Polymer 44 (2003) 2599–2604

polymer

www.elsevier.com/locate/polymer

Modeling of high-conversion binary copolymerization

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Received 25 November 2002; received in revised form 24 January 2003; accepted 25 January 2003

Abstract

In this paper, the Three Stage Polymerization Model (TSPM) proposed in our previous publication for free radical homopolymerization was extended to describe high-conversion copolymerization reactions exhibiting a strong gel effect. Moreover, the literature data on conversion history for styrene (St)–methyl methacrylate (MMA), MMA–ethylene glycol dimethacrylate (EGDMA) and acrylonitrile (AN)-α-methylstyrene (AMS) copolymerizations were used to examine applicability of the model. It was found that TSPM is still suitable for kinetic description of the copolymerization systems mentioned above.

Keywords: Free radical binary copolymerization; Three Stage Polymerization Model; Kinetic modeling

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1. Introduction

In order to obtain the reaction rate equation of free radical copolymerization, it is necessary to determine which chain propagation and chain termination models will be employed first. The most remarkable models at present for chain propagation are the terminal model and the penultimate model, the latter includes two different versions, the explicit penultimate model and the implicit penultimate model [1]. Other models, such as the radical-complex model and the monomer-complex-participation model, are only suitable for certain cases in which the complex of some kinds comes into being [2]. For chain termination, long controversial problem had been that whether the termination was chemically controlled or diffusion-controlled. Fortunately, the viewpoints on this problem at present are relatively consistent with each other in the literature, most researchers consider that the termination reaction is diffusion-controlled [2].

If chain propagation models were in combination with chain termination models, the reaction rate equations could be obtained. For example, when the terminal model was coupled with the termination model of chemically control, famous Walling equation could be derived [3]. Similarly, if the terminal model was in combination with the termination model of diffusion-controlled, North equation should be obtained [4]. Unfortunately, these rate equations could not be applied to high conversion range due to the gel effect or so-called Trommsdorff effect. Some researchers, therefore, used a free volume approach to describe changes caused by increasing of polymer concentration on the reaction rate constants [5,6]. Although the approach acquired success to certain extent, its calculating procedure was complicated and adjustable parameters were used.

In order to simplify mathematical expression of the chain propagation rate R_p, some researchers used the Pseudo-kinetic rate constant method to obtain the propagation rate equation of copolymerization [7,8]. According to the method, a rate equation, which was in the same form as for homopolymerization, could be derived from either of the terminal model or the penultimate model [8]. Kinetic constant in the equation, thus, could be measured directly by modern techniques, for instance, the pulse-laser polymerization (PLP) technique [9,10] or the electron spin resonance (ESR) spectroscopy [11–13]. Li et al. [14] and Zhu et al. [12] used this rate equation to study methylmethacrylate (MMA)–ethylene glycol dimethacrylate (EGDMA) bulk copolymerizatiom with an on-line electron spin resonance (ESR) spectrometer. They found that the apparent propagation rate constant, k_p, in the equation did not vary with conversions within conversion of 0–80%. The fact shows that varying rule of k_p with conversion is similar to bulk

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doi:10.1016/S0032-3861(03)00097-1

homopolymerization. In addition, Lau et al. [15] extended ESR analysis to a semicontinuous acrylic emulsion copolymerization and found that the rate equation mentioned above was still valid.

In a previous publication from our group [16], a simple model, Three Stage Polymerization Model (TSPM) was proposed to describe free radical bulk homopolymerization exhibiting strong gel and glass effects. This model described the polymerization process over entire course of reaction. Model predictions agreed well with literature data on conversion history and product molecular weights for bulk homopolymerizations of MMA, styrene (St) and ethylmethacrylate (EMA) [16,17]. In the present paper, this basic homopolymerization model will extend to describe copolymerization reactions to high conversions where both gel and glass effects are important. Experimental data found in the literature for MMA–St, acrylonitrile (AN)-α-methylstyrene (AMS) and EGDMA–MMA copolymerizations are used to examine the model.

2. Development of kinetic model

Since the rate equation of chain propagation R_{p} for copolymerization can be expressed as that for homopolymerization [8] and k_{p} in the equation is a constant within a wide conversion range [12,14], a copolymerization system, thus, can be approximately referred to as a pseudo-homopolymerization system when its initiative monomer composition is given.

If considering that the termination reaction for copolymerization is diffusion-controlled [2], its rate, R_{t}, should be out of relation to the terminal radical type for a system given initiative composition. In such a case, it seems that the termination equation of homopolymerization can also extend to describe copolymerization.

Based on above discussions, in order to develop the rate equations of a bulk binary copolymerization, the following assumptions are made:

1. A copolymerization system can be approximately referred as a pseudo-homopolymerization system when its initiative composition of monomers is given.
2. TSPM concept [16] is applicable for bulk copolymerization, i.e. whole course of binary copolymerization can be still divided into three different stages: low conversion, gel effect and glass effect stages as in the case of bulk homopolymerization.
3. In each stage, the kinetic constants do not vary with conversion. In addition, the initiator efficiency, f_{i}, is also a constant in each stage as has been hypothesized and proven in the TSPM [16,17].

In order to illustrate the model, an initiator-initiating bulk free radical copolymerization is introduced here as an example. Based on Pseudo-kinetics rate constant method [7,8], the chain propagation rate, R_{p}, can be expressed as

$$R_{\mathrm{p}} = -\frac{\mathrm{d}[\mathrm{M}]}{\mathrm{d}\theta} = k_{\mathrm{p}}[\mathrm{M}^*][\mathrm{M}] \tag{1}$$

where k_{p} is the apparent propagation rate constant; [M∗] and [M] are total mole concentration of radicals and monomers, respectively, in a bulk copolymerization system; θ is the reaction time.

Under the quasi-steady-state approximation and by assuming that termination reaction is diffusion-controlled, the following equation is written [16]

$$R_{\mathrm{i}} = 2f_{\mathrm{i}}k_{\mathrm{d}}[\mathrm{I}] = R_{\mathrm{t}} = 2k_{\mathrm{t}}[\mathrm{M}^*]^2 \tag{2}$$

where R_{i} and R_{t} are the chain initiation reaction rate and the chain termination reaction rate, respectively; f_{i} is the initiator efficiency; k_{d} is the initiator decomposition rate constant; [I] is the initiator concentration and k_{t} is the chain termination rate constant.

Eliminating $[\mathrm{M}^*]$ from Eqs. (1) and (2) and considering that $[\mathrm{I}] = [\mathrm{I}]_0 \exp(-k_{\mathrm{d}}\theta)$, the following equation can be obtained

$$-\frac{\mathrm{d}[\mathrm{M}]}{[\mathrm{M}]} = k_{\mathrm{p}}\left(\frac{f_{\mathrm{i}}k_{\mathrm{d}}}{k_{\mathrm{t}}}\right)^{1/2}[\mathrm{I}]_0^{1/2}\exp\left(-\frac{k_{\mathrm{d}}\theta}{2}\right)\mathrm{d}\theta \tag{3}$$

where $[\mathrm{I}]_0$ is the initial initiator concentration.

Based on the model assumption, since $k_{\mathrm{p}}(f_{\mathrm{i}}k_{\mathrm{d}}/k_{\mathrm{t}})^{1/2}[\mathrm{I}]_0^{1/2}$ is the constant at different copolymerization stage, the integrals of Eq. (3) are easy to perform as has been mentioned in the TSPM [16].

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

Integrating Eq. (3) under the condition $[\mathrm{M}] = [\mathrm{M}]_0$ at $\theta = 0$ and defining $x = 1 - [\mathrm{M}]/[\mathrm{M}]_0$ gives

$$-\ln(1 - x) = K_1[\exp(-k_{\mathrm{d}}\theta/2) - 1] \tag{4}$$

where $K_1 = (2/k_{\mathrm{d}})k_{\mathrm{p1}}(f_{\mathrm{i1}}k_{\mathrm{d}}/k_{\mathrm{t1}})^{1/2}[\mathrm{I}]_0^{1/2} = 2([\mathrm{I}]_0/k_{\mathrm{d}})^{1/2}k_{\mathrm{a1}}$, which is referred to as the overall reaction rate constant at low conversion stage in this paper; $k_{\mathrm{a1}} = k_{\mathrm{p1}}(f_{\mathrm{i1}}/k_{\mathrm{t1}})^{1/2}$, is the apparent reaction rate constant at low conversion stage. The definitions of f_{i1}, and k_{p1} and $k_{\mathrm{t}}1$ are the same as those mentioned above, but ‘1’ in subscripts denotes the stage within low conversion stage; x is the conversion and x_1 is the critical conversion for the transition from low conversion stage to gel effect stage.

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

Similarly, integrating Eq. (3) with the condition $[\mathrm{M}] = [\mathrm{M}]_1$ at $\theta = \theta_1$ and setting $[\mathrm{M}] = [\mathrm{M}]_0(1 - x)$ and $[\mathrm{M}]_1 = [\mathrm{M}]_0(1 - x_1)$, the following equation can be obtained

$$-\ln(1 - x) = -\ln(1 - x_1) - K_2[\exp(-k_{\mathrm{d}}\theta/2) - \exp(-k_{\mathrm{d}}\theta_1/2)] \tag{5}$$

where $K_2 = (2/k_{\mathrm{d}})k_{\mathrm{p2}}(f_{\mathrm{i2}}k_{\mathrm{d}}/k_{\mathrm{t2}})^{1/2}[\mathrm{I}]_0^{1/2} = 2([\mathrm{I}]_0/k_{\mathrm{d}})^{1/2}k_{\mathrm{a2}}$, which is the overall reaction rate constant at gel effect stage; $k_{a2} = k_{p2}(f_{i2}/k_{t2})^{1/2}$, is the apparent reaction rate constant at gel effect stage; The definitions of f_{i2}, k_{p2} and k_{t2} are the same as those mentioned above, but '2' in subscripts denotes the stage within gel effect stage; x_2 is the critical conversion for the transition from gel effect stage to glass effect stage; θ_1 is the reaction time correspond to x_1.

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

Similarly, we have

$$-\ln(1-x) = -\ln(1-x_2) - K_3[\exp(-k_d\theta/2) - \exp(-k_d\theta_2/2)] \tag{6}$$

where $K_3 = (2/k_d)k_{p3}(f_{i3}k_d/k_{t3})^{1/2}[\mathrm{I}]_0^{1/2} = 2([\mathrm{I}]_0/k_d)^{1/2}k_{a3}$, which is the overall reaction rate constant at glass effect stage; $k_{a3} = k_{p3}(f_{i3}/k_{t3})^{1/2}$, is the apparent reaction rate constant at glass effect stage. The definitions of f_{i3}, k_{p3} and k_{t3} are also the same as those mentioned above, but '3' in subscripts denotes the stage within glass effect stage.

It is observed from Eqs. (4)–(6) that if copolymerization kinetics can be described by the model proposed in this paper, three straight lines should be obtained in a plot of $-\ln(1-x)$ vs. $-\ln(1-x)$ vs. $\exp(-k_d\theta/2)$ for three different stages. The slopes of three straight lines are K_1, K_2 and K_3, respectively. The intersection points of three straight lines are the critical conversions x_1 and x_2.

3. Experimental data plots and model examination

3.1. St–MMA copolymerization

O'Driscoll and Huang [18] studied bulk homopolymerizations and copolymerizations of St (M_1) and MMA (M_2) initiated with 2,2′-azodiisobutyrate (AIBME) at 60° ($k_d = 6.78 \times 10^{-4}$ min^{-1}, reactivity ratios $r_1 = 0.472$ and $r_2 = 0.454$). The concentration of AIBME was identical and equal to 0.01 mol/l in all of experiments. The initial St (M_1) mole fractions, f_{10}, were 0, 0.3, 0.52, 0.7 and 1, respectively. In addition, Dionisio and O'Driscoll [19] studied bulk St–MMA copolymerization initiated with benzoyl peroxide (BPO) at 60 °C ($k_d = 1.56 \times 10^{-4}$ min^{-1}) and $f_{10} = 0.6$. Since the data of conversion vs. time were measured in these experiments, plots of $-\ln(1-x)$ vs. $\exp(-k_d\theta/2)$ are easy to perform by using their experimental data. Figs. 1 and 2 show such plots.

It is observed from Figs. 1 and 2 that the experimental points fall satisfactorily on two or three straight lines for each f_{10}, showing that the model is correct for typical St–MMA copolymerization and the copolymerization experiments of O'Driscoll and Huang [18] were within low conversion and gel effect stages approximately since there was no such stage at which conversion was roughly independent of time. In fact, the plots of experimental data for $f_{10} = 0$ and 1 in Fig. 1 are that of homopolymerizations for MMA and St, which indicate that TSPM still holds true although the kind of initiator is different from that in our prevous study [16]. It shows again that TSPM has extensive applicability.

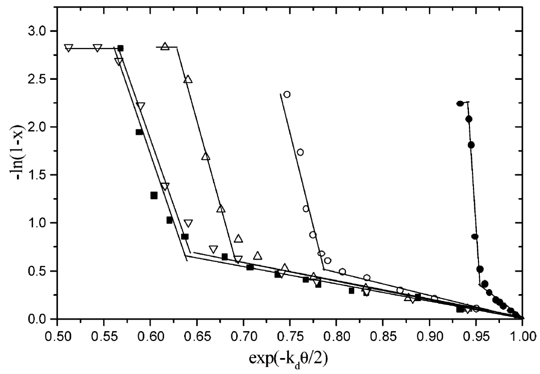

Fig. 1. Plots of experimental data presented by O'Driscoll and Huang [18] St(1)/MMA(2) copolymerization, 60 °C, $[\mathrm{I}]_0 = 0.01$ mol/l (AIBME). Experimental points: (●) $f_{10} = 0$, $K_1 = 7.2$, $K_2 = 110$, $x_1 = 0.265$, $x_2 = 0.88$; (○) $f_{10} = 0.3$, $K_1 = 2.5$, $K_2 = 40$, $x_1 = 0.4084$; (△) $f_{10} = 0.52$, $K_1 = 1.92$, $K_2 = 32$, $x_1 = 0.4385$, $x_2 = 0.94$; (■) $f_{10} = 0.7$, $K_1 = 1.7$, $K_2 = 27$, $x_1 = 0.4580$; (▽) $f_{10} = 1$, $K_1 = 1.91$, $K_2 = 25$, $x_1 = 0.485$, $x_2 = 0.943$. (—) Model.

By contrast with homopolymerization, experimental studies of the kinetics of copolymerization taken to high conversion are quite rare in the literature. In particular, smaller ampoule reactor must be used in experiments to avoid the non-isothermal effect [16], which causes difficulty in finding useful literature data. To obtain predictive equations of kinetic constants and x_1 with classical kinetic treatment, more literature data at different temperatures and initiator concentrations are necessary. Perhaps proposal for fuether mechanism to correlate x_1 and kinetic constants at different f_{10} would be needed. Unfortunately, no further data can be found in the literature. Moreover the cause of gel effect or x_1 is an interesting subject in recent times and a consistent viewpoint on its mechanism has not been yet eatablished [20]. Based on the background mentioned

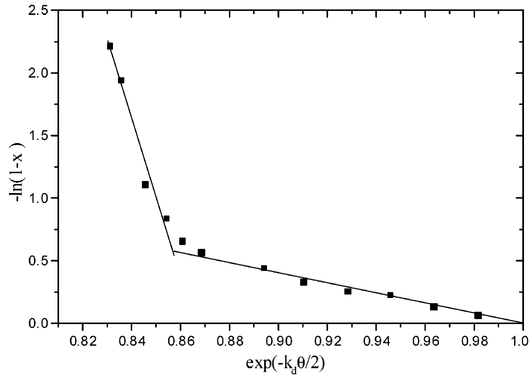

Fig. 2. Plots of experimental data presented by Dionisio and O'Driscoll [19] St(1)/MMA(2) copolymerization, 60 °C, $[\mathrm{I}]_0 = 0.0083$ mol/l (BPO). Experimental points: (■) $f_{10} = 0.6$, $K_1 = 3.9$, $K_2 = 60$, $x_1 = 0.4264$. (—) Model.

above, it is clear that theoretical treatments of x_1 and kinetic constants are difficult to perform only by using the data listed in Figs. 1 and 2, futher theoretical and experimental studies are necessary for consummating the treatment.

Using the values of K_1, K_2 and x_1 taken directly from Fig. 1 and substituting these values into Eqs. (4) and (5), the curve of conversion vs. time can be predicted. Fig. 3 shows the comparisons between predictions and experimental data presented by O'Driscoll and Huang [18]. Fig. 4 shows similar comparson between predictions and experimental data presented by Dionisio and O'Driscoll [19], but the values of K_1, K_2 and x_1 are directly taken from Fig. 2.

It is observed from Figs. 3 and 4 that the predicted results are well coincided with the experimental data. As for Fig. 3, perhaps this is because annular ampules were used at high rates of polymerization in the experiments of O'Driscoll and Huang [18] and annular gap was only 2 mm. In such a case, the ampules have better heat transfer ability, hence non-isothermal effect becomes smaller when gel effect occurs in kinetic experiments. However, since the non-isothermal effect may not be entirely removed by improvement of heat transfer, some experimental points around x_1 still deviate slightly from the model predictions.

3.2. EGDMA–MMA copolymerization

Free radical polymerization with crosslinking has been receiving more attention recently due to its potential for development of new polymer products, such as thermosetting moulding compounds, superabsorbents and ion exchange resins. Although some successes have been achieved in the manufacture of these materials, an understanding of the kinetics has not progressed far. Li et al. [14] studied the kinetics of EGDMA(M_1)–MMA(M_2) bulk copolymerization initiated with 2,2′-azoisobutyronitrile (AIBN) at 70 °C ($r_1 = 1.49$ and $r_2 = 0.67$). The levels of EGDMA used in the experiments of conversion vs. time were 0, 0.3, 1, 5, 15 and 25 wt%, respectively. Assuming that EGDMA is monomer 1, the correspondent f_{10} should be 0, 0.0015, 0.0051, 0.026, 0.0818 and 0.144. The concentration of AIBN was 0.3 wt% in all experiments of Li et al. [14]. By using their experimental data, plots of $-\ln(1-x)$ vs. $\exp(-k_d\theta/2)$ can be similarly performed. The value of k_d used in data processing for AIBN is calculated by the following equation [20]

$$k_d(\text{min}^{-1}) = 6.32\times10^{16}\exp(-15.43\times10^3/T) \tag{7}$$

where T is the reaction temperature, K.

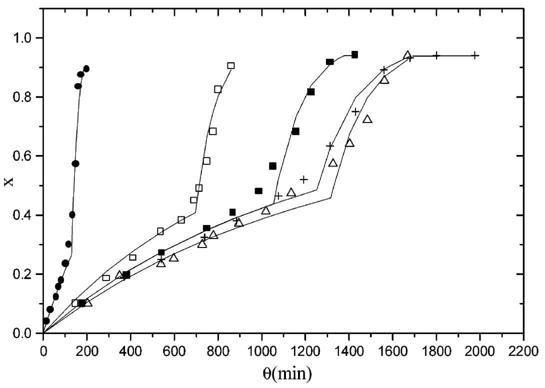

Fig. 3. The comparisons between the predictions and experimental data presented by O'Driscoll and Huang [18], St–MMA copolymerization, 60 °C, $[I]_0 = 0.01$ mol/l (AIBME). Experimental points: (●) $f_{10} = 0$, (□) $f_{10} = 0.3$, (■) $f_{10} = 0.52$, (+) $f_{10} = 0.7$, (△) $f_{10} = 1$. (—) Predicted values.

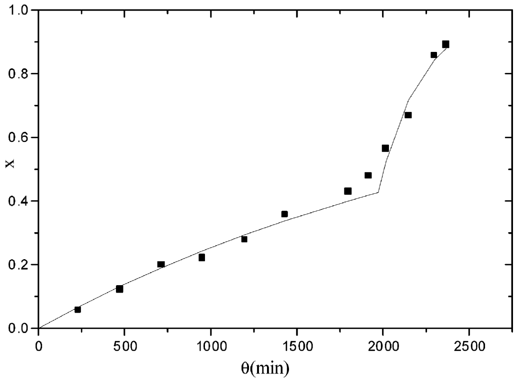

Fig. 4. The comparison between the predictions experimental data presented by Dionisio and O'Driscoll [19], St–MMA copolymerization, 60 °C, $[I]_0 = 0.0083$ mol/l (BPO). Experimental points: (■) $f_{10} = 0.6$. (—) Predicted values.

Fig. 5 shows the plots. It is observed from Fig. 5 that experimental data of Li et al. [14] are extended through to glass effect stage since the stages at which the conversion is basically independent of time, are in existence. In addition, the experimental points fall roughly on three straight lines for the same level of EGDMA, meaning that the model proposed in this paper is similarly suitable for EGDMA–MMA copolymerization with the crosslinking.

It is also observed from Fig. 5 that there are some deviation between the experimemtal points and the model

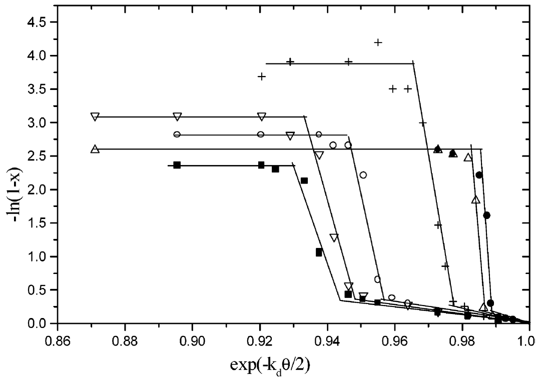

Fig. 5. Plots of data presented by Li et al. [14] EGDMA(1)/MMA(2) copolymerization, 70 °C, $[I]_0 = 0.3$ wt% (AIBN). Experimental points: (■) $f_{10} = 0$, $K_1 = 6.7$, $K_2 = 146$, $K_3 = 0$, $x_1 = 0.32$, $x_2 = 0.905$; (▽) $f_{10} = 0.0015$, $K_1 = 7$, $K_2 = 170$, $K_3 = 0$, $x_1 = 0.3075$, $x_2 = 0.945$; (○) $f_{10} = 0.0051$, $K_1 = 7.9$, $K_2 = 215$, $K_3 = 0$, $x_1 = 0.2936$, $x_2 = 0.933$; (+) $f_{10} = 0.026$, $K_1 = 9.7$, $K_2 = 340$, $K_3 = 0$, $x_1 = 0.2$, $x_2 = 0.98$; (△) $f_{10} = 0.0818$, $K_1 = 10.7$, $K_2 = 460$, $K_3 = 0$, $x_1 = 0.1299$, $x_2 = 0.925$; (●) $f_{10} = 0.144$, $K_1 = 11$, $K_2 = 570$, $K_3 = 0$, $x_1 = 0.114$, $x_2 = 0.925$. (—) Model.

for 5 wt% EGDMA level at high conversions, perhaps this is because $\ln(1-x)$ is very sensitive to x at high conversion.

As pointed out by Li et al. [14], they had no obvious explanation about strange variation of the limiting conversion with EGDMA levels, the critical conversions x_2 obtained from the plots of Fig. 5, are also ruleless.

Due to the same reason as mentioned in Section 3.1, the values of K_1, K_2, K_3, x_1 and x_2 are directly taken from Fig. 5 and the curve of conversion vs. time is predicted by using Eqs. (4)–(6). Fig. 6 shows the comparisons between predictions and experimental data presented by Li et al. [14]. It is observed from Fig. 6 that the experimental points are satisfactorily consistent with the predicted curves expect that some points near x_1 deviate slightly from the predictions due to the reason of non-isothermal effect.

3.3. AN–AMS copolymerization

It was generally believed that the AN–AMS copolymerization had so-called penultimate unit effect in the literature [21]. Using experimental data of AN–AMS copolymerization to examine applicability of the model proposed in this paper, hence, is of interest. Capek and Barton [22] studied high conversion bulk copolymerizations of AN(M_1)–AMS(M_2) at 50, 90 and 120 °C ($r_1 = 0.06$ and $r_2 = 0.1$). The data of conversion vs. time were measured in their experiments. The concentration of initiators was 0.05 mol/l, but different initiators were used at different temperatures: AIBN at 50 °C, *t*-butylperoxybenzoate (TBPB) at 90 °C and di-*t*-butyl peroxide (TBP) at 120 °C. f_{10} were 0.5 in all of experiments. In data processing, the value of k_d for AIBN is predicted by Eq. (7), while the values of k_d for TBPB and TBP are directly taken from Capek and Barton [22], which are $6\times10^{-5}\ \mathrm{min}^{-1}$ and $4.5\times10^{-4}\ \mathrm{min}^{-1}$, respectively.

Fig. 7 shows the plots of $-\ln(1-x)$ vs. $\exp(-k_d\theta/2)$ performed by using experimental data of Capek and Barton [22]. It is observed from Fig. 7 that the experimental data similarly fall on the straight lines except one point at high conversion for 120 °C. The results mean that the model proposed in this paper is also suitable for AN–AMS copolymerization system, although it was generally believed that the system had penultimate unit effect in the literature as mentioned above.

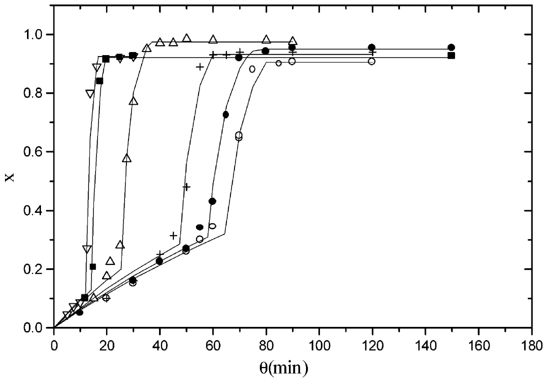

Fig. 6. The comparisons between predictions and experimental data presented by Li et al. [14] EGDMA/MMA copolymerization, 70 °C. Experimental points: $[\mathrm{I}]_0 = 0.3$ wt% (AIBN). Experimental points: (▽) $f_{10} = 0.144$, (■) $f_{10} = 0.0818$, (△) $f_{10} = 0.026$, (+) $f_{10} = 0.0051$, (○) $f_{10} = 0.0015$, (●) $f_{10} = 0$. (—) Predicted values.

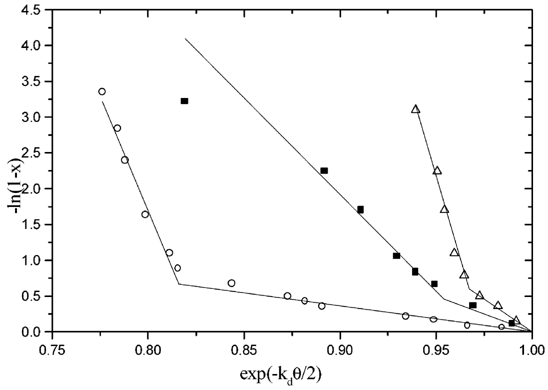

Fig. 7. Plots of data presented by Capek and Barton [22] AN(1)/AMS(2) copolymerization, $f_{10} = 0.5$, $[\mathrm{I}]_0 = 0.05$ mol/l. Experimental points: (○) 50 °C, AIBN, $K_1 = 3.64$, $K_2 = 64$, $x_1 = 0.4883$; (■) 120 °C, TBP, $K_1 = 11.8$, $K_2 = 27$, $x_1 = 0.3687$; (△) 90 °C, TBPB, $K_1 = 18.35$, $K_2 = 90$, $x_1 = 0.4512$. (—) Model.

Capek and Barton [22] pointed out that composition of AN–AMS copolymer was in accord with the integrated form of the Mayo–Lewis equation at 50 °C, while the compositions at 90 and 120 °C were different to predicted one if assuming that reactivity ratios, r_1 and r_2, did not vary with reaction temperature. They concluded that this was because the ceiling temperature for polymerization of AMS was 61 °C and depropagation effects, hence, could be important at the polymerization temperatures of 90 and 120 °C. Clearly, if the explanation is correct, it seems that the experimental data at 90 and 120 °C are impossible to be treated by our model because which do not take the depropagation effects into account. However, it is marvelous that the data of conversion vs. time at 90 and 120 °C are still described well by the model proposed in this paper as shown in Fig. 7. The results bring on a doubt whether r_1 and r_2 reliably do not vary with reaction temperature since the

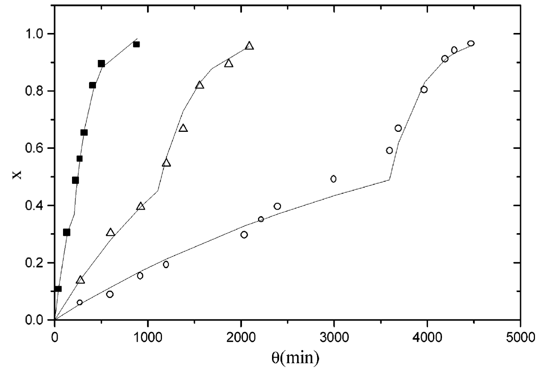

Fig. 8. The comparisons between predictions and experimental data presented by Capek and Barton [22] AN/AMS copolymerization, $[\mathrm{I}]_0 = 0.05$ mol/l. Experimental points: (○) 50 °C, AIBN; (△) 90 °C, TBPB; (■) 120 °C, TBP. (—) Predicted values.

variation of reaction temperature is remarkable in the experiments of Capek and Barton [22] and reactivity ratios may be related to reaction temperature [21]. In order to beat out this question, further study is necessary.

Substituting K_1, K_2 and x_1 directly taken from Fig. 7 into Eqs. (4) and (5), the curve of conversion vs. time can be predicted as mentioned above for St–MMA and EGDMA–MMA copolymerizations. Fig. 8 shows the comparisons between predictions and experimental data of Capek and Barton [22]. It is observed from Fig. 8 that the agreement is satisfactory.

4. Conclusions

1. Based on the concept of TSPM, a simple model is proposed to discribe the kinetics of bulk free radical copolymerizatiom in this paper.
2. The model can discribe satisfactorily experimental data found in the literature on conversion history for St–MMA, EGDMA–MMA and AN–AMS copolymerizations.

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