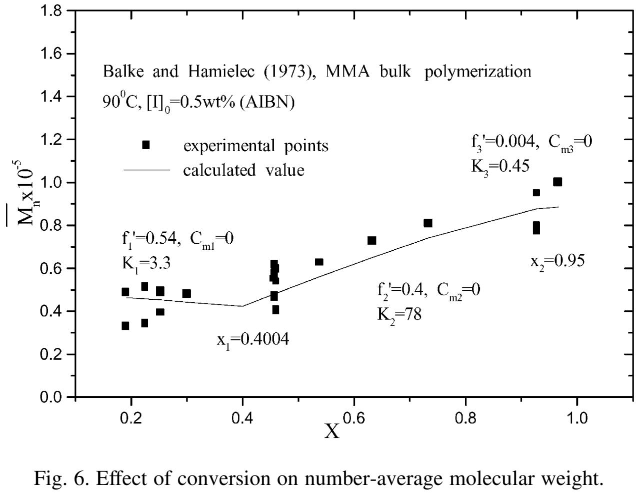

Fig. 6. Effect of conversion on number-average molecular weight.

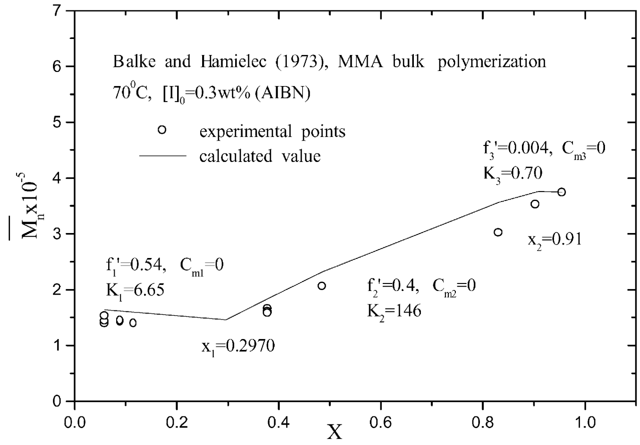

Fig. 7. Effect of conversion on number-average molecular weight.

Pan [5] and Marten and Hamielec [14] pointed out that the termination by combination might play a major role in the whole chain termination for St polymerization. According to this viewpoint, the fraction of termination rate constants by disproportionation, α_{td}, should be equal to zero approximately. Therefore, the real initiator efficiencies should be roughly equal to or somewhat less than 0.9 at low conversion stage and 0.12 at gel effect stage, which are twice the values of the apparent initiator efficiency obtained above.

Moreover, the value of 0.9 at low conversion stage is

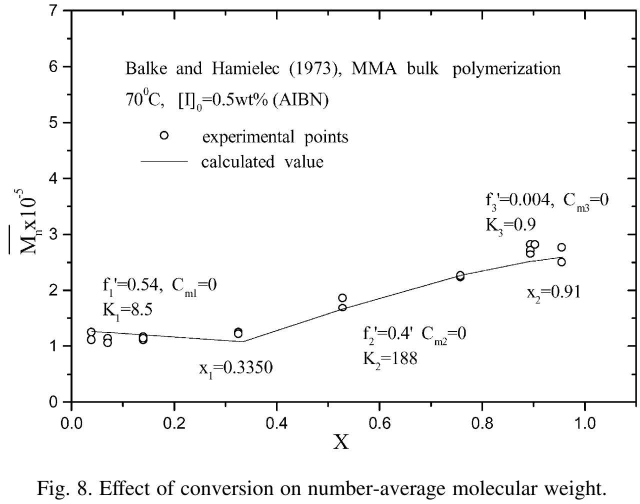

Fig. 8. Effect of conversion on number-average molecular weight.

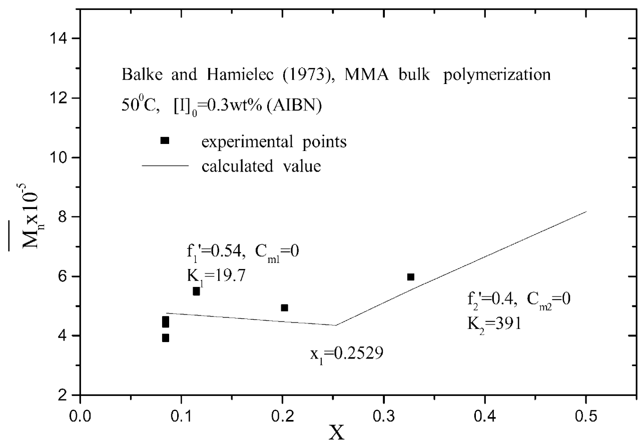

Fig. 9. Effect of conversion on number-average molecular weight.

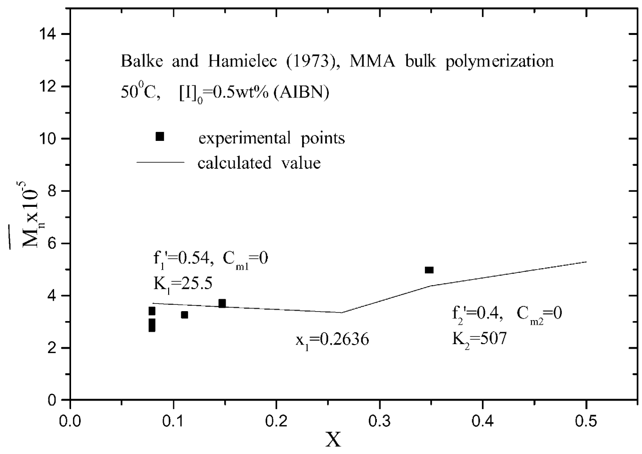

Fig. 10. Effect of conversion on number-average molecular weight.

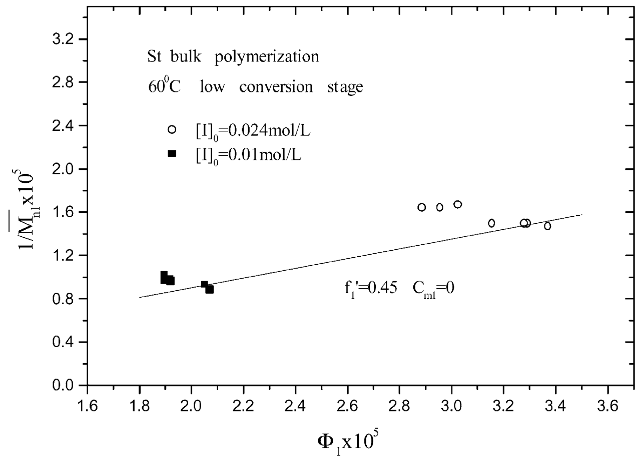

Fig. 11. Plot of data presented by Braks at low conversion stage.

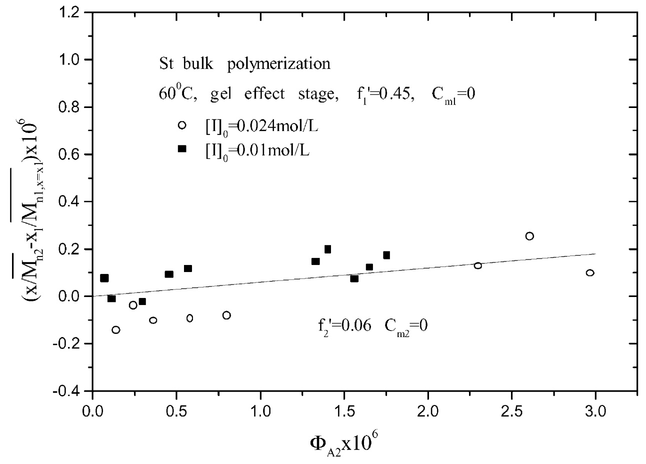

Fig. 12. Plot of data presented by Braks at gel effect stage.

approximately consistent with 0.8 recommended by Pan [5] and 0.7 suggested by Marten and Hamielec [14]. However, since the predicted initiator efficiencies for St polymerization in this section reduce obviously from low conversion stage to gel effect stage, the concept proposed by Russell et al. [3] that the initiator efficiencies only reduce slightly at intermediate conversion probably cannot be extended to St bulk polymerization.

It is also observed from the figures that all of the straight lines pass through the origin and the chain transfer to monomer can be neglected. Therefore, the constant of chain transfer to monomer for St polymerization is also equal to zero as that for MMA bulk polymerization.

Based on the apparent initiator efficiencies obtained and the constant of chain transfer to monomer, the values of the number-average molecular weight varying along with conversions for St bulk polymerization can be calculated and compared with the experimental data of Braks as shown in Figs. 13 and 14. It is found that the agreement is acceptable.

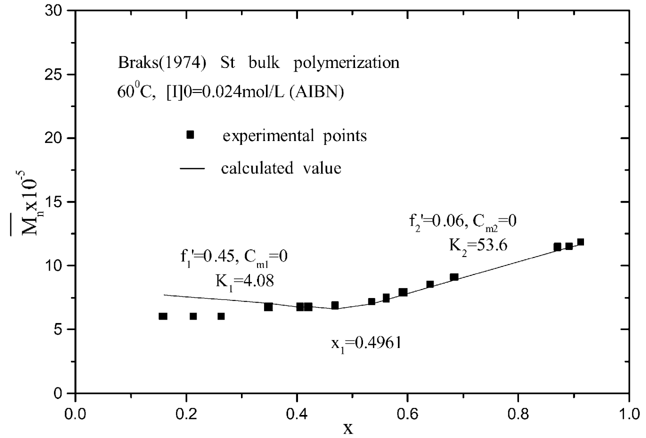

Fig. 13. Effect of conversion on number-average molecular weight.

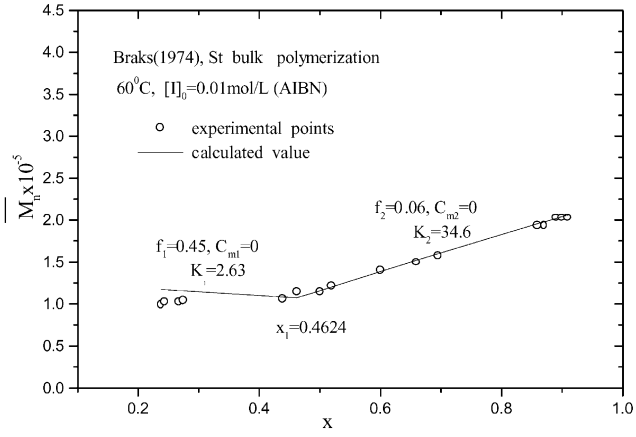

Fig. 14. Effect of conversion on number-average molecular weight.

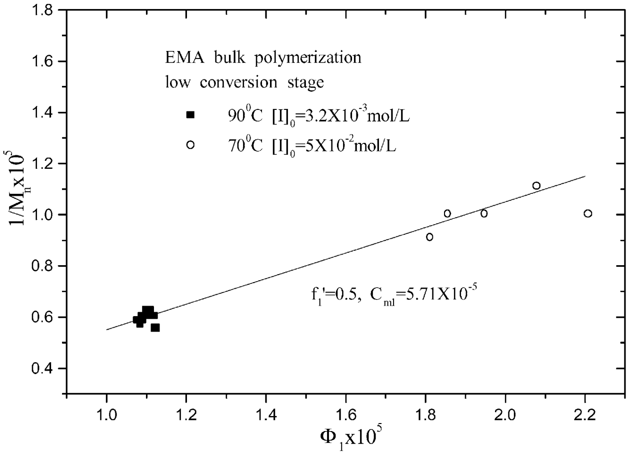

Fig. 15. Plot of data presented by Cardenas and O'Driscoll at low conversion stage.

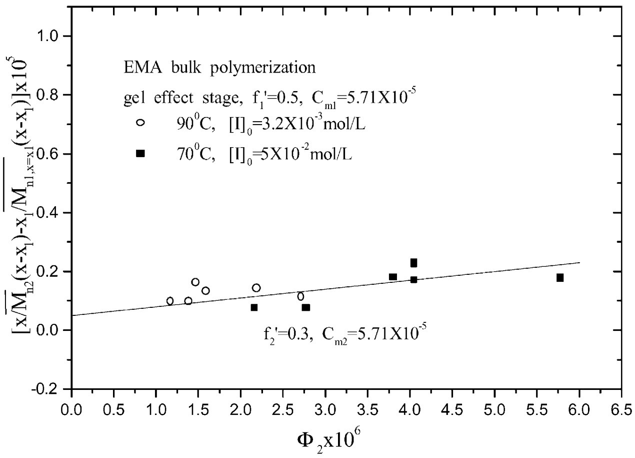

Fig. 16. Plot of data presented by Cardenas and O'Driscoll at gel effect stage.

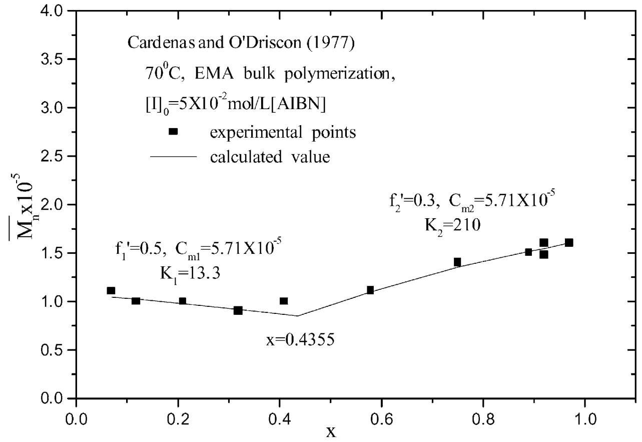

Fig. 17. Effect of conversion on number-average molecular weight.

3.3. EMA bulk free radical polymerization

The data for EMA presented by Cardenas and O'Driscoll [6] are similarly processed and the predicted number-average molecular weights are then compared with the experimental data as shown in Figs. 15–18.

Figs. 15 and 16 show that the chain transfers to monomer for EMA bulk polymerization cannot be neglected. It is found that the constants of chain transfer to monomer are identical in the value of 5.71×10^{-5} and independent of reaction temperature and initiator concentration for both low conversion and gel stages. In addition, the apparent initiator efficiencies at low conversion and gel effect stages are also independent of reaction temperature and initiator concentration with the values of 0.5 and 0.3, respectively.

Figs. 17 and 18 show that the predicted number-average molecular weights well coincided with the experimental results presented by Cardenas and O'Driscoll [6], which means that the proposed model in this paper is also suitable for EMA bulk polymerization.

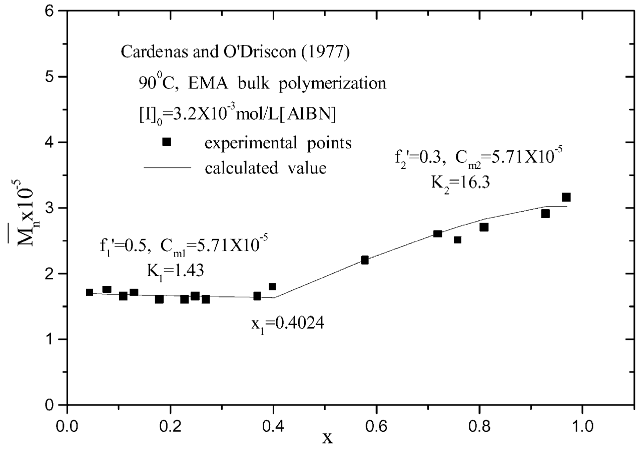

Fig. 18. Effect of conversion on number-average molecular weight.

4. Conclusions

1. By using the equations derived in this paper on the basis of the TSPM, the apparent initiator efficiency and the constant of chain transfer to monomer at each polymerization stage can be determined. The calculated number-average molecular weights varying with conversions coincided very well with the experimental data.
2. Chain transfer to monomer can be neglected for MMA and St bulk polymerization. The values of the apparent initiator efficiency are independent of reaction temperature and initiator concentration. In addition, the apparent initiator efficiency for MMA bulk polymerization at gel effect stage reduces slightly compared to that at low conversion stage, but for St bulk polymerization it reduces significantly at gel effect stage.
3. On the other hand, the chain transfer to monomer for EMA bulk polymerization cannot be neglected. The constants of chain transfer to monomer at low conversion stage and gel effect stage are the same with the value of 5.71×10^{-5} and independent of reaction temperature and initiator concentration. The variation of the apparent initiator efficiency at different polymerization stages is similar to MMA bulk polymerization and also the values are independent of reaction temperature and initiator concentration.

Acknowledgements

The authors wish to thank Professor Zuren Pan and Professor Gantang Chen of Zhejiang University for the valuable suggestions.

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