ELSEVIER

Polymer 43 (2002) 1163–1170

polymer

www.elsevier.com/locate/polymer

# Modeling of the bulk free radical polymerization up to high conversion—three stage polymerization model
# I. Model examination and apparent reaction rate constants

Jiguang Qin, Wenping Guo, Zheng Zhang*

*College of Chemical Engineering, Beijing University of Chemical Technology, Beijing 100029, People's Republic of China*

Received 17 July 2000; received in revised form 11 October 2001; accepted 16 October 2001

**Abstract**

In this paper, a simple and useful model, the three stage polymerization model (TSPM) is proposed on the basis of recent experimental evidence and our preliminary treatment of the experimental kinetic results found in the literature. The model accounts for gel effect and glass effect in bulk free-radical polymerization. Equations for calculating the conversion of the polymerization reaction are derived based on TSPM. Using experimental kinetic data available in the literature, general expressions for apparent reaction rate constants in three stages for methylmethacrylate (MMA) and styrene (St) are obtained. In general, the experimental kinetic data can be treated very well with the TSPM from the low conversion stage to high conversion, except for some experimental data near the transition points. However, the deviation for this data may be reasonably explained by the non-isothermal effects that occur in this regime of experiments. This deviation is smaller for a smaller ampoule reactor used in polymerization experiments because of its better heat transfer ability. In order to establish that there is no glass effect stage when the reaction temperature is greater than the glass transition temperature for a polymerization process, some experimental data for ethylmethacrylate (EMA) bulk polymerization at a reaction temperature higher than its glass transition temperature were checked with TSPM. The plots show that the model is also suitable for EMA bulk polymerization. © 2001 Elsevier Science Ltd. All rights reserved.

*Keywords*: Bulk free radical polymerization; Kinetics; Three stage polymerization model

## 1. Introduction

There are a number of mathematical models for bulk free polymerization proposed in Refs. [1,2]. Recently, Tefera et al. [3] tried to classify the models into five different groups according to their theoretical background or to the types of correlations for reaction rate parameters with specific variables. Almost all models appearing in the literature contain adjustable parameters for fitting model predictions to experimental data. In addition, critical break points are often introduced to simulate the onset of gel effect occurring in the polymerization. Although the developed models are successful to varying degrees at fitting the experimental data for certain conditions, doubts about the basic mechanism of the models have also been raised. For example, Tefera et al. [3] pointed out that the models correlating the reactor rate parameters with the macro-viscosity of the reaction medium proposed by Duerksen and Hamielec [4] and Brooks [5] might not be applicable for other reaction conditions. The diffusion limitation of the reaction rate might be caused by the increase of the micro-viscosity at reaction sphere, rather than by the increase of the macro-viscosity. This doubt should also be applicable to the models [6–10] correlating the rate parameters with conversion or weight fraction of the polymer. O'Neil et al. [1] conducted an experiment to examine the gel effect in free radical polymerization and raised doubt about the model based on entanglement arguments [13]. Since reputation theory is closely related to entanglement arguments, doubt about the models based on entanglement arguments should also be applicable for the models [13–16] based on reputation theory. Several investigations [17–21] cast doubt on the models based on free volume theory. Russell et al. [22] pointed out that the free volume theory could not explain some experimental results. For example, direct measurements of the chain propagation rate $k_p$ in emulsion polymerization showed that the measured $k_p$ for methylmethacrylate (MMA) at 50 °C and very high conversions was many orders of magnitude greater than that predicted by free volume models. Stickler

---

* Corresponding author.
*E-mail addresses:* zhangzh1@hotmail.com (Z. Zhang), zhangzh1@yahoo.com (Z. Zhang).

PII: S0032-3861(01)00715-7

## Nomenclature

| | |
|---|---|
| $f$ | initiator efficiency |
| $[I]$ | initiator concentration, mol l$^{-1}$ |
| $[I]_0$ | initial initiator concentration, mol l$^{-1}$ |
| $K_{1a}$ | apparent reaction rate constant at low conversion stage, l$^{1/2}$ mol$^{-1/2}$ min$^{-1}$ |
| $K_{2a}$ | apparent reaction rate constant at gel effect stage, l$^{1/2}$ mol$^{-1/2}$ min$^{-1}$ |
| $K_{3a}$ | apparent reaction rate constant at glass effect stage, l$^{1/2}$ mol$^{-1/2}$ min$^{-1}$ |
| $K_1$ | overall reaction rate constant at low conversion stage |
| $K_2$ | overall reaction rate constant at gel effect stage |
| $K_3$ | overall reaction rate constant at glass effect stage |
| $k_d$ | initiator decomposition rate constant, min$^{-1}$ |
| $k_p$ | chain propagation rate constant, l mol min$^{-1}$ |
| $k_t$ | chain termination rate constant, l mol min$^{-1}$ |
| $[M]$ | monomer concentration, mol l$^{-1}$ |
| $[M^*]$ | free radical concentration, mol l$^{-1}$ |
| $R_i$ | chain initiation reaction rate, mol l min$^{-1}$ |
| $R_p$ | chain propagation reaction rate, mol l min$^{-1}$ |
| $R_t$ | chain termination reaction reaction rate, mol l min$^{-1}$ |
| $\theta$ | time, min |
| $x$ | conversion |

[23] pointed out that complete conversion could be achieved in bulk systems as long as the reaction time was large enough. This refuted the notion that the bulk polymerization stopped at the glass transition point.

As the gel effect is present in bulk polymerization, the non-isothermal effect might always occur if the reaction heat in the gel stage is not removed on time. In general, the experiments of bulk free radical polymerization in the literature were performed in ampoule reactors and the water bath (or oil bath) temperature was often adopted as the reaction temperature. Although the bath temperature might remain unchanged in the experiments, the temperature of the reaction mass in the ampoule would increase rapidly when the gel effect occurs. Hence, polymerization was under a non-isothermal condition at this regime [24]. Therefore, in this case, an isothermal assumption may lead to a misunderstanding of the process [2].

In order to establish the mathematical model of kinetics for bulk free radical polymerization, it is important to understand the variation of reaction rate constants and initiator efficiencies with conversion as well as to obtain these parameters more directly and accurately. Therefore, the electron spin resonance (ESR) spectroscopy [25] and pulsed-laser polymerization (PLP) technique [26] were used to obtain the propagation rate constant $k_p$ directly. The results [25] showed that the propagation rate constant was unchanged within the range of wider conversion.

Carswell et al. [27] reported a study of the polymerization of MMA to high conversion, in which the Fourier transform infrared spectroscopy (FTIR) was used to measure the concentration of monomer and the ESR was used to obtain the radical concentration. The results showed that the polymerization could be obviously divided into several stages and $k_p$ was a constant in a much wider conversion range. The chain termination rate constant $k_t$ was also different at the low conversion stage and the gel effect stage.

For the initiator efficiency $f$, only limited experimental data at low conversion has been reported. In the past, $f$ was assumed to be a constant throughout the polymerization up to very high conversion. However, some investigators [22,28–30] challenged this hypothesis. For example, Russell et al. [22] pointed out that the initiator efficiency at intermediate conversion was reduced slightly compared with that at low conversion, and that it would decrease drastically in many orders of magnitude beyond a certain critical conversion.

It may be concluded from the brief review above that it is necessary to develop a new model for describing the kinetics of bulk free radical polymerization.

## 2. Kinetic model

Based on recent experimental evidence and our preliminary data processing of kinetic experimental results in the literature, a simple and useful model, the three stage polymerization model (TSPM), is proposed. The major content of TSPM is as follows:

1. The whole course of the bulk free radical polymerization is divided into three different stages: low conversion stage, gel effect stage and glass effect stage.
2. The kinetics of each stage can be described by the kinetic mechanism of the classical free radical polymerization. In each stage, the values of kinetic constants and initiator efficiency remain constant.
3. Glass effect stage occurs only when the reaction temperature is lower than the glass transition point of the polymer.

In order to illustrate the model, an initiator-initiating bulk free radical polymerization is introduced here as an example. Under a long chain hypothesis for monomer consumption, a quasi-steady-state approximation for radical concentration, and on the assumption that the total polymerization rate is equal to the rate of the monomer consumption [31], the following differential equations are obtained:

$$R_p = -\frac{d[M]}{d\theta} = k_p[M^*][M] \tag{1}$$

$$R_i = 2fk_d[I] = R_t = 2k_t[M^*]^2 \tag{2}$$

Eliminating $[M^*]$ from Eqs. (1) and (2),

$$R_p = -\frac{d[M]}{d\theta} = k_p(fk_d/k_t)^{1/2}[I]^{1/2}[M] \tag{3}$$

According to the classical kinetics of free radical polymerization, we have

$$[I] = [I]_0 \exp(-k_d\theta) \tag{4}$$

Substituting Eq. (4) into Eq. (3), the following equation is obtained

$$-\frac{d[M]}{[M]} = K_a[I]_0^{1/2}\exp(-k_d\theta/2)d\theta \tag{5}$$

where

$$K_a = k_p(fk_d/k_t)^{1/2} \tag{6}$$

### 2.1. Low conversion stage ($x \leq x_1$, $K_a = K_{1a}$)

Integrating Eq. (5) under the condition $[M] = [M]_0$ at $\theta = 0$ and defining $x = 1 - [M]/[M]_0$ gives

$$-\ln(1-x) = -K_1[\exp(-k_d\theta/2) - 1] \tag{7}$$

where

$$K_1 = (2/k_d)K_{1a}[I]_0^{1/2} \tag{8}$$

$$K_{1a} = k_{p1}(f_1k_d/k_{t1})^{1/2} \tag{9}$$

### 2.2. Gel effect stage ($x_1 \leq x \leq x_2$, $K_a = K_{2a}$)

Similarly, integrating Eq. (5) with the condition $[M] = [M]_1$ at $\theta = \theta_1$ and setting $[M] = [M]_0(1-x)$ and $[M]_1 = [M]_0(1-x_1)$, we obtain the following:

$$-\ln(1-x) = -\ln(1-x_1) - K_2[\exp(-k_d\theta/2) - \exp(-k_d\theta_1/2)] \tag{10}$$

where

$$K_2 = (2/k_d)K_{2a}[I]_0^{1/2} \tag{11}$$

$$K_{2a} = k_{p2}(f_2k_d/k_{t2})^{1/2} \tag{12}$$

### 2.3. Glass effect stage ($x \geq x_2$, $K_a = K_{3a}$)

Similarly, we have:

$$-\ln(1-x) = -\ln(1-x_2) - K_3[\exp(-k_d\theta/2) - \exp(-k_d\theta_2/2)] \tag{13}$$

where

$$K_3 = (2/k_d)K_{3a}[I]_0^{1/2} \tag{14}$$

$$K_{3a} = k_{p3}(f_3k_d/k_{t3})^{1/2} \tag{15}$$

It is obvious from Eqs. (7), (10) and (13) that if the polymerization kinetics can be described by the TSPM, three straight lines should be obtained in the plots of $-\ln(1-x)$ vs. $\exp(-k_d\theta/2)$ in three different stages. The slopes of the three straight lines are $K_1$, $K_2$ and $K_3$, respectively. The intersection points of the three straight lines are the critical conversion $x_1$ for the transition from low conversion stage to gel effect stage and the critical conversion $x_2$ for the transition from gel effect stage to glass effect stage. It is clear that $K_{1a}$, $K_{2a}$ and $K_{3a}$ can be calculated from $K_1$, $K_2$ and $K_3$ for a given initial initiator concentration $[I]_0$ and initiator decomposition rate constant $K_d$. In addition, $K_{1a}$, $K_{2a}$ and $K_{3a}$ obtained by means of Eqs. (8), (11) and (14) are independent of the value of the initiator concentration. According to the definitions in Eqs. (9), (12) and (15), the obtained $K_{1a}$, $K_{2a}$ and $K_{3a}$ under the TSPM can be correlated to temperature by the Arrhenius equation.

## 3. Model examination and discussion

### 3.1. The three stage polymerization model plots of kinetic data

In order to treat the experimental data, $k_d$ is given by the following equation [2,20]

$$k_d(\text{AIBN})/\text{min} = 6.32 \times 10^{16}\exp(-15.43 \times 10^3/T[K]) \tag{16}$$

#### 3.1.1. Three stage polymerization model plots of methylmethacrylate bulk polymerization data

Zhu and Hamielec [24] studied the heat effect for bulk free radical polymerization of MMA using 2,2′-azobisisobutyronitrile (AIBN) as the initiator in glass ampoule reactors and reported a set of conversion data obtained in a 5 mm outer diameter ampoule. The TSPM plot of the data adopted from Zhu and Hamielec [24] is shown in Fig. 1. It can be seen that the experimental data basically, falls on three straight lines with different slopes, as TSPM predicted.

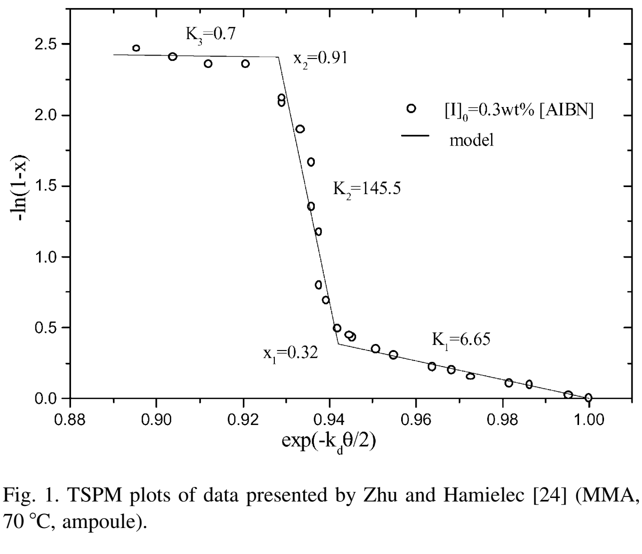

Fig. 1. TSPM plots of data presented by Zhu and Hamielec [24] (MMA, 70 °C, ampoule).

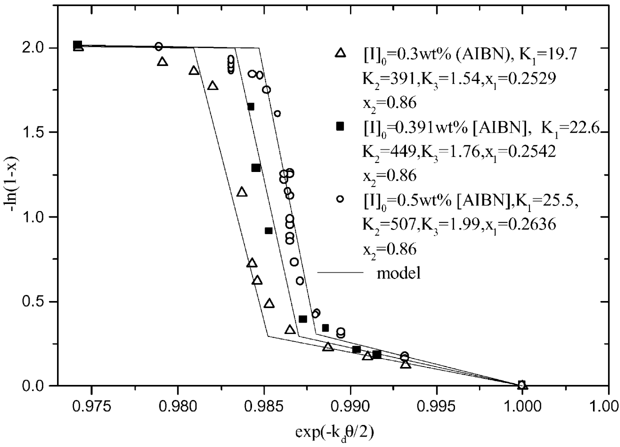

Fig. 2. TSPM plots of data presented by Balke and Hamielec [32] (MMA, 50 °C, ampoule).

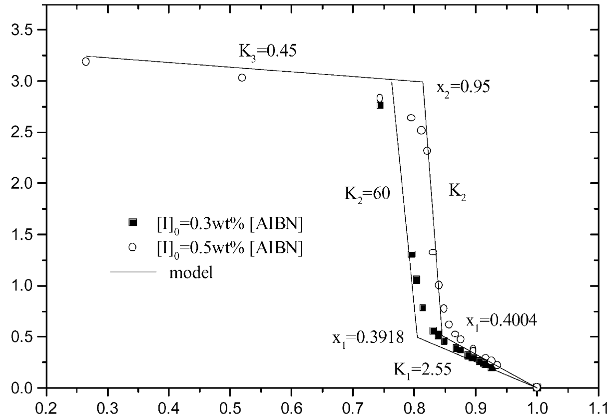

Fig. 4. TSPM plots of data presented by Balke and Hamielec [32] (MMA, 90 °C, ampoule).

It may also be seen that some experimental points around the transition point $x_1$ from the low conversion stage to the gel effect stage deviate slightly from the TSPM. This can be explained by the non-isothermal effect in this regime as discussed previously.

Figs. 2–4 show the TSPM plots of the data presented by Balke and Hamielec [32] at 50, 70 and 90 °C, respectively. It can be seen that the data at different temperature and initiator concentration are described well by TSPM. It can be found that the experimental points around the transition point $x_1$ deviate from the TSPM more obviously in Fig. 4, compared to that in Figs. 2 and 3. This can be explained by the fact that the experiments in Fig. 4 are performed in a larger, 7 mm inner diameter ampoule, where the non-isothermal effect might be greater than that performed in a smaller ampoule (3 mm inner diameter), as used for the experiments plotted in Figs. 2 and 3.

It is also seen that there is some deviation between the experimental data near the transition point from the gel effect stage to the glass effect stage. This may be attributed to the fact that $\ln(1-x)$ is very sensitive to $x$ at high conversion.

Balke and Hamielec [32] presented some long-term kinetic data in the glass effect stage. For example, in the case of 50 °C 0.391 wt% AIBN, the reaction lasted for 266.6 h. These data show that there is no limiting conversion, and complete conversion could be achieved as long as the reaction time is sufficient.

O'Neil and Wisnudel [2] studied the kinetics of MMA bulk polymerization at 20 °C (4 wt% AIBN) and 75 °C (5 wt% AIBN) by DSC with a small sample mass. Figs. 5 and 6 show the TSPM plots of data presented by O'Neil and Wisnudel [2]. From the plots, it can be seen that the experimental points generally fall on three straight lines with different slopes. However, the experimental data around the transition point $x_1$ still deviate slightly from TSPM for such small reactor. These results show that the non-isothermal effect might be an inherent character of the gel effect and might not be entirely removed by the improvement of heat transfer.

Ito [33] studied MMA bulk polymerization kinetics with

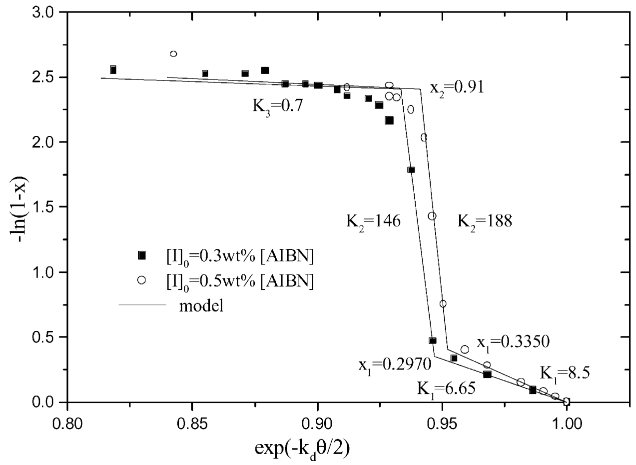

Fig. 3. TSPM plots of data presented by Balke and Hamielec [32] (MMA, 70 °C, ampoule).

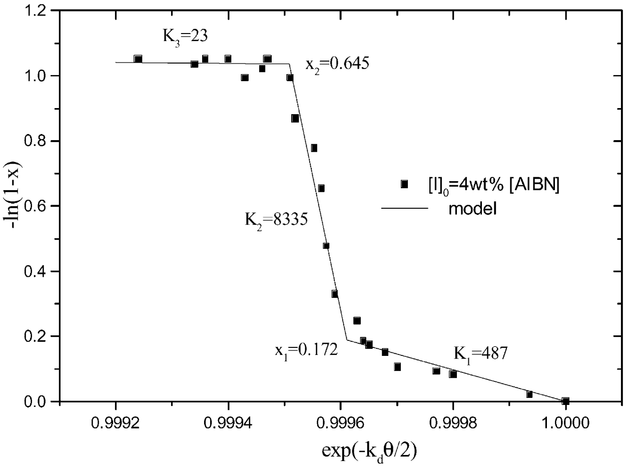

Fig. 5. TSPM plots of data presented by O'Neil and Wisnudel [2] (MMA, 20 °C, DSC).

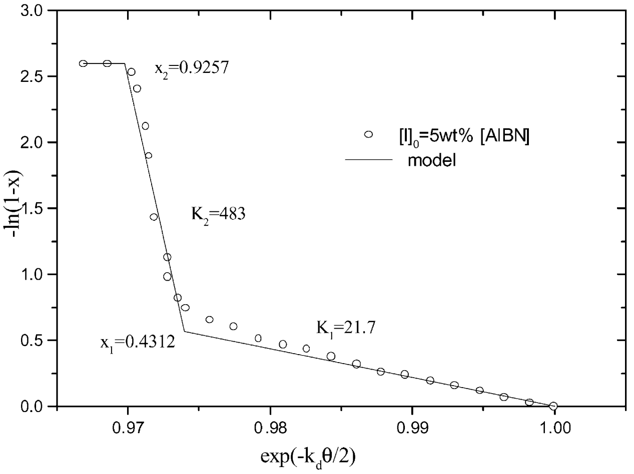

Fig. 6. TSPM plots of data presented by O'Neil and Wisnudel [2] (MMA, 75 °C, DSC).

an ampoule at 45 °C. His data has been used as a source of kinetic and molecular weight in some modeling and simulation exercises, and hence is of particular significance. Therefore these data are adopted to examine the correctness of TSPM. Fig. 7 shows the TSPM plots of Ito's data, from which it is seen that again Ito's data can be described well by the TSPM.

O'Neil et al. [1] reported a study of polymerization of MMA up to high conversion at 50 °C with high concentration AIBN as the initiator in a 15 ml ampoule reactor. The data are plotted in Fig. 8, which shows that the experimental data of O'Neil et al. can also be described well by TSPM.

### 3.1.2. Three stage polymerization model plots of styrene bulk polymerization data

Although a lot of kinetic data of St bulk polymerization has been published in the literature, only a very few experimental data have covered the glass effect stage, since most experiments for the kinetic study of St bulk polymerization stopped once the glass effect stage was reached. Therefore, it is difficult to determine $K_3$ by means of these data, and $x_2$ may only be roughly estimated.

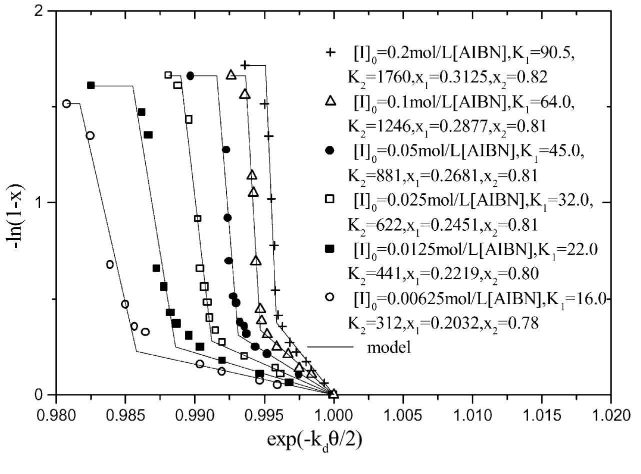

Fig. 7. TSPM plots of data presented by Ito [33] (MMA, 45 °C, ampoule).

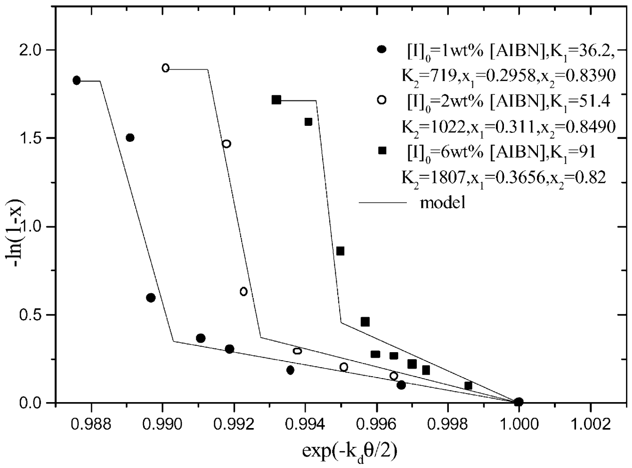

Fig. 8. TSPM plots of data presented by O'Neil et al. [1] (MMA, 50 °C, ampoule).

Fig. 9 shows the data of St bulk polymerization at 80 °C presented by O'Neil and Wisnudel [2], Nishmura [34] and Toboisky et al. [35] with TSPM plots. It is worth noting that the data given by O'Neil and Wisnudel [2] and Nishmura [34] fall on the same lines of TSPM, since they used same initiator concentration, 0.05 mol/l. However, the data from Toboisky et al. has been dropped on different lines since they used a different initiator concentration, 0.02 mol/l.

Fig. 10 shows the TSPM plots of St bulk polymerization data at 60 °C presented by O'Neil and Wisnudel [2], Nishmura [34] and Braks (data taken from Marten and Hamielec [36]) for four different initiator concentration, respectively. This figure clearly demonstrates that the experimental can be well represented by the data of TSPM.

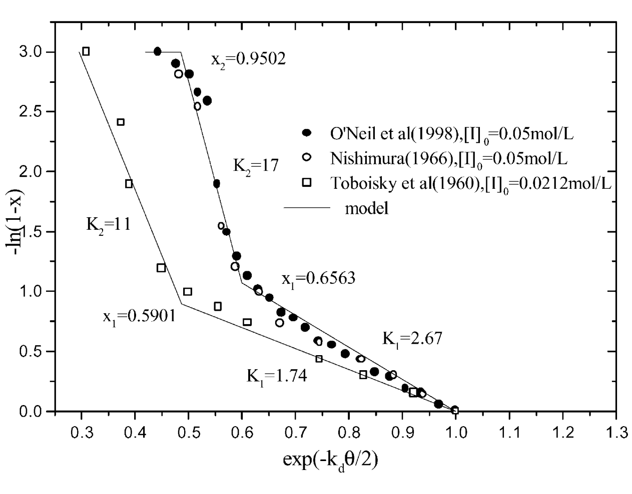

Fig. 9. TSPM plots of St bulk polymerization data (80 °C, DSC and ampoule).

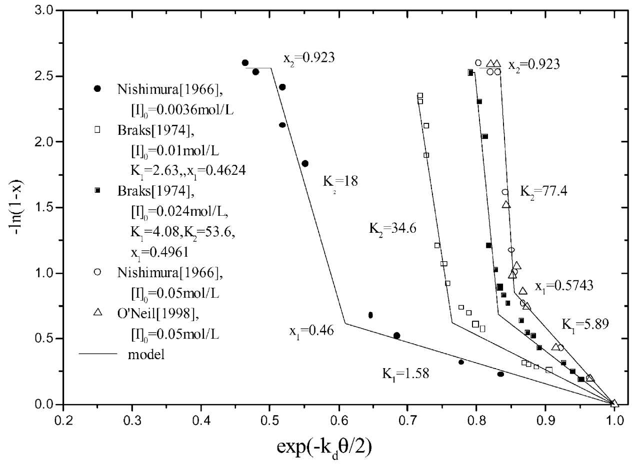

Fig. 10. TSPM plots of St bulk polymerization data (60 °C, DSC and ampoule).

Arai and Sato [37] also studied the kinetics of St bulk polymerization at 60 °C, by using an ampoule reactor. Fig. 11 shows the TSPM plots of the data presented by Arai and Sato [37]. It can be seen from the figure that the experimental data falls near to the straight lines of different slopes, except for some experimental data around the transition point $x_1$.

Ito [33] studied St bulk polymerization at 45 °C with AIBN as initiator in an ampoule reactor. The plots of data are shown in Fig. 12. Again, it can be seen from the plots that the experimental points are described well by TSPM, except for data near the transition point. However, Marten and Hamielec [36] pointed out that Ito's data might be inaccurate at higher conversion (≥85%). Our TSPM plots indicate that Ito's experiments have not captured the trend of the glass effect stage at high conversion. It seems that Ito's data only covers two stages.

Fig. 13 shows the TSPM plot of the kinetic data of St bulk polymerization at 70 °C with higher AIBN concentration (6.5 wt%) presented by O'Neil et al. [1]. It can be seen from this figure that there is a good match between the experimental data and the preditions of the TSPM.

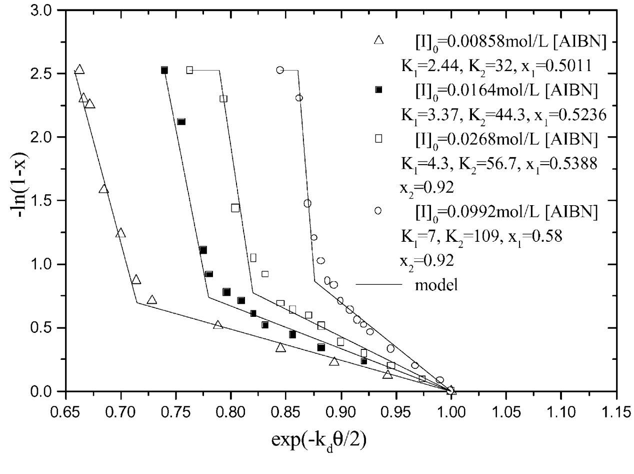

Fig. 11. TSPM plots of data presented by Arai and Sato [37] (St, 60 °C, ampoule).

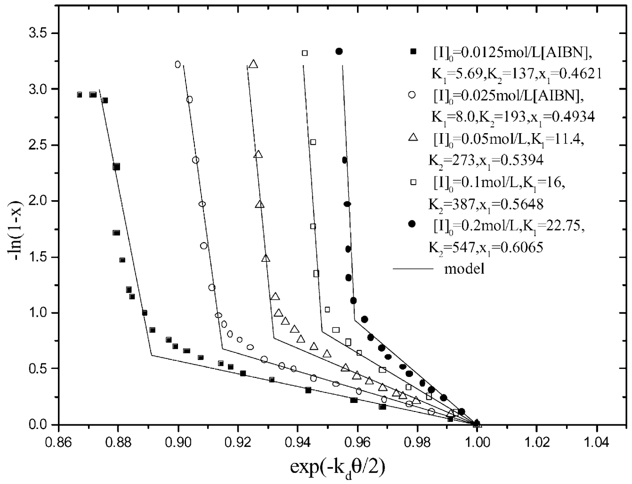

Fig. 12. TSPM plots of data presented by Ito [33] (St, 45 °C, ampoule).

### 3.1.3. Three stage polymerization model plots of ethylmethacrylate bulk polymerization data

Cardenas and O'Driscoll [11,12] studied the kinetics of EMA bulk polymerization at 70 and 90 °C with AIBN as initiator in a 3 mm outer diameter ampoule reactor. In most experiments, the conversions were higher than 97%. Since the reaction temperatures were higher than the glass transition temperature of the Polyethylmethacrylate (PEMA), 65 °C [38], the data of Cardenas and Driscoll [11,12] can be used to examine the hypothesis of TSPM as there will be no glass effect stage when the reaction temperature is greater than the glass transition temperature. The TSPM plots of the data presented by Cardenas and O'Driscoll are shown in Figs. 14 and 15 for reaction temperatures 70 and 90 °C, respectively. Indeed, the polymerization courses in these figures only include low conversion and gel effect

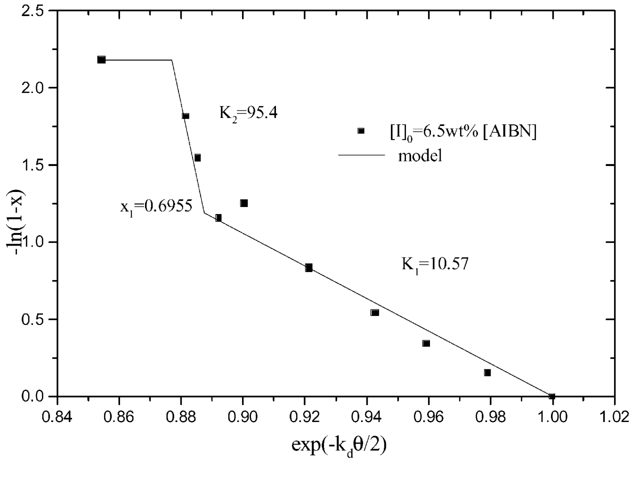

Fig. 13. TSPM plots of data presented by O'Neil et al. [1] (St, 70 °C, ampoule).

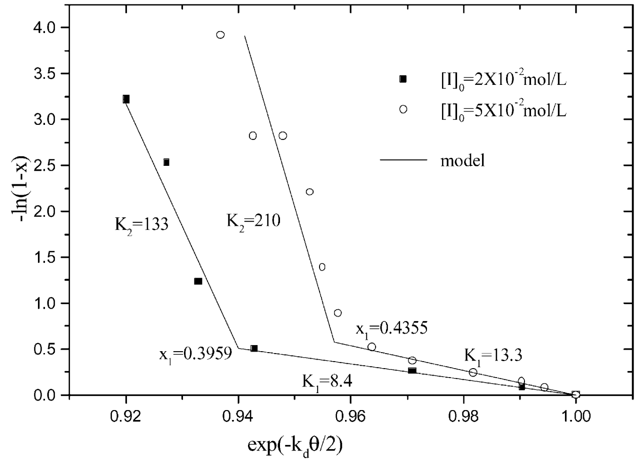

Fig. 14. TSPM plots of data presented by Cardenas and O'Driscoll [12] (EMA, 70 °C, ampoule).

stage. Again, these results show that the TSPM is correct for a case without glass effect stage.

### 3.2. Correlation of apparent reaction rate constants

As mentioned previously, the apparent reaction rate constants for all three stages, $K_{1a}$, $K_{2a}$ and $K_{3a}$, should be independent of the initial initiator concentration and can be correlated to reaction temperature by means of the Arrhenius equation.

#### 3.2.1. Correlation of apparent reaction rate constants for methylmethacrylate bulk polymerization

Using the $K_1$, $K_2$ and $K_3$ for MMA bulk polymerization in Figs. 1–8, the $K_{1a}$, $K_{2a}$ and $K_{3a}$ can be calculated by means of Eqs. (8), (11) and (14). The logarithm of the calculated $K_{1a}$, $K_{2a}$ and $K_{3a}$ are plotted against the reciprocal of the reaction temperature, 1/*T* in Fig. 16. All of the data falls on three straight lines for the different stages. This demonstrates that all three apparent rate constants, $K_{1a}$, $K_{2a}$ and $K_{3a}$ are well fitted with Arrhenius correlations to the reaction temperature.

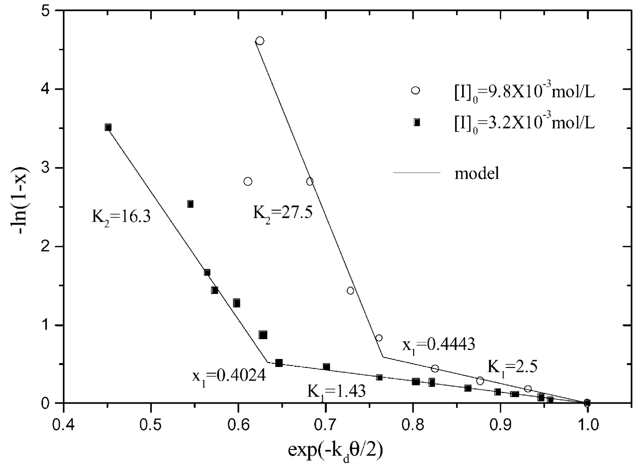

Fig. 15. TSPM plots of data presented by Cardenas and O'Driscoll [12] (EMA, 90 °C, ampoule).

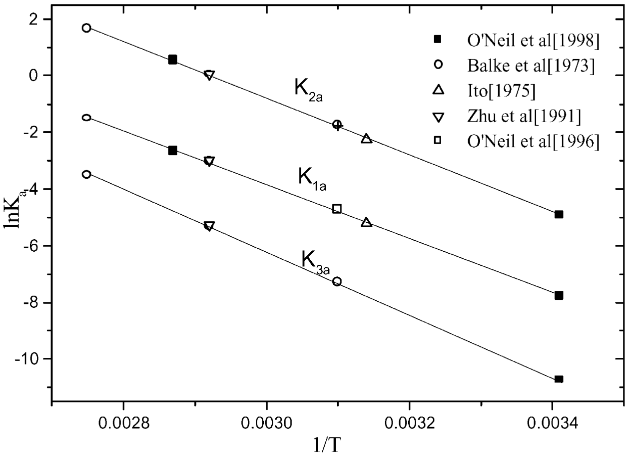

Fig. 16. Apparent reaction rate constants for MMA bulk polymerization.

Based on Fig. 16, general calculation equations of $K_{1a}$, $K_{2a}$ and $K_{3a}$ for MMA bulk polymerization are obtained as follows:

$$K_{1a} = 5.44 \times 10^{10} \exp[-9520/T(\mathrm{K})] \tag{17}$$

$$K_{2a} = 4.80 \times 10^{12} \exp[-10\,000/T(\mathrm{K})] \tag{18}$$

$$K_{3a} = 5.68 \times 10^{11} \exp[-11\,100/T(\mathrm{K})] \tag{19}$$

#### 3.2.2. Correlation of apparent reaction rate constants for styrene bulk polymerization

Using the $K_1$ and $K_2$ data for St bulk polymerization in Figs. 9–13, $K_{1a}$ and $K_{2a}$ can be calculated and treated in a similar manner as for MMA bulk polymerization mentioned above. It is shown that the $K_{1a}$ and $K_{2a}$ calculated from $K_1$ and $K_2$ are functions of the reaction temperature only. They are independent of the initial initiator concentration as shown in Fig. 17. Once again, from Fig. 17, equations for

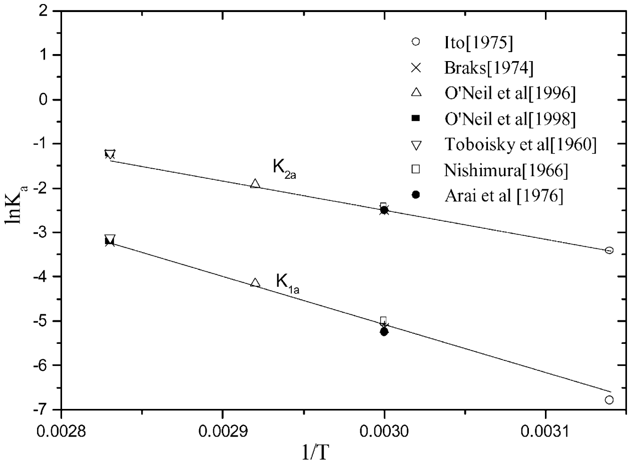

Fig. 17. Apparent reaction rate constants for St bulk polymerization.

$K_{1a}$ and $K_{2a}$ of St bulk polymerization can be derived:

$$K_{1a} = 7.40 \times 10^{11} \exp[-10\,790/T(\mathrm{K})] \tag{20}$$

$$K_{2a} = 2.62 \times 10^{7} \exp[-6520/T(\mathrm{K})] \tag{21}$$

However, due to the absence of available experimental data for $K_3$ in the literature, it is not possible to obtain a calculation equation of $K_{3a}$. To achieve this, it is neccesary to perform some kinetic experiments for long reaction time.

## 4. Conclusions

Based on the current study, the following observations can be made:

1. The free radical bulk polymerization can be satisfactorily described by means of the TSPM. The model is very simple and useful for engineering purposes.
2. Using the experimental data published in the literature, the general Arrhenius-type equations for the apparent reaction rate constants at three different polymerization stages for bulk free radical polymerization of MMA and St have been obtained. This gives strong support to the correctness of TSPM.
3. Using the experimental data of EMA bulk polymerization, the hypothesis that there will be no glass effect stage when the reaction temperature is greater than the glass transition temperature of polymer has been verified.

## Acknowledgements

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

## References

[1] O'Neil GA, Wisnudel MB, Torkelson JM. Macromolecules 1996;29:7477.
[2] O'Neil GA, Wisnudel MB. AIChE J 1998;44:1226.
[3] Tefera N, Weickert G, Westerterp KR. J Appl Polym Sci 1997;63:1663.
[4] Duerksen JH, Hamielec AE. J Polym Sci 1968;C25:155.
[5] Brooks BW. Proc R Soc Lond 1977;A357:1311.
[6] Ray WH, Jaisinghani R. Chem Engng Sci 1977;32:811.
[7] Hui AW, Hamielec AE. J Appl Polym Sci 1972;16:749.
[8] Ballard MJ, Gilbert RG, Napper DH. J Polym Sci 1984;32:3225.
[9] Ballard MJ, Gilbert RG, Napper DH. Macromolecules 1986;19:1303.
[10] Buback M. Macromol Chem 1990;191:1575.
[11] Cardenas JN, O'Driscoll KF. J Polym Sci, Polym Chem Ed 1976;14:883.
[12] Cardenas JN, O'Driscoll KF. J Polym Sci, Polym Chem Ed 1977;15:1883 see also page 2097.
[13] Tulig TJ, Tirrell MV. Macromolecules 1982;15:459.
[14] Ito K. J Polym 1980;12(8):499.
[15] Ito K. J Polym 1981;13(8):127.
[16] Ito K. J Polym 1984;16(10):761.
[17] Marten FL, Hamielec AE. ACS Symp Ser 1979;104:43.
[18] Schmidt AD, Ray WH. Chem Engng Sci 1981;36:1401.
[19] Soh SK, Sundberg DC. J Polym Sci, Polym Chem Ed 1982;20, see also pages 1299, 1315, 1331, 1345.
[20] Chiu WY, Carratt GM, Soong DS. Macromolecules 1983;16:348.
[21] Achilias D, Kiparissides C. Macromolecules 1992;25:3739.
[22] Russell GT, Napper DH, Gilbert RC. Macromolecules 1988;21:2141.
[23] Stickler M. Macromol Chem 1982;184:2563.
[24] Zhu S, Hamielec AE. Polymer 1991;32:3021.
[25] Parker HY, Westmoreland DG, Chang HR. Macromolecules 1996;29:5119.
[26] Hutchinson PA, Aronson MT, Richards AR. Macromolecules 1993;26:6410.
[27] Carswell TG, Hill DJT, Londero DI, O'Donnell JH, Pomery PT, Winzor CL. Polymer 1992;33:137.
[28] Shen J, Tian Y, Wang G, Yang M. Macromol Chem 1991;192:2669.
[29] Zhu S, Tian Y, Hamielec AE, Eaton DR. Polymer 1990;31:154.
[30] Tefera N, Weickert G, Bloodworth R, Schweer J. Macromol Chem Phys 1994;195:3067.
[31] Pan Z. Macromolecular chemistry. Beijing, China: Chemical Industry Press, 1997 (in Chinese).
[32] Balke ST, Hamielec AE. J Appl Polym Sci 1973;17:905.
[33] Ito K. J Polym Sci, Part A 1975;13:401.
[34] Nishimura N. J Macromol Sci 1966;1:257.
[35] Toboisky AV, Rogers CE, Brickman RD. J ACS 1960;82:1277.
[36] Marten FL, Hamielec AE. J Appl Polym Sci 1982;27:489.
[37] Arai K, Saito S. J Chem Engng Jpn 1976;4:302.
[38] Li S, Lu G, Liang Z. Macromolecular chemistry. Beijing, China: Science Press, 1982 (in Chinese).