

# Diffusion-Limited Kinetics Modeling of One-Step Polyimide Formation

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**ABSTRACT:** A diffusion-limited kinetic model was developed to describe the imidization of one-step polythioetherimide formation based on an endgroup diffusion model. The changes of conversion and viscosity during the imidization were monitored with thermogravimetric analysis and dynamic stress rheometry, respectively. It was observed that the imidization rate began to decelerate after a fast early stage, whereas the viscosity in the system increased dramatically after a period of low value. Amic acid and imide formations concurrently take place in the one-step polyimide formation, but the formation of amic acid is much slower than that of imide and is the rate-limiting step of imidization. When a second-order kinetic model was used to describe the imidization, the effect of viscosity on the diffusion resistance of reactive groups needed to be included. In order to predict the change of viscosity during the imidization, the Lipshitz-Macosko model was modified and introduced into the diffusion-limited kinetic model by the Stokes-Einstein equation. The comparison of the modeled results with experimental data indicated that the diffusion-limited kinetic model and the modified Lipshitz-Macosko model were able to efficiently predict the changes of conversion and viscosity with temperature and time during the one-step polythioetherimide formation. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 2052–2059, 2001

**Key words:** diffusion; kinetics modeling; polyimide formation

## INTRODUCTION

In the manufacture of fiber-reinforced polyimide composites, polyimides are often formed by thermal imidization between a diamine and a di(acid-ester) or tetra-acid at a temperature in excess of 120°C, which is called one-step formation of polyimides.<sup>1,2</sup> In this approach, both amic acid and imide are formed concurrently with the removal of alcohol and water. One-step polyimide forma-

tion involves a series of complex physicochemical phenomena, which is different from the process of two-step polyimide formation. To produce high-quality composite parts, it is very important to model and control the entire reaction process of polyimide formation.

The kinetics of one-step polyimide formation has received much less study to date.<sup>2–7</sup> However, because of an increasingly wide variety of applications in advanced composites, there is an impending requirement to deeply understand and study the one-step polyimide formation kinetics for the sake of optimizing the processing cycle and reducing the production cost of polyimide composites. During the formation of polyimides, each imide formation step is faster than the preceding

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amic acid formation, which minimizes the formation of amide-linked oligomers, and therefore, amic acid formation is the rate-controlled step of the reaction.<sup>2</sup> In the early kinetic studies of one-step polyimide formation, amic acid and imide formations were described with second- and first-order kinetics, respectively. When the steady-state approximation is applied to the amic acid, imidizations are expected to follow second-order kinetics. However, nonlinearities in second-order plots begin at low conversion of less than 30%.<sup>5</sup> To solve the problem, Lauver<sup>7</sup> used two first-order models to describe the kinetic behavior of polymerization of monomer reactants (PMR)-15 (a polyimide with molecular weight of 1500). Almost unchanged activation energies, about 25 kJ/mol, were obtained. The value is similar to the result obtained by Kreuz et al.<sup>8</sup> in the study of thermal cyclizations between pyromellitic dianhydride and 4,4'-diaminodiphenyl ether. It was explained that the different pre-exponential factors and the inability to attain favorable conformations (because of the reduction of fractional free volume) were responsible for the decrease of the reaction rate. However, the two first-order models were unable to give good agreement in the entire reaction process, especially in the intermediate transition stage.<sup>9</sup> This seems to indicate that there are other factors influencing the entire kinetic process of one-step imidization.

In the manufacture of fiber-reinforced polyimide composites through the PMR approach, most solvents are usually removed before the beginning of imidization.<sup>10,11</sup> Because of the high glass transition temperature of polyimides, the imidization in the poststage can be carried out in a solid state. With the transition of system states from melt to solid, the transfer resistance of reactive groups will rapidly increase, which certainly leads to a decrease of the process rate. Therefore, the effect of diffusion resistance of groups on the reaction rate of one-step polyimide formation must be considered. The nonlinearities of second-order plots can mainly result from the diffusion-limited factors of reactive groups not included in second-order kinetic models.

Our purpose for the current work was to develop a diffusion-limited kinetic model by considering the effect of viscosity on the diffusion rate of reactive groups, which can be used to simulate the kinetic behavior of the imidization occurring in the manufacture of fiber-polyimide composites through the PMR approach.

## EXPERIMENTAL

### Materials

3,3',4,4'-Thioetherdiphthalic dianhydride was prepared from 4-chlorophthalic anhydride in our laboratory<sup>19,20</sup>; 4,4-methylene dianiline (MDA) was obtained commercially. Both were purified by sublimation or recrystallization before use. 3,3',4,4'-Thioetherdiphthalic dianhydride was esterified with excess dry ethanol under nitrogen.<sup>12,20</sup> After removal of solvent, the mixture species of diethyl ester of 3,3',4,4'-thioetherdiphthalic tetracarboxylic acid (TDPE) and MDA was obtained by mixing equimolar amounts of TDPE and MDA. The dry powder samples obtained were used in thermoanalytical and rheological experiments.

### Thermogravimetry Analysis (TGA)

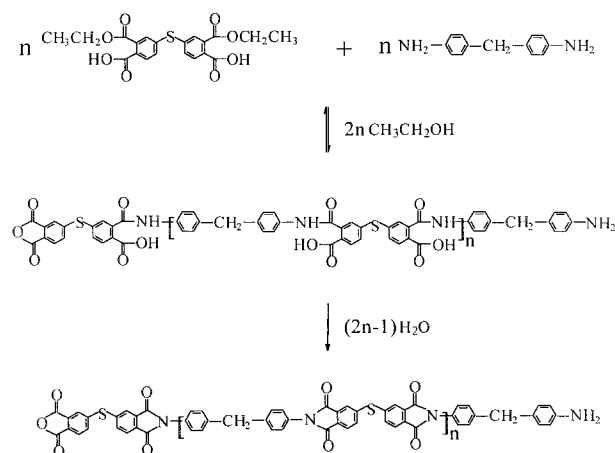
In this work, it was assumed that the magnitude of volatile components (ethanol and water) released during the polymerization would be directly proportional to the conversion of the monomer (TDPE or MDA). The polymerization between TDPE and MDA was traced with TGA (Perkin Elmer TGA-7) at 140, 160, 180, and 200°C, respectively. The sample weight was about 5 mg. The flow rate of nitrogen was 50 mL/min. The conversion of monomer,  $\alpha$ , at any time was determined by the following equation:

$$\alpha = \frac{\text{weight loss fraction of sample at any time } t (w_t)}{\text{weight loss fraction of sample at completion of the polymerization } (w_p)} \quad (1)$$

where no detectable weight loss observed in a 2°C/min dynamic experiment from ambient temperature to 400°C was taken as the completion of polymerization.

### Rheology Analysis

A dynamic stress rheometer produced by Rheometrics Incorporation was used to measure the viscosity. Parallel plate geometry (20 mm in diameter) was used with a gap size of 1 mm. All the experiments were performed with 1–2 g samples under the condition of 80 Pa stress and 10 s<sup>-1</sup> shear rate. The viscosity data were collected and calculated with special software, Rhios. For such a stiff polymer chain as aromatic polythioetherimides, the dependence of viscosity on the tem-



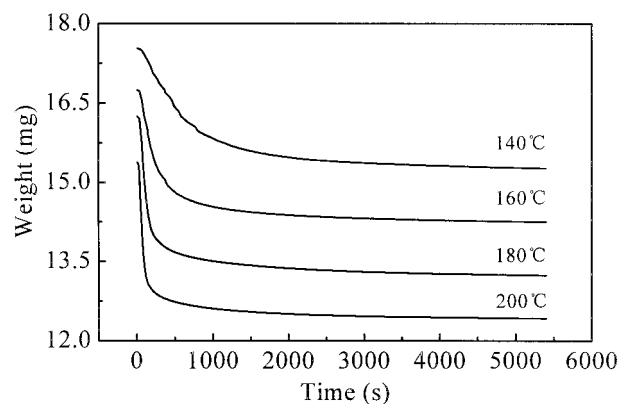
**Scheme 1** The chemistry of imidization occurring between di(acid ester)s and diamines in the PMR approach.

perature is obviously higher than on the shear rate. Hence, the influence of shear rate was not included in this work.

## RESULTS AND DISCUSSION

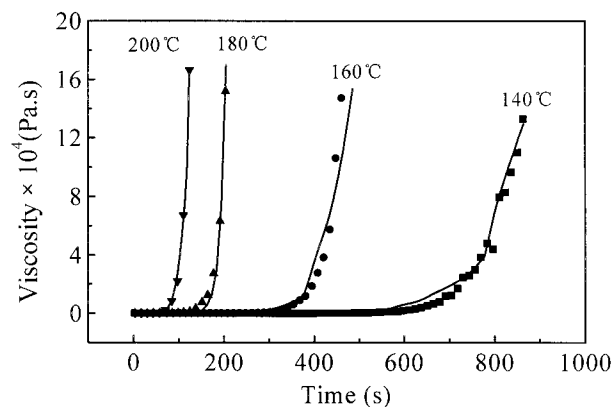
The chemistry of one-step polythioetherimide formation from TDPE and MDA is shown in Scheme 1. As the imidization proceeded, water and ethanol were released, which led to the weight loss of the samples. In preparing the mixture samples of TDPE and MDA, the solvent was removed as thoroughly as possible.<sup>12</sup> We assumed that all the sample weight losses monitored by TGA were from the evaporation of both water and ethanol released during the imidization. Figure 1 shows the weight-loss curves of the mixture samples at reaction temperatures from 140 to 200°C. It was seen that the initial reaction rates at the four temperatures were rapid, and then began to gradually decline at a certain time, finally continuing to the end of reaction at a very slow rate. Elevating reaction temperature made the initial weight loss rate faster and the time to begin deceleration sooner.

The changes of viscosity with time during the reaction are given in Figure 2. The viscosity at the early stage of imidization was low and increased slightly with time; the increase in viscosity began to accelerate dramatically after a period of time. Moreover, the time to keep low viscosity became shorter with the rise of reaction temperature.

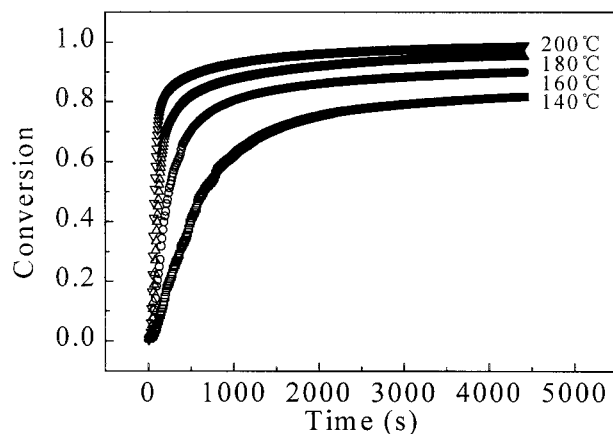


**Figure 1** The weight-loss curves of mixture samples of TDPE and MDA at 140, 160, 180, and 200°C, respectively.

Figure 3 shows the conversion curves obtained at different temperatures in terms of eq. (1). The imidization process of one-step polyimide formation can be divided into three stages: a kinetics-controlled stage (fast early stage), a diffusion-controlled stage (slow final stage), and the transition stage between these two stages (intermediate stage).<sup>9</sup> In the early stage, because the system mainly consists of monomers and oligomers, the viscosity is low; the transfer of reactive groups is unrestrained, and the reactions are kinetically controlled. Therefore, the reaction rate only depends on the inherent reactivity and concentration of reactive groups in the system. As the reaction proceeds, the viscosity increases rapidly because of chain growth and reduction of free volume. The reaction rate gradually becomes dependent not only on the reactivity of groups but



**Figure 2** The viscosity curves of mixture samples of TDPE and MDA at 140, 160, 180, and 200°C, respectively.



**Figure 3** The changes of conversion with time at 140, 160, 180, and 200°C, respectively.

also on their diffusion rate. In the final stage, the reaction rate primarily relates to the mass transfer rate of reactive groups, which depends significantly on the magnitude of viscosity. When the viscosity increases to such an extent that the reaction rate is far higher than the diffusion rate of reactive groups, the reaction becomes completely controlled by the diffusion of reactive groups. In this period, it is acceptable that the reaction will be accomplished instantaneously as soon as the reactive groups approach each other to a certain distance. Hence, the reaction rate can be expressed with the diffusion rate of reactive groups.

When we consider the effect of diffusion on the imidization rate, the overall reaction rate can be written as:

$$\frac{1}{R} = \frac{1}{R_{\text{chem}}} + \frac{1}{R_{\text{diff}}} \quad (2)$$

where  $R$  is the overall reaction rate,  $R_{\text{chem}}$  is the rate of fully kinetics-controlled reaction, and  $R_{\text{diff}}$  is the diffusion rate of reactive endgroups in the fully diffusion-controlled stage. When  $R_{\text{chem}} \gg R_{\text{diff}}$ , that means,  $R \approx R_{\text{chem}}$ , the reaction is fully kinetics-controlled; when  $R_{\text{chem}} \ll R_{\text{diff}}$ , that is,  $R \approx R_{\text{diff}}$ , the reaction is in a fully diffusion-controlled stage.

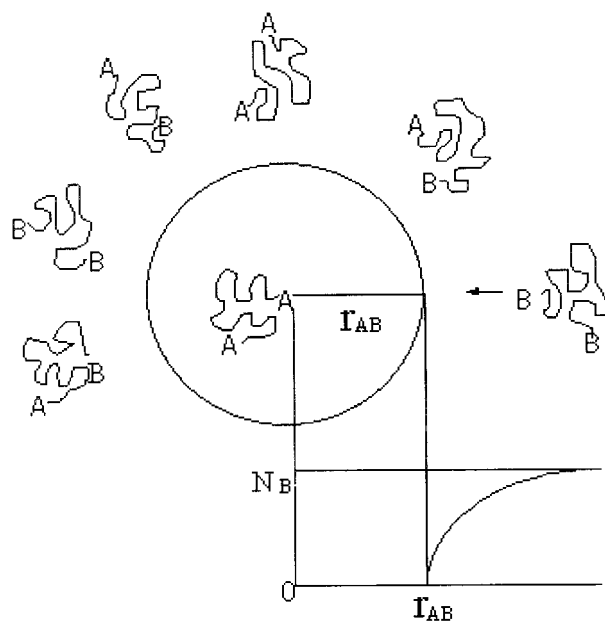
For concurrent amic acid and imide formations, the former is an intermolecular reaction and the latter belongs to an intramolecular reaction.<sup>2</sup> The intermolecular process involves reactive groups' diffusion, collision, and reaction. With the increase of viscosity, the group diffusion rate will decline significantly and, hence, the re-

action rate. In contrast, as far as the intramolecular reaction, the effect of viscosity on the conformational transition of reactive groups between the activated and inactivated states is far weaker. Consequently, the rate difference of both will be more obvious with the process of reaction. Under such conditions, amic acid formation should be the rate-controlling step of the entire reaction and subject to second-order kinetics.<sup>5</sup> In the kinetics-controlled stage, therefore, the overall imidization rate only depends on the reactivity and concentration of groups at a certain temperature, which can be expressed as:

$$\frac{d\alpha}{dt} = k_{\text{chem}}(1 - \alpha)^2 \quad (3)$$

where  $\alpha$  is the conversion of monomers during the imidization and  $k_{\text{chem}}$  is the rate constant in the fully kinetics-controlled stage.

In the diffusion-controlled stage, we consider any one molecule with endgroup  $A$  surrounded by other molecules with endgroups  $B$  and  $A$  (see Fig. 4). Here,  $A$  and  $B$  represent amine and anhydride endgroups [because a di(acid-ester) will lose an alcohol to form an anhydride before the reaction with an amine to form an amic acid<sup>2-4,6</sup>]. In a small sphere with the radius  $r_{AB}$ , one end of a molecule with endgroup  $A$  is located at the center of this sphere. The collision and reaction between



**Figure 4** Schematic diagram of an endgroup diffusion model during one-step polyimide formation.

two endgroups occur mainly by the diffusion of endgroups on molecular chains rather than by the transmission of the whole chain. Once an endgroup  $B$  diffuses to  $r_{AB}$ , the reaction between endgroup  $A$  and  $B$  will occur. Hence, there exists a concentration gradient of endgroup  $B$  in the vicinity of endgroup  $A$  located at the center of this sphere. The difference in concentration results in endgroup  $B$  diffusing to this sphere.

We assume that the diffusion is in a steady state. Because the rate of diffusion is much slower than that of reaction, the reaction can be taken as instantaneously completed as soon as endgroup  $B$  diffuses to  $r = r_{AB}$ . Therefore, the concentration of endgroup  $B$  at  $r_{AB}$  can be viewed as zero. Considering the above-mentioned assumption and boundary condition, which is similar to the diffusion-controlled process of small molecular reactions, the diffusion rate of endgroups to  $r_{AB}$  is

$$R_{\text{diff}} = 4\pi DN_A N_B N_B r_{AB} \quad (4)$$

where  $D$  is the diffusion coefficient of reactive endgroups (including  $A$  and  $B$ ) in the system, equal to  $D_A + D_B$ .  $N_A$ ,  $N_B$  are the number of endgroup  $A$ ,  $B$  in a unit volume, that is, the concentrations of endgroups  $A$  and  $B$ . The Stokes-Einstein equation can be used to describe the dependence of the diffusion coefficient of endgroups on temperature and viscosity, which has been found to be successful in many cases<sup>13,14</sup>.

$$D = \frac{k_B T}{6\pi\eta r} \quad (5)$$

where  $k_B$  is the Boltzman constant,  $r$  is the distance between endgroups  $A$  and  $B$ , and  $T$  is temperature. Substituting eq. (5) into eq. (4) leads to:

$$R_{\text{diff}} = \frac{8k_B T}{3\eta} N_A N_B = \frac{k_D}{\eta} N_A N_B \quad (6)$$

For two monomers of equal molar number, by substituting  $N_A$  and  $N_B$  with  $(1 - \alpha)$ , the following expression is obtained:

$$R_{\text{diff}} = \frac{k'_D}{\eta} (1 - \alpha)^2 \quad (7)$$

where  $k'_D$  is a constant only relative to temperature,  $\eta$  is the viscosity in the system, which de-

pends on temperature and the conversion of monomers.

For a linear polymer, the viscosity is directly relative to the weight-average molecular weight.<sup>15</sup> As a result, it can be assumed that the viscosity in the reactive system is directly proportional to the  $m$ th power of weight-average molecular weight, which has been suggested by Fox and Berry<sup>16</sup> and confirmed by Lipshitz and Macosko.<sup>17</sup> By combining the expression of weight-average degree of polymerization,<sup>18</sup>  $\bar{X}_w = (1 + \alpha)/(1 - \alpha)$ , into the Lipshitz-Macosko model,<sup>17</sup> the following chemorheological model can be used to describe the changes of viscosity with conversion:

$$\eta(\alpha, T) = k_\eta \left( \frac{1 + \alpha}{1 - \alpha} \right)^m \quad (8)$$

where  $k_\eta = \ln A + (D/RT)$  and  $m = s + (C/RT)$ .  $A$ ,  $C$ ,  $D$ , and  $s$  are constants.

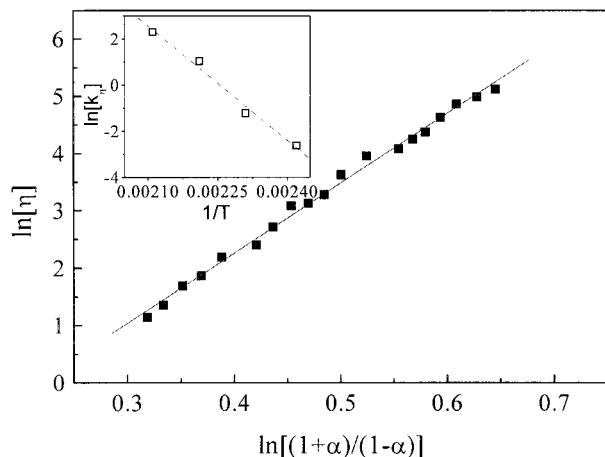
After combining eqs. (3), (7), and (8) into eq. (2), as well as algebraic and integral manipulations, a diffusion-limited kinetics model is obtained:

$$\frac{2\alpha}{1 - \alpha} + \frac{k_{\text{chem}} k_\eta}{(m + 1) k'_D} \left[ \left( \frac{1 + \alpha}{1 - \alpha} \right)^m - 1 \right] = 2k_{\text{chem}} t \quad (9)$$

The parameters in eq. (9) are necessary to identify their specific values in the kinetics-controlled and diffusion-controlled stage, respectively.

$k_m$  and  $m$  in eq. (9) were obtained by fitting rheological and thermogravimetric experiment data. A plot of  $\ln \eta$  versus  $\ln[(1 + \alpha)/(1 - \alpha)]$  as well as  $\ln k_\eta$  versus  $1/T$  at 140°C is shown in Figure 5. The values of  $C$  and  $A$  are 137.012 and  $1.38 \times 10^{16}$ , respectively. A plot of  $m$  versus  $1/T$  is shown in Figure 6. The values of  $s$  and  $D$  are  $-34.17$  and  $159.097$ , respectively. The modeled results of eq. (8) are also given in Figure 2.

The overall imidization rate in the kinetics-controlled stage can be expressed by eq. (3). Its integral expression is  $1/(1 - \alpha) - 1 = k_{\text{chem}} t$ . A typical plot of  $1/(1 - \alpha)$  versus time  $t$  at 140°C is given in Figure 7. The values of  $k_{\text{chem}}$  at different temperatures were obtained by linear regression. Using the Arrhenius relationship, the activation energy and pre-exponential factor were obtained from the plot of  $\ln k_{\text{chem}}$  against  $1/T$  (see the inset of Figure 7). The activation energy and pre-exponential factor in kinetics-controlled stage are respectively 62.447 kJ/mol and  $9.05 \times 10^4$ , which are higher than the values of AFR-700B<sup>9</sup> but lower than the values calculated with first-order

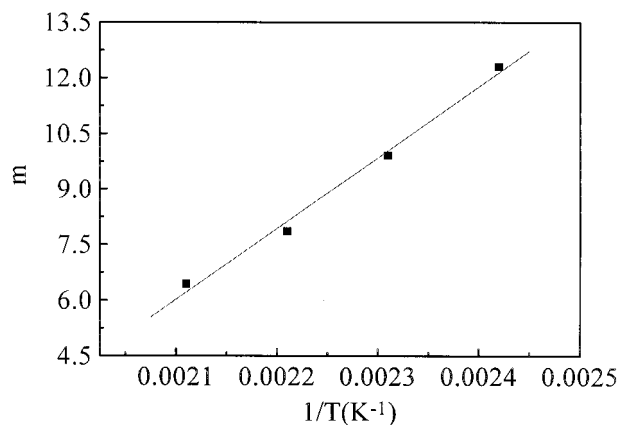


**Figure 5** A typical plot of  $\ln[\eta]$  versus  $(1 + \alpha)/(1 - \alpha)$ ; inset is the plot of  $\ln[k_\eta]$  versus  $1/T$ .

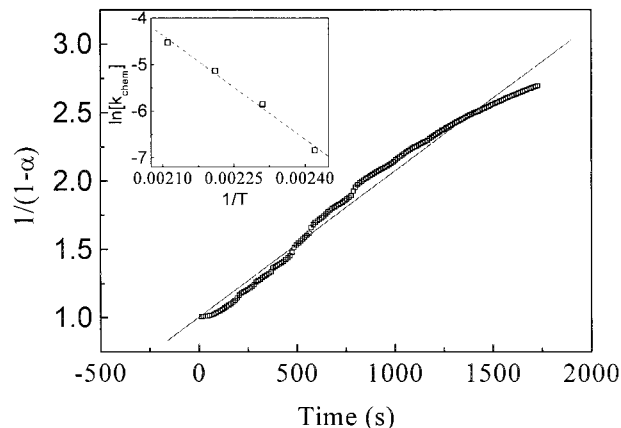
kinetics by Lauer<sup>7</sup> for the PMR-15 system. It was found that the values of  $k_{\text{chem}}$  increased from  $1.0710 \cdot 10^{-3}$  to  $1.08410 \cdot 10^{-2}$  L/mol  $\cdot$  s with increasing temperature. It was explained that the increasing temperature enhances the fractional free volume in the system and the transfer rate of reactive groups, and contributes to the diffusion of reactive groups and the transition between different conformations.

To simulate the overall imidization by eq. (9), we need to determine another important parameter  $k'_D$ . At the fully diffusion-controlled stage, eq. (7) becomes valid to describe the conversion changing with time. Substituting eq. (7) into eq. (1) and integrating from  $\alpha = \alpha_i$ , to  $\alpha$  and  $t$  from  $t = t_i$  to  $t$ , eq. (10) can be obtained:

$$\left(\frac{1 + \alpha}{1 - \alpha}\right)^{n+1} - \left(\frac{1 + \alpha_i}{1 - \alpha_i}\right)^{n+1} = \frac{2(n + 1)k'_D}{k_\eta} (t - t_i) \quad (10)$$

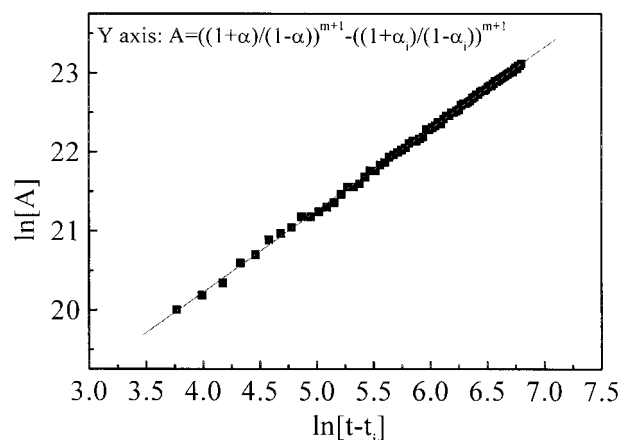


**Figure 6** A plot of power-index  $m$  versus  $1/T$ .



**Figure 7** A typical plot of  $1/(1 - \alpha)$  versus time  $t$  at  $140^\circ\text{C}$ ; inset is the plot of  $\ln[k_{\text{chem}}]$  versus  $1/T$ .

Linearizing eq. (10) by taking the logarithm of both sides, plotting  $\ln[(1 + \alpha)/(1 - \alpha)]^{n+1} - [(1 + \alpha_i)/(1 - \alpha_i)]^{n+1}$  versus  $\ln(t - t_i)$  will give the values of  $k'_D$  at various temperatures by regression analysis. Figure 8 shows a typical sample at  $140^\circ\text{C}$  and the values of  $k'_D$  at different temperatures are given in Table I. Similarly, according to the deductive analysis process of the diffusion-limited kinetics model, the value of  $k'_D$  should be a constant only relative to temperature, and increase with temperature. However, the values of  $k'_D$  obtained by correlating the thermogravimetric and rheological data did not display regularity. We inferred that  $k'_D$  played a certain role in correlating two experimental data because in the two experiments there were certain deviations, such as that slight differences between starting points to collect data were inevitable.



**Figure 8** A typical plot of  $\{[(1 + \alpha)/(1 - \alpha)]^{n+1} - [(1 + \alpha_i)/(1 - \alpha_i)]^{n+1}\}$  versus  $\ln[t - t_i]$  at  $140^\circ$ .

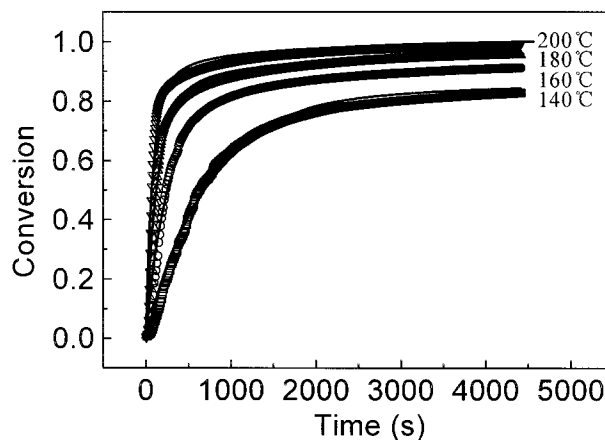
The parameters needed in modeling the one-step polythioetherimide formation by the diffusion-limited kinetic model are summarized in Table I. The modeled results obtained are shown in Figure 9, which shows good agreement between the modeled results and the experimental data.

## CONCLUSION

In one-step polyimide formations from diamines and di(acid-esters), amic acid and imide formations take place concurrently, but the rate of imide formation is more rapid than that of amic acid formation. Therefore, the amic acid formation is the rate-limiting step. The overall imidization rate can be described with a second-order kinetic model, but diffusion-limited factors must be included in the kinetic models.

The changes of conversion and viscosity in the imidization of TDPE and MDA were monitored with TGA and a dynamic stress rheometer at four reaction temperatures. It was found that the initial imidization rate was rapid, and then followed by a much slower rate. Meantime, the viscosity displayed an initial low value, followed by a dramatic increase. The imidization of polythioetherimide formation from TDPE and MDA is a diffusion-limited process. The increase of viscosity in the system made the diffusion resistance of reactive groups rise, which was a primary factor resulting in the reduction of overall imidization rate.

The imidization process of one-step polythioetherimide formation was divided into three stages: a kinetics-controlled stage, a diffusion-controlled stage, and the transition stage from kinetics-controlled stage to diffusion-controlled stage. The reciprocal of the overall reaction rate was equal to the reciprocal sum of the reaction



**Figure 9** The comparison of the results fitted by the diffusion-limited kinetic model and experimental data at 140, 160, 180, and 200°, respectively.

rates in the kinetics-controlled stage and the diffusion-controlled stage. On the basis of an endgroup diffusion model, similar to the diffusion-controlled reaction mechanism of small molecules, the effect of viscosity on the reaction rate was introduced into the diffusion-limited kinetic model by the Stokes-Einstein equation. All the parameters needed in the diffusion-limited kinetic model were necessarily obtained separately for the kinetics-controlled stage and diffusion-controlled stage.

To examine the validity of the new models, the results predicted by the models were compared with the experimental data. Very good agreement with experimental results indicated that the diffusion-limited kinetic model and modified Lipshitz-Mocasco model were able to efficiently predict the changes of conversion and viscosity with temperature and time during the one-step polythioetherimide formation.

**Table I** The Parameter Values in the Diffusion-Limited Kinetics Model Used to Model the Imidization

Temperature (°C)	$k_{\text{chem}}$ ( $\text{s}^{-1}$ )	$k_{\eta}$	$M$	$k'_D$
140	0.00107	0.0732	12.388	27072.8
160	0.00289	0.2975	9.961	334.388
180	0.00592	2.8318	7.897	1938.4
200	0.01084	9.9661	6.436	19305.38

Kinetic parameters:  $E_a = 62.447$  kJ/mol,  $A = 9.05 \times 10^4$ .

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