



# A kinetic study on bulk thermal polymerization of styrene

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## Abstract

The kinetics of bulk thermal polymerization of styrene over the range of 100–200 °C has been studied based on three stage polymerization model (TSPM) in this paper. TSPM plots showed that the whole polymerization course only exhibits two stages, low conversion stage and gel effect stage, which is consistent with TSPM as the reaction temperature is higher than the glass transition temperature of polystyrene. It was found that the critical conversion,  $x_1$ , for the transition from low conversion stage to gel effect stage is independent of the reaction temperature and approximately equal to 0.5. In addition, the apparent reaction rate constants obtained from TSPM plots could be correlated to temperature by Arrhenius equation. Expressions predicting number-average molecular weight were also derived according to TSPM. Using the expressions to treat experimental data available in the literature, it was found that number-average molecular weight is independent of the conversion and relative to the reaction temperature at low conversion stage. However, it varies with the conversions at gel effect stage and the variations are more obvious as the reaction temperature rises. © 2002 Elsevier Science Ltd. All rights reserved.

**Keywords:** Bulk thermal polymerization of styrene; Polymerization kinetics; Three stage polymerization model

## 1. Introduction

In order to simulate the kinetics of bulk thermal polymerization of styrene (St), two types of model have been proposed, i.e. the microscopic and macroscopic kinetics models [1]. Although the microscopic kinetics model was based on polymerization mechanism, the kinetic equation derived was complicated and adjustable parameters were used. For instance, Arai et al. [2] proposed a kinetic model by considering the effects for a decrease in a jump frequency of a polymer segment on the rate of each elementary reaction, in which five adjustable parameters were included. Hui and Hamielec [3] assumed that all of the rate constants could vary with conversions and proposed a so-called macroscopic kinetics model. Since the classical kinetics mechanism holds true at least within low conversion stage, where the apparent reaction rate constant should be independent of conversions, the assumption may have some problems. In addition, Arai et al. [2] as well as Hui and Hamielec [3] hypothesized in their models that the chain transfer constant to monomer would vary on conversions,

which is also in conflict with the classical kinetics mechanism.

Many researchers studied the effects of conversion and reaction temperature on the molecular weight of the polymer formed. Unfortunately, some conclusions deviate from each other. Arai et al. [2] measured the variations of molecular weight with conversions at five different temperatures (100.1, 120.4, 140.2, 160.8, and 179.5 °C) and found that the molecular weights reduced abnormally at 179.5 °C within the limits of higher conversion. Arai et al. [2] pointed out that this phenomenon could not be explained clearly, but they still supposed that it might result from  $\beta$ -scission of C–C bond of the product due to the chain transfer to the carbon atom linked to the phenyl group of polystyrene (PS). Hui and Hamielec [3] studied the variations of number-average molecular weight with conversions at four temperatures (100, 140, 170, and 200 °C) and concluded that the molecular weights reduced throughout with the increase in conversion. Shi et al. [4] also conducted similar study at four different temperatures (140, 160, 180, and 200 °C) and found that the number-average molecular weights did not vary significantly with conversions. In order to clarify the above inconsistency, further study is needed.

To establish the equations predicting both conversion

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### Nomenclature

$C_m$	constant of chain transfer to monomer
$K_1$	overall reaction rate constant at low conversion stage ( $\text{min}^{-1}$ )
$K_2$	overall reaction rate constant at gel effect stage ( $\text{min}^{-1}$ )
$k_{1a}$	apparent reaction rate constant at low conversion stage ( $\text{mol/l min}$ )
$k_{2a}$	apparent reaction rate constant at gel effect stage ( $\text{mol/l min}$ )
$k_p$	chain propagation rate constant ( $\text{l/mol min}$ )
$k_i$	chain initiation reaction rate constant ( $\text{l/mol min}$ )
$k_t$	chain termination rate constant ( $\text{l/mol min}$ )
$k_{tr,m}$	rate constant of chain transfer to monomer ( $\text{l/mol min}$ )
$[M]$	monomer concentration ( $\text{mol/l}$ )
$[M^*]$	free radical concentration ( $\text{mol/l}$ )
$R_p$	chain propagation reaction rate ( $\text{mol/l min}$ )
$R_i$	chain initiation reaction rate ( $\text{mol/l min}$ )
$R_t$	chain termination reaction rate ( $\text{mol/l min}$ )
$R_{tr,m}$	reaction rate of chain transfer to monomer ( $\text{mol/l min}$ )
$T$	reaction temperature (K)
$w$	molecular weight of monomer
$x$	conversion
$x_1$	critical conversion
$\theta$	time (min)

history and molecular weight, it is necessary to determine thermal-initiated mechanism first. There are two viewpoints on the mechanism at present. One is the second-order initiation [5], in which polymerization rate is assumed to be proportional to the square of St concentration. Another is the third-order initiation [3], i.e. polymerization rate is proportional to the third power of St concentration. Although there are some inconsistencies, most researchers agree with the rate as second-order initiation. Bengough and Park [6] as well as Barr et al. [7] studied the thermal-initiated rate at different temperatures within a wide conversion range and concluded that the rate was related to the square of St concentration. The work of Shi et al. [4] also supported the mechanism of second-order initiation.

In our recent papers [8,9], a simple but useful model, the three stage polymerization model (TSPM) was proposed to describe high-conversion free radical polymerization exhibiting a strong gel effect. The main content of TSPM is that the whole course of bulk polymerization is divided into three stages, i.e. low conversion, gel effect and glass effect stages, and that the values of the kinetic constants and of the initiator efficiency do not vary with conversions in each stage. In addition, there will be no glass effect stage when the reaction temperature is greater than the glass transition

temperature of the polymer formed. The model agreed well with a lot of data available in the literature on conversion history and product molecular weight for methylmethacrylate (MMA), St and ethylmethacrylate (EMA) bulk polymerizations initiated with the initiator, 2,2'-azobisisobutyronitrile (AIBN).

In this paper, the applicability of TSPM on the bulk thermal polymerization of St is examined and equations predicting both conversion history and number-average molecular weight are derived. Moreover, the experimental data on conversion history and number-average molecular weight found in the literature are used to check the equations.

## 2. Model development

To obtain the equations predicting both conversion history and number-average molecular weight, the following assumptions are made:

1. TSPM [8] is still suitable for bulk free radical thermal polymerization of St.
2. Polymerization rate is proportional to the square of St concentration, i.e. the second-order initiation is preferred for bulk thermal polymerization of St [4,6,7].

### 2.1. Conversion history

Since the glass transition temperature of PS is 100 °C [10] and the temperatures range studied in this paper are within 100–200 °C, it is clear that only low conversion and gel effect stages should be included under this condition according to TSPM. Assuming that the quasi-steady-state approximation for radical concentration holds true and that total polymerization rate is equal to the rate of monomer consumption, we have

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

$$R_i = 2k_i[M]^2 = R_t = 2k_t[M^*]^2 \quad (2)$$

Using Eqs. (1) and (2),  $[M^*]$  can be cancelled from the equations, thus Eq. (1) becomes

$$R_p = -\frac{d[M]}{d\theta} = k_p \left( \frac{k_i}{k_t} \right)^{1/2} [M]^2 \quad (3)$$

#### 2.1.1. Low conversion stage ( $x \leq x_1$ )

Integrating Eq. (3) under the condition  $[M] = [M]_0$  at  $\theta = 0$  and defining  $x = 1 - [M]/[M]_0$ , we have

$$\begin{aligned} \frac{1}{1-x} &= 1 + k_{p1} \left( \frac{k_{i1}}{k_{t1}} \right)^{1/2} [M]_0 \theta = 1 + k_{1a} [M]_0 \theta \\ &= 1 + K_1 \theta \end{aligned} \quad (4)$$

where

$$k_{1a} = k_{p1} \left( \frac{k_{i1}}{k_{t1}} \right)^{1/2} \quad (5)$$

$$K_1 = k_{1a}[M]_0 \quad (6)$$

2.1.2. Gel effect stage ( $x \geq x_1$ )

Integrating Eq. (3) with the conditions  $[M] = [M]_0$  at  $\theta = 0$  and  $[M] = [M]_1$  at  $\theta = \theta_1$ , as well as defining  $x_1 = 1 - [M]_1/[M]_0$  gives

$$\begin{aligned} \frac{1}{1-x} &= \frac{1}{1-x_1} + k_{p2} \left( \frac{k_{i2}}{k_{t2}} \right)^{1/2} [M]_0 (\theta - \theta_1) \\ &= \frac{1}{1-x_1} + k_{2a}[M]_0 (\theta - \theta_1) \\ &= \frac{1}{1-x_1} + K_2 (\theta - \theta_1) \end{aligned} \quad (7)$$

where

$$k_{2a} = k_{p2} \left( \frac{k_{i2}}{k_{t2}} \right)^{1/2} \quad (8)$$

$$K_2 = k_{2a}[M]_0 \quad (9)$$

It is observed from Eqs. (4) and (7) that there should be two straight lines in the plot of  $1/(1-x)$  vs.  $\theta$  if the experimental data of conversion history can be described by the model. The slopes of two straight lines are  $K_1$  and  $K_2$ , respectively. Using Eqs. (6) and (9),  $k_{1a}$  and  $k_{2a}$  can be calculated from  $K_1$  and  $K_2$ . In addition,  $k_{1a}$  and  $k_{2a}$  should be able to correlate to temperature with Arrhenius equation according to the definitions of Eqs. (5) and (8). The intersection point of two straight lines is the critical conversion,  $x_1$ , for the transition from low conversion stage to gel effect stage.

2.2. Number-average molecular weight

Based on the classical theory of free radical polymerization, the cumulative number-average degree of polymerization,  $\bar{P}_n$ , can be expressed as

$$\frac{1}{\bar{P}_n} = \frac{\int_{[M]_0}^{[M]} \frac{1}{p_n} d[M]}{-([M]_0 - [M])} \quad (10)$$

In Eq. (10), the instantaneous number-average degree of polymerization,  $p_n$ , is

$$\begin{aligned} \frac{1}{p_n} &= \frac{(R_t/2) + R_{tr,m}}{R_p} = \frac{k_t[M^*]^2 + k_{tr,m}[M^*][M]}{k_p[M^*][M]} \\ &= \frac{k_t[M^*]}{k_p[M]} + \frac{k_{tr,m}}{k_p} \end{aligned} \quad (11)$$

According to the quasi-steady-state approximation for radical concentration, the following equation can be written

as

$$R_i = 2k_i[M]^2 = R_t = 2k_t[M^*]^2 \quad (12)$$

Eq. (12) yields

$$[M^*] = \left( \frac{k_i}{k_t} \right)^{1/2} [M] \quad (13)$$

Substituting Eq. (13) in Eq. (11) gives

$$\frac{1}{p_n} = \frac{k_t}{k_p} \left( \frac{k_i}{k_t} \right)^{1/2} + \frac{k_{tr,m}}{k_p} \quad (14)$$

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

For low conversion stage, Eq. (14) can be rewritten as

$$\frac{1}{p_{n1}} = \frac{k_{t1}}{k_{p1}} \left( \frac{k_{i1}}{k_{t1}} \right)^{1/2} + \frac{k_{tr,m1}}{k_{p1}} \quad (15)$$

Substituting Eq. (15) in Eq. (10), then integrating the equation obtained and considering  $\bar{M}_{n1} = \bar{P}_{n1}w$ , we have

$$\begin{aligned} \frac{1}{\bar{M}_{n1}} &= \frac{1}{\bar{P}_{n1}w} = \frac{\int_{[M]_0}^{[M]} \frac{1}{p_{n1}} d[M]}{-w([M]_0 - [M])} \\ &= \frac{1}{w} \left[ \frac{k_{t1}}{k_{p1}} \left( \frac{k_{i1}}{k_{t1}} \right)^{1/2} + \frac{k_{tr,m1}}{k_{p1}} \right] = A_1 \end{aligned} \quad (16)$$

where  $A_1$  should be a constant since the reaction rate constants do not vary with conversions at low conversion stage on the basis of TSPM and  $w$  is the molecular weight of monomer.

2.2.2. Gel effect stage ( $x \geq x_1$ )

For gel effect stage, Eqs. (10) and (14) can be rewritten as

$$\frac{1}{\bar{P}_{n2}} = \frac{\int_{[M]_0}^{[M]_1} \frac{1}{p_{n1}} d[M] + \int_{[M]_1}^{[M]} \frac{1}{p_{n2}} d[M]}{-([M]_0 - [M])} \quad (17)$$

and

$$\frac{1}{p_{n2}} = \frac{k_{t2}}{k_{p2}} \left( \frac{k_{i2}}{k_{t2}} \right)^{1/2} + \frac{k_{tr,m2}}{k_{p2}} \quad (18)$$

Substituting Eqs. (15) and (18) in Eq. (17), then integrating the equation obtained and considering  $\bar{M}_{n2} = \bar{P}_{n2}w$ , we have

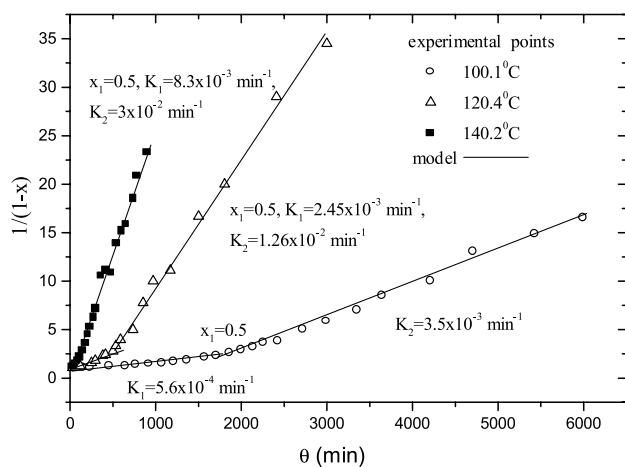
$$\begin{aligned} \frac{1}{\bar{M}_{n2}} &= \frac{1}{\bar{P}_{n2}w} = \frac{1}{w} \left[ \frac{1}{p_{n1}} \frac{x_1}{x} + \frac{1}{p_{n2}} \left( 1 - \frac{x_1}{x} \right) \right] \\ &= A_2 + (A_1 - A_2) \frac{x_1}{x} \end{aligned} \quad (19)$$

where

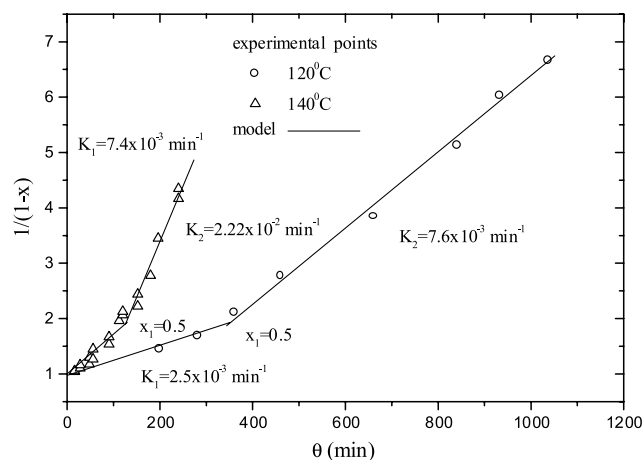
$$A_2 = \frac{1}{wp_{n2}} = \frac{1}{w} \left[ \frac{k_{t2}}{k_{p2}} \left( \frac{k_{i2}}{k_{t2}} \right)^{1/2} + \frac{k_{tr,m2}}{k_{p2}} \right]$$

which is also a constant according to TSPM.

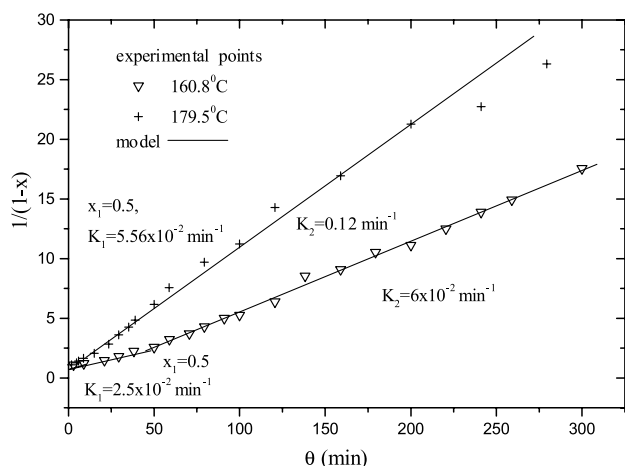
It is clear that if the model is correct, Eq. (19) should be able to treat the experimental data at gel effect stage.



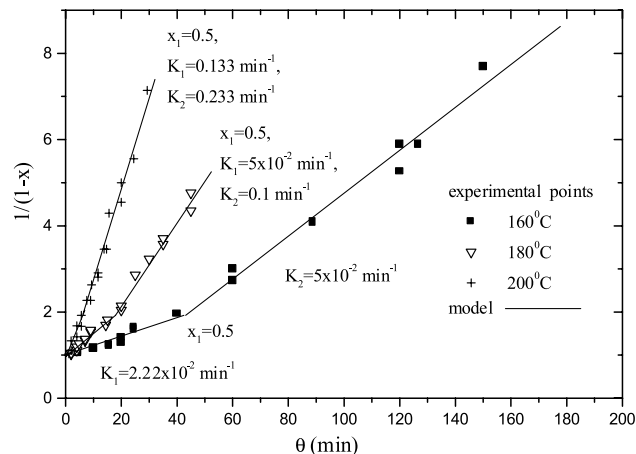
(a)



(a)



(b)



(b)

Fig. 1. TSPM plots of data presented by Arai et al. [2].

Fig. 2. TSPM plots of data presented by Shi et al. [4].

### 3. Model examination and data correlation

#### 3.1. Conversion history

##### 3.1.1. Plots of conversion history data

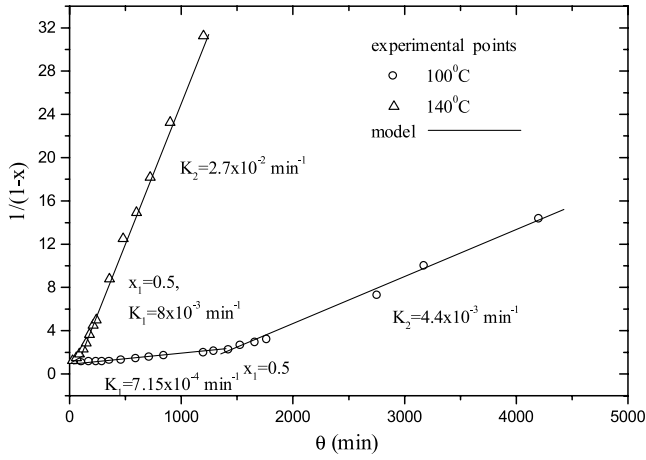
In order to examine the model, the plots of  $1/(1-x)$  vs.  $\theta$ , i.e. TSPM plots are performed by using the conversion vs. time data found in the literature.

Fig. 1 shows the plots using the data presented by Arai et al. [2]. It is observed from Fig. 1 that the data fall basically on the straight lines. The polymerization course only exhibits two stages, i.e. the low conversion stage and the gel effect stage as expected by TSPM. In addition, the critical conversion,  $x_1$ , is approximately equal to 0.5 and independent of the reaction temperature.

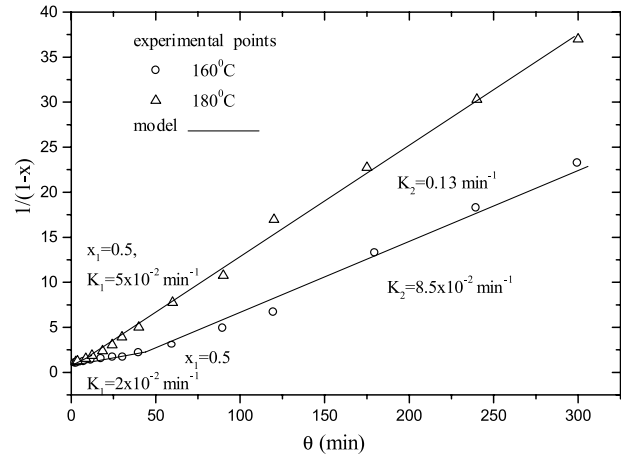
Fig. 2 shows the plots of the data presented by Shi et al. [4]. It is seen from the figure that all of the experimental data at 120–200 °C can be satisfactorily described by TSPM and there occur only two stages. The critical conversion,  $x_1$ , is still equal to 0.5.

Fig. 3 shows the plots of the data presented by Hui and Hamielec [3]. Similarly, the experimental data fall on the straight lines except for 200 °C data at conversion beyond 0.95. The conversions up to 0.95 were measured by gravimetry and the conversions beyond 0.94, by UV spectrophotometry in the experiments of Hui and Hamielec [3], which may cause the deviation of data measured from each other. In fact, if the plot of conversion history at 200 °C in the paper of Hui and Hamielec [3] is carefully observed, it can be found that conversion data appear abruptly on the high side when the conversion is beyond 0.95. In particular, due to the fact that  $1/(1-x)$  is very sensitive to  $x$  at high conversion, which may also cause the deviation of experimental data from the model. As expected by TSPM, it is observed from Fig. 3 that only two stages are in existence. The critical conversion  $x_1$  is equal to 0.5 roughly.

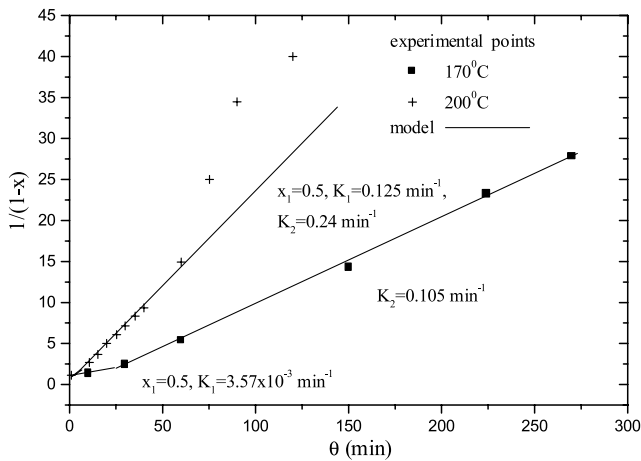
The experimental data of Taherzadeh was referenced in the paper of Hui and Hamielec [3]. In order to examine the model extensively, the plots of the data presented by Taherzadeh are also performed as shown in



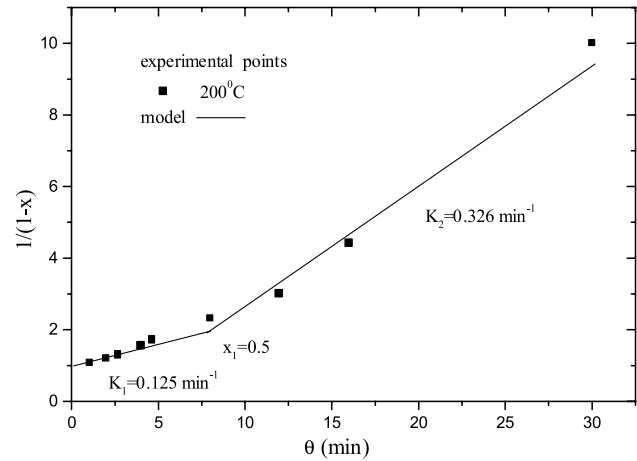
(a)



(a)



(b)



(b)

Fig. 3. TSPM plots of data presented by Hui and Hamielec [3].

Fig. 4. TSPM plots of data presented by Taherzadeh (1972) [3].

Fig. 4. Hui and Hamielec [3] pointed out that the data of Taherzadch at 160 °C were unreliable because the reaction temperature was remarkably increased during polymerization progress, these data, hence, are cancelled in the plots. It is observed from Fig. 4 that the data of Taherzadeh at different temperatures can also be described by the TSPM. The polymerization course only includes two stages and the critical conversion,  $x_1$ , is equal to 0.5.

Since the cause of gel effect is an interesting subject in recent times and a consistent viewpoint on its mechanism has not been yet established [11], it is difficult to explain why  $x_1$  is equal to 0.5. Further study on this question is necessary.

### 3.1.2. Correlation of apparent reaction rate constants

According to the definitions of Eqs. (5) and (8), the apparent reaction rate constants should be able to correlate to temperature with Arrhenius plot. Fig. 5 shows such plots. As seen from the figure,  $k_{1a}$  and  $k_{2a}$  obtained with the

conversion data of different researchers fall satisfactorily on the two straight lines, respectively.

Based on Fig. 5, the general expressions predicting  $k_{1a}$  and  $k_{2a}$  can be obtained

$$k_{1a} = 9.46 \times 10^6 \exp(-9500/T) \quad (20)$$

$$k_{2a} = 2.73 \times 10^5 \exp(-7500/T) \quad (21)$$

It is worth to notice that the volume expansion in the modeling of St bulk thermal polymerization was often considered in former works [2,3]. We also considered the volume expansion in preliminary data processing, but the results showed that the influence of volume expansion could be neglected when the TSPM was employed.

### 3.2. Number-average molecular weight

#### 3.2.1. Plots of molecular weight data

When  $x_1/x$  is used as the abscissa and  $1/\bar{M}_n$  as the

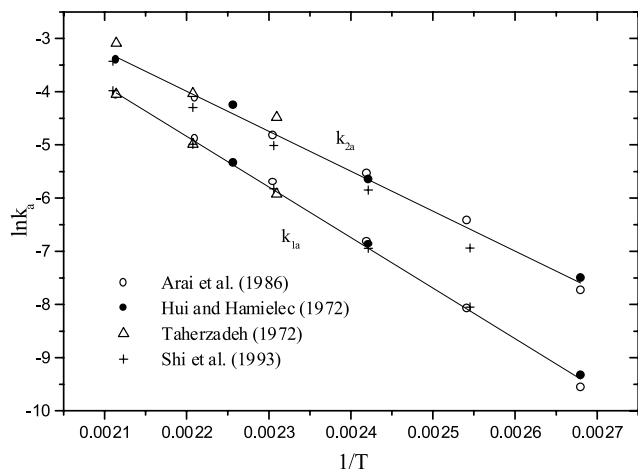


Fig. 5. Correlation of apparent reaction rate constants.

ordinate to plot the experimental data of number-average molecular weight, it is observed from Eqs. (16) and (19) that a horizontal line should be obtained in the zone of  $x_1/x \geq 1$ . The ordinate of horizontal line is  $A_1$ . In the zone of  $x_1/x \leq 1$ , another straight line should also be obtained, the slope and intercept of the straight line are  $(A_1 - A_2)$  and  $A_2$ , respectively.

Fig. 6 shows such plots, in which the data presented by different researchers are used. It is observed from Fig. 6 that the data trends are basically consistent with Eqs. (16) and (19). Although there are some data dispersion, the polymerization course is obviously divided into two stages.

It is also observed from Fig. 6 that the number-average molecular weight is independent of conversions and only relative to reaction temperature at low conversion stage. However, it varies with conversions at gel effect stage and the variations are more obvious as the reaction temperature rises. The values of  $A_2$  are also related to reaction temperatures only. As pointed out by Arai et al. [2], due to the presence of the possible error in analysis of the elution curves, the dispersion of experimental points in Fig. 6 is understandable.

### 3.2.2. Correlation of $A_1$ and $A_2$

It is found that  $A_1$  and  $A_2$  in Fig. 6 can be correlated to  $1/T$  as shown in Fig. 7. The equations of straight lines are as follows

$$A_1 = 0.034 \exp\left(-\frac{3534}{T}\right) \quad (22)$$

$$A_2 = 0.223 \exp\left(-\frac{4230}{T}\right) \quad (23)$$

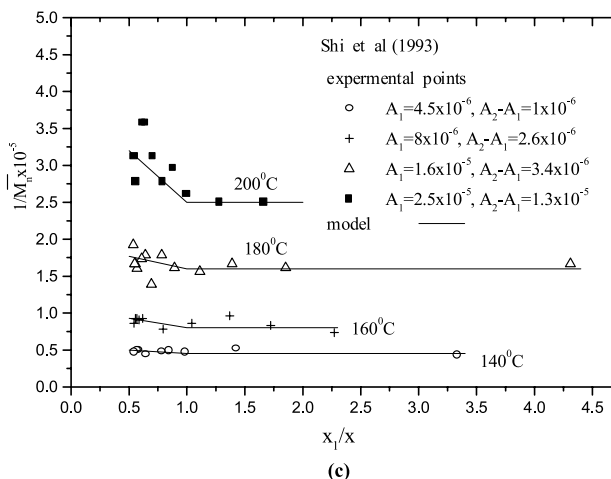
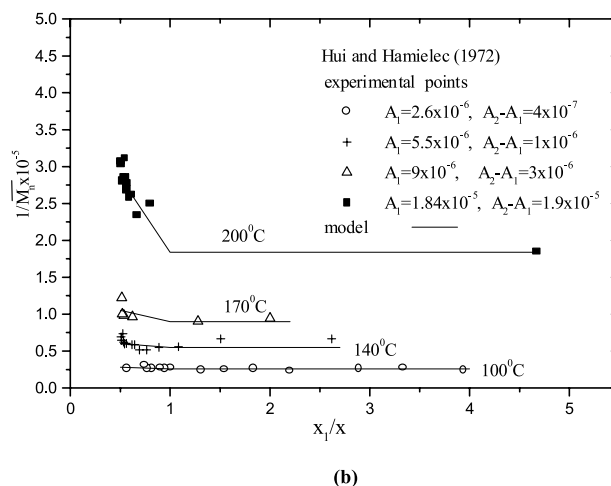
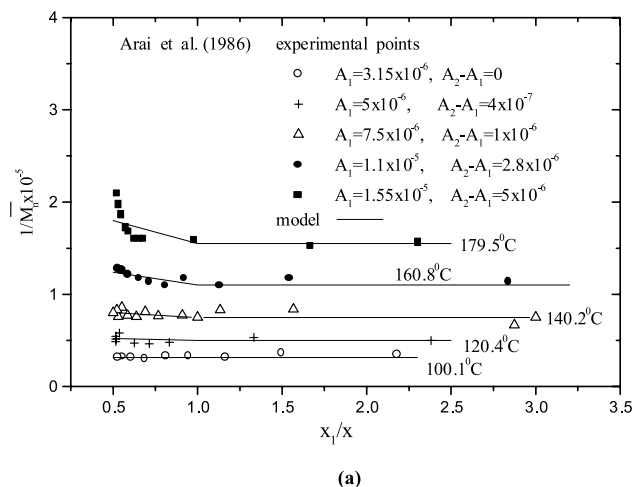


Fig. 6. Relation between number-average molecular weight and conversion.

According to TSPM, since all of the reaction rate constants at each polymerization stage do not vary with conversions, they are only dependent on reaction temperatures and should be able to correlate with Arrhenius plot. The following equations, hence, can be written according to

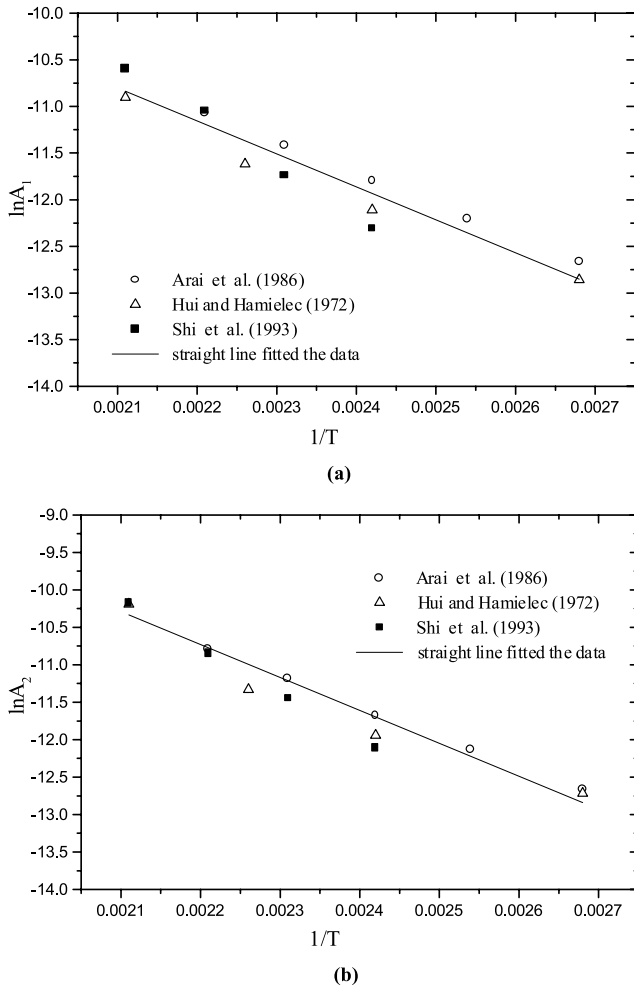


Fig. 7. Plots of  $A_1$  or  $A_2$  vs.  $1/T$ .

the definitions of  $A_1$  and  $A_2$

$$A_1 = \frac{1}{w} \left[ \frac{k_{t1}}{k_{p1}} \left( \frac{k_{i1}}{k_{t1}} \right)^{1/2} + \frac{k_{tr,m1}}{k_{p1}} \right] = B_1 \exp\left(-\frac{C_1}{T}\right) + B_2 \exp\left(\frac{C_2}{T}\right) \quad (24)$$

$$A_2 = \frac{1}{w} \left[ \frac{k_{t2}}{k_{p2}} \left( \frac{k_{i2}}{k_{t2}} \right)^{1/2} + \frac{k_{tr,m2}}{k_{p2}} \right] = B_3 \exp\left(-\frac{C_3}{T}\right) + B_4 \exp\left(-\frac{C_4}{T}\right) \quad (25)$$

where  $B_1, B_2, C_1,$  and  $C_2$  as well as  $B_3, B_4, C_3,$  and  $C_4$  are constants.

Comparing Eqs. (22) and (23) with Eqs. (24) and (25), it is clear that Eqs. (22) and (23) will correspond to Eqs. (24) and (25), respectively, if  $B_2 \exp(C_2/T) = 0$  in Eq. (24) and  $B_4 \exp(C_4/T) = 0$  in Eq. (25). It gives a hint that the constant of chain transfer to monomer,  $C_m (= k_{tr,m}/k_p)$ , is equal to zero, which is consistent with the result obtained in our previous study on St bulk polymerization initiated with the initiator [9].

#### 4. Conclusions

1. The kinetics of bulk thermal polymerization of St can be satisfactorily described by the TSPM.
2. Critical conversion,  $x_1$ , is independent of the reaction temperature and equal to 0.5.
3. Apparent reaction rate constants obtained with TSPM plots can be correlated to temperatures by Arrhenius equation.
4. Number-average molecular weight is independent of the conversion and only relative to the reaction temperature at low conversion stage. However, it varies with the conversions at gel effect stage and the variations are more obvious as the reaction temperature rises.

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