

# Thermal Cure of Phenylethynyl-Terminated AFR-PEPA-4 Imide Oligomer and a Model Compound

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**ABSTRACT:** The thermal cure reactions of phenylethynyl terminated AFR-PEPA-4 oligomer and a model compound *N*-phenyl-[4-(phenylethynyl) phthalimide] were investigated. The kinetics analysis of the thermal cure of AFR-PEPA-4 was determined using DSC, with modified DiBenedetto equation. The activation energy of thermal cure reaction of AFR-PEPA-4 oligomer is 34.1 kcal/mol with the kinetic order of one, when the reaction conversion is less than 80%. The activation energy of thermal reaction of

*N*-phenyl-[4-(phenylethynyl) phthalimide] is 41.5 kcal/mol with the kinetic order of 0.95. The cure reaction of AFR-PEPA-4 imide oligomer can be described as a fast first-order reaction stage for the formation of polyenes followed by a slow diffusion-controlled crosslinking reaction stage. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 4446–4453, 2006

**Key words:** polyimides; thermal cure; kinetics

## INTRODUCTION

Polyimides possess outstanding key properties such as high use temperature (above 300°C), thermooxidative stability, high mechanical strength, high modulus, excellent electrical properties, and superior chemical resistance.<sup>1</sup> Because of these merits, polyimides have become one of the leading polymer materials for high temperature composites in aerospace structural applications. Compared with norbornyl/amine or ethynyl terminated polyimides, phenylethynyl terminated polyimides exhibit many advantages<sup>2–5</sup> such as (1) no evolution of volatiles during the cure reaction, (2) larger processing window, (3) excellent mechanical properties, in particular outstanding fracture toughness value, and (4) higher hydrolytical stabilities. NASA's PETI-5, for example, received enormous attention during the development of the high speed civil transportation program. It crosslinks between 320 and 371°C range and at a pressure of 1 MPa, which can be easily processed by resin transfer molding (RTM).<sup>6</sup> PETI-5 polyimides demonstrated excellent hot/wet properties and high toughness (strain to failure from 14 to 84% in the 23–177°C temperature range).<sup>6</sup> However, the glass transition temperature ( $T_g$ ) of PETI-5 is low, which is about 270°C.

It was found that polyimides synthesized from 2,2'-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA), with the structure of perfluoromethyl substituents, always have extremely high use temperatures and stabilities.<sup>7</sup> The fluorinated polyimide AFR-700B, developed by the Air Force, showed excellent thermo-oxidative resistance and a high  $T_g$  above 400°C. Unfortunately, AFR 700B polyimide experienced significant decreases in strength (~70%) and  $T_g$  (75°C) after 1000 h at 160°C in a hygrothermal pressure bomb environment.<sup>8,9</sup> The hydrolyzable weak link was found to be norbornene crosslinks, which originate from the nadic end-caps. Recently, AFR-PEPA-N imide oligomer was synthesized with the fluorinated backbone 6FDA and the phenylethynyl end-caps, 4-(phenylethynyl)phthalic anhydride (PEPA).<sup>7</sup> AFR-PEPA-N exhibited only a 3–5% decrease in dry  $T_g$  after hygrothermal exposure, which is similar to PETI-5.<sup>7</sup> In addition, AFR-PEPA-N polyimides showed (1) extremely high  $T_g$ s (435–455°C), (2) significantly improved mechanical properties at 300°C compared with AFR 700B, (3) the potential to be processed by RTM, (4) high ductility for a high temperature polyimide (ambient temperature elongation to break of 5%), and (5) slightly lower thermo-oxidative stability compared with AFR 700B.<sup>7</sup> Therefore, AFR-PEPA-N polyimides were promptly deployed on ultrahigh temperature light weight composites for aerospace structural applications. However, no studies, as yet, have been performed to characterize the network of AFR-PEPA-N polyimides and the effects of thermal history on the cured products. Cure reactions and kinetics of AFR-PEPA-N oligomers need to be

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investigated, to further understand the structure-property-processing relations of AFR-PEPA-N polyimides.

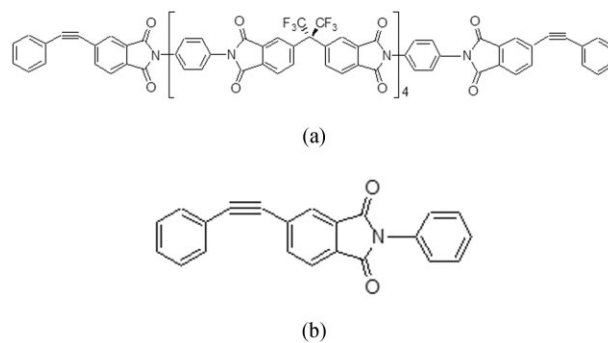
Several studies on the thermal cure of phenylethynyl terminated imide oligomers have been reported. Johnston et al.<sup>10</sup> synthesized and characterized a series of phenylethynyl end-capped imide oligomers with PEPA and substituted PEPA's containing electron-withdrawing groups. Takekoshi and Terry<sup>11</sup> studied thermal reactions of two PEPA model compounds, *N*-[3-(phenylethynyl)phenyl]phthalimide and *N*-phenyl-4-(phenylethynyl)phthalimide, by using high-pressure liquid chromatography (HPLC) and field-desorption mass spectroscopy. Fang et al.<sup>12</sup> studied the kinetic mechanism of thermal cure of PETI-5 oligomer by thermal analysis using the modified DiBenedetto equation. It was found that thermal cure reaction of PETI-5 was 1.5th order, which suggested that complicated reaction mechanisms such as intramolecular and bimolecular double bond addition reactions are involved to form a highly crosslinked polyimide. Solid-state <sup>13</sup>C NMR was also used to analyze the chemical structure of cured acetylene-terminated polyimides or acetylene containing model compounds.<sup>13–15</sup> Although phenylethynyl groups are expected to react by chain extension, crosslinking, and branching, it is still difficult to elucidate the cure kinetics and mechanism of thermal cure of phenylethynyl-terminated imide oligomer because of the steric effect of the phenyl-ended functional groups, low concentration of phenylethynyl groups in the oligomers, and insolubility of the cured products.

In the present study, thermal cure reactions of phenylethynyl-terminated AFR-PEPA-4 imide oligomer and a model compound *N*-phenyl-4-(phenylethynyl)phthalimide were characterized by infrared spectroscopy (IR). The kinetics analysis of thermal cure of AFR-PEPA-4 imide oligomer was determined using differential scanning calorimetry (DSC) by following the  $T_g$  of the cured polyimides as a function of cure, which was simulated by the modified DiBenedetto equation. The aim of this work is to understand the thermal cure kinetics and mechanism of phenylethynyl-terminated imide oligomer AFR-PEPA-N.

## EXPERIMENTAL

### Materials

2,2'-Bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA), 1,4-diaminobenzene (*p*-PDA), and 4-(phenylethynyl)phthalic anhydride (PEPA) were obtained from Performance Polymer Solutions, OH. *N*-methyl-2-pyrrolidinone (NMP), aniline, acetic acid, and methanol were obtained from Aldrich. All chemicals were used as received.



**Figure 1** Chemical structures of AFR-PEPA-4 imide oligomer and PEPA model compound. (a) Phenylethynyl-terminated imide oligomer AFR-PEPA-4; (b) *N*-phenyl-4-(phenylethynyl) phthalimide].

### Phenylethynyl-terminated imide oligomer AFR-PEPA-4

Imide oligomer AFR-PEPA-4 was prepared from *p*-PDA, 6FDA, and PEPA in NMP solvent by the method reported by Lincoln.<sup>7</sup> *p*-PDA (7.034 g, 0.065 mol) was dissolved in 150 mL NMP in a 500-mL, three-neck round-bottom flask equipped with a Teflon stirring bar and a gas adaptor, under a nitrogen atmosphere at room temperature. 6FDA (23.117 g, 0.052 mol) was dissolved in 150 mL NMP under a nitrogen atmosphere protection. The solution of 6FDA/NMP was then added in *p*-PDA/NMP solution, in three portions over 3 h. Once all of the 6FDA solution was added, stirring continued for 20 h at room temperature. PEPA (6.459 g, 0.026 mol) was added as a solid and was stirred until it completely reacted (4 h) under nitrogen. The NMP used is 10% solids by weight during the whole synthesis. Toluene was then added, and the resulting mixture was then imidized under reflux in 180°C-oil bath with the removal of water via azeotropic distillation. The reaction mixtures were finally added into distilled water, filtered, and washed in boiling water and then in warm methanol to remove the NMP. This produced very fine yellow powders that were dried under vacuum for 24 h at 160°C. The yield was 33.387 g (97.5%). The oligomer had a theoretical molecular weight of 2634 g/mol and a glass transition temperature of 250°C (DSC) at 20°C/min. The chemical structure of AFR-PEPA-4 imide oligomer is shown in Figure 1(a).

### *N*-Phenyl-4-(phenylethynyl) phthalimide

Phenylethynyl model compound *N*-phenyl-4-(phenylethynyl) phthalimide was prepared following the method reported by Takekoshi and Terry.<sup>11</sup> PEPA (31.029 g, 0.125 mol), aniline (12.200 g, 0.131 mol), and 225 mL of acetic acid were placed in a 500-mL, three-necked flask. The mixture was stirred under nitrogen

and heated to reflux for 1.5 h. A total of 50 mL of water and acetic acid mixture was distilled off during the following 0.5-h period. The reaction mixture was cooled and the yellow crystalline solid was filtered. The product was washed with methanol and dried. The yield was 38.883 g (96.2%), mp 210–212°C. Elemental analysis calculated for C<sub>22</sub>H<sub>13</sub>O<sub>2</sub>N: C, 81.72%, H, 4.05%, N, 4.33%; found: C, 81.66%, H, 4.02%, N, 4.26%. FTIR (KBr): 2216 (C≡C), 1780 (C=O), 1713 (C=O), 1611 (C=C) cm<sup>-1</sup>; <sup>13</sup>C NMR (CDCl<sub>3</sub>): 166.62, 137.17, 132.20, 131.84, 131.52, 130.33, 129.27, 129.12, 128.52, 126.53, 126.49, 123.72, 122.03, 94.19, 87.70 ppm; Mass spectrum *m/e* 323 M<sup>+</sup>. The chemical structure of AFR-PEPA-4 is shown in Figure 1(b).

### Cure reactions of the model compound and AFR-PEPA-4 oligomer

The range of reaction temperatures chosen for thermal cure of AFR-PEPA-4 oligomer and the model compound was determined by thermal analysis. Thermogravimetric analysis (TGA) of AFR-PEPA-4 oligomer was performed on a TGA Q500 thermal analyzer. The heating atmospheres were air or nitrogen. The samples were heated to 800°C at 10°C/min. DSC analysis was performed by a Perkin–Elmer DSC Pyris 7 system. Temperature was scanned from 100 to 450°C at 20°C/min.

About 0.2 g samples were cured in small glass vials in a preheated furnace. After curing at the desired temperature for a certain time (from 2 min to 8 h), the samples were cooled promptly and removed from the vials for characterization. FTIR analysis was used to monitor the reaction conversion after curing. A Nicolet AVATAR 360 spectrometer was used in this study. Samples were prepared as KBr pellets. The number of accumulations was set at 64 with a resolution of 2 cm<sup>-1</sup>.

*T<sub>g</sub>*s of cured AFR-PEPA-4 were measured by DSC at a heating rate of 20°C/min under nitrogen atmosphere. The modified DiBenedetto equation<sup>12,16,17</sup> was used to calculate the reaction extent *x* according to *T<sub>g</sub>* as follows

$$\frac{T_g - T_{g0}}{T_{g\infty} - T_{g0}} = \frac{\lambda x}{1 - (1 - \lambda)x} \quad (1)$$

where *T<sub>g0</sub>*, *T<sub>g∞</sub>*, and *T<sub>g</sub>* are the glass transition temperatures before complete cure, after complete cure, and the glass transition temperature of the sample after curing at a cure temperature for a specified cure time, respectively. *λ* is the ratio of isobaric heat specified time of the fully cured material to that of uncured material. The isobaric heat capacities can be determined by DSC. It should be noted that even if the selected *T<sub>g∞</sub>* does not correspond to the theoretically ideal fully cured system, cure extent *x* is still valid for kinetic analysis according to this equation.<sup>12</sup>

TABLE I  
TGA Results of AFR-PEPA-4 Oligomer

Weight loss (%)	Temperature (°C)	
	Air	N <sub>2</sub>
1	339.6	342.8
2	480.1	488.6
5	524.2	527.4
10	543.8	548.7
20	564.8	584.5

Heating rate = 10°C/min.

## RESULTS AND DISCUSSION

### Cure characterization of AFR-PEPA-4 oligomer

The temperatures for various weight losses of AFR-PEPA-4 oligomer calculated from TGA are listed in Table I. In nitrogen atmosphere, the temperatures for 1, 2, 5, 10, and 20% weight losses of AFR-PEPA-4 oligomer are higher than those in air. The oligomer has less than 2% weight loss in both air and N<sub>2</sub> when the temperature is lower than 480°C. A DSC study of AFR-PEPA-4 oligomer shows that the cure reaction starts at 370°C and reaches the peak at 410°C. On the basis of the thermal analysis results, the temperature window for thermal curing of AFR-PEPA-4 oligomer can be chosen from 340 to 430 °C to ensure the occurrence of crosslinking reaction without serious thermal degradation. In this article, the cure temperatures 350, 370, 390, and 410°C were chosen to study the effect of temperature on cure reactions of AFR-PEPA-4 oligomer.

FTIR spectra of AFR-PEPA-4 oligomer is shown in Figure 2. Since the absorption around 2213 cm<sup>-1</sup> is attributed to *ν*<sub>C≡C</sub> in ethynyl group, the reaction conversion of AFR-PEPA-4 oligomer during the curing can be given by the consumption of C≡C triple bonds through the calculation of the decreased intensities of the bands at 2213 cm<sup>-1</sup>. The absorption of imide C=O stretching around 1726 cm<sup>-1</sup> and 1785 cm<sup>-1</sup>, inert from the reactions, can be used as internal standard. Absorption bands around 1511 cm<sup>-1</sup> and 1367 cm<sup>-1</sup> are attributed to benzene ring and aromatic imide C—N stretching, respectively. The reaction conversion can be calculated by relative intensity ratio compared between the intensity of the reaction involved peaks and that of internal standard. The reaction conversion *α* can be calculated by eq. (2)

$$\alpha = \left( \frac{I^{2213}}{I^{1785}} \right)_t \bigg/ \left( \frac{I^{2213}}{I^{1785}} \right)_{t=0} \quad (2)$$

The quantitative results are shown in Figure 3. The reaction conversion of AFR-PEPA-4 oligomers in-

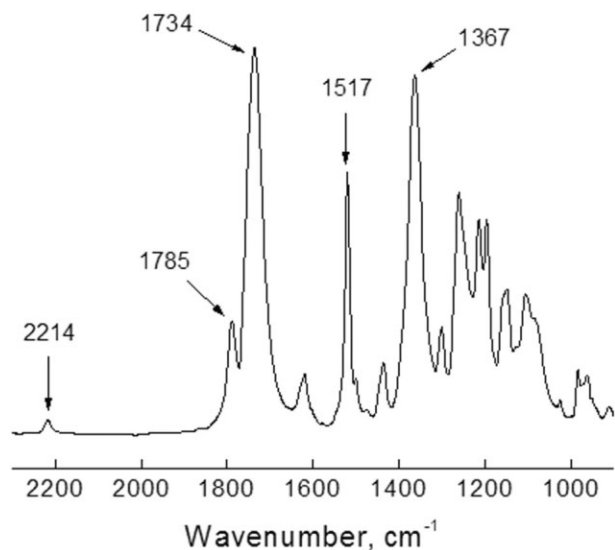


Figure 2 FTIR spectra of AFR-PEPA-4 imide oligomer.

creased with the increase of cure time, when they were cured at 350°C in air atmosphere. However, when the cure time is longer than 1 h and the reaction conversion is more than 85%, FTIR cannot detect the 2213  $\text{cm}^{-1}$  band because of the limited resolution and the relatively low concentration of phenylethynyl groups in AFR-PEPA-4 oligomer. On the basis of the calculation from residual exothermal reaction  $\Delta H$  in DSC test, the curing is not complete even over 8-h cure at 350°C and the degree of cure is about 90%.

A plot  $\ln [1 - \alpha]$  versus  $t$  for the cure reaction of AFR-PEPA-4 oligomer at 350°C in 1 h yields a straight line, which is shown in Figure 4. Therefore, according to cure conversion calculated from FTIR data, the cure kinetic obeys first order during the first 1 h at 350°C.

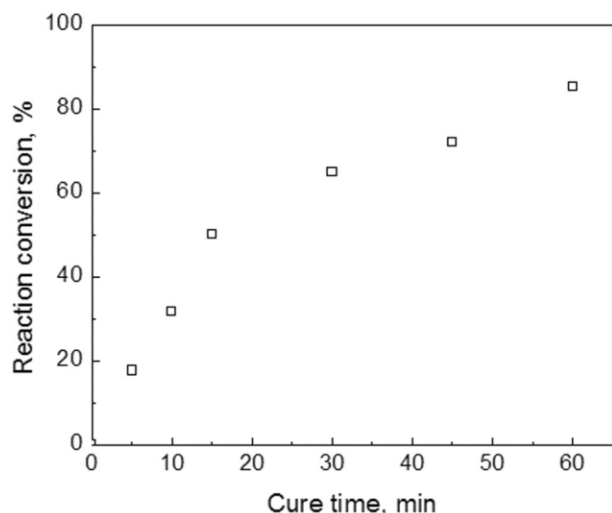


Figure 3 Reaction conversion of AFR-PEPA-4 oligomer versus cure time at 350°C from FTIR data.

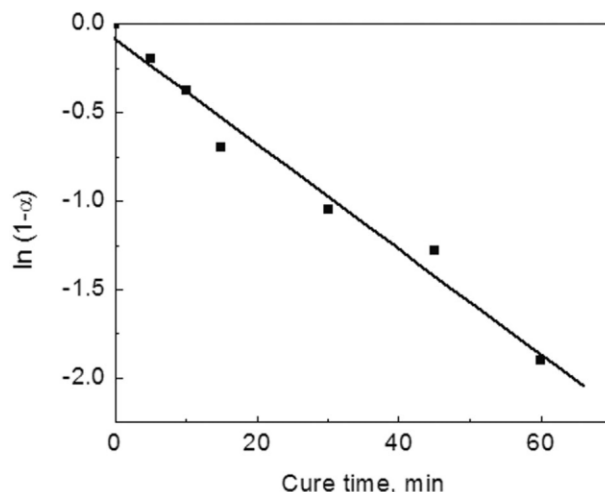


Figure 4 Reaction kinetic plot of  $\ln(1 - \alpha)$  versus time for thermal cure of AFR-PEPA-4 at 350°C from FTIR data.

$T_g$ s of cured AFR-PEPA-4 were determined by DSC. An illustration of the  $T_g$  before and after cure at 350°C is shown in Figure 5. The plot of  $T_g$  versus cure time of AFR-PEPA-4 oligomer cured at 350°C is shown in Figure 6. The increase of  $T_g$  is almost linear in the first 1 h of curing. After that, the increase of  $T_g$  has a remarkable drop due to diffusion restriction. On the basis of the modified DiBenedetto eq. (1), the dependence of  $T_g$  on reaction conversion of phenylethynyl  $\text{C}\equiv\text{C}$  in AFR-PEPA-4 oligomers can be simulated, which is shown in Figure 7, indicating that good agreement between the simulated curve and experimental data from FTIR. Therefore, this simulation method is reliable to calculate the reaction conversions based on measured  $T_g$ s.

The dependences of  $T_g$  of cured oligomers on cure time at various cure temperatures in air are shown in

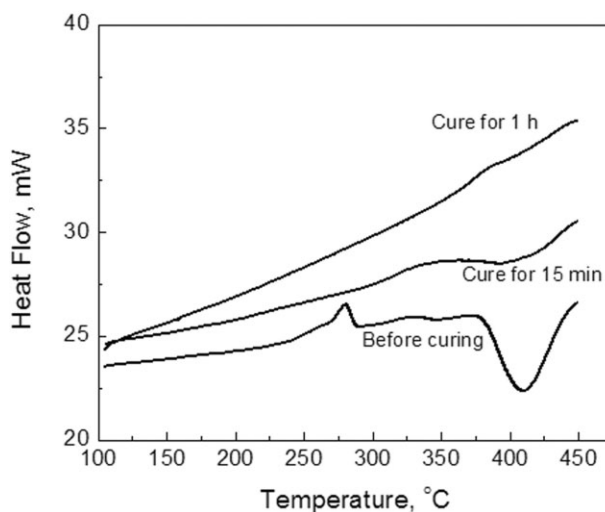
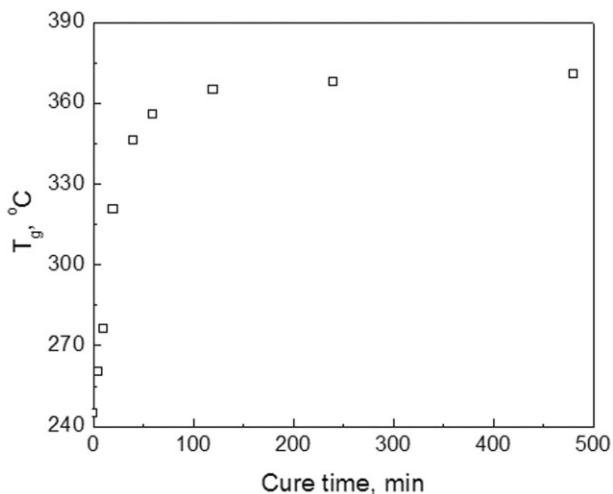


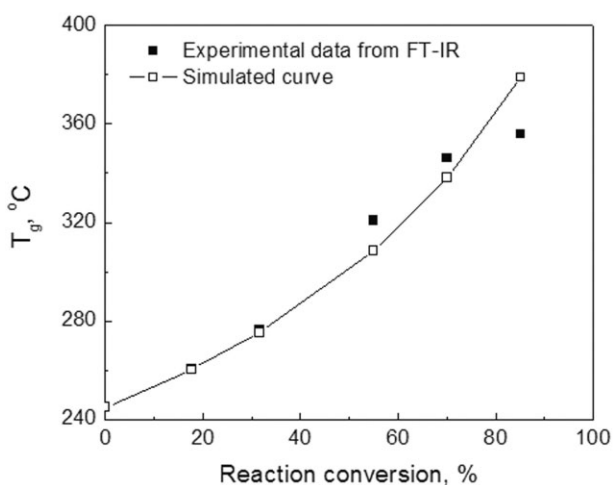
Figure 5 DSC curves of AFR-PEPA-4 oligomer before and after cure at 350°C.



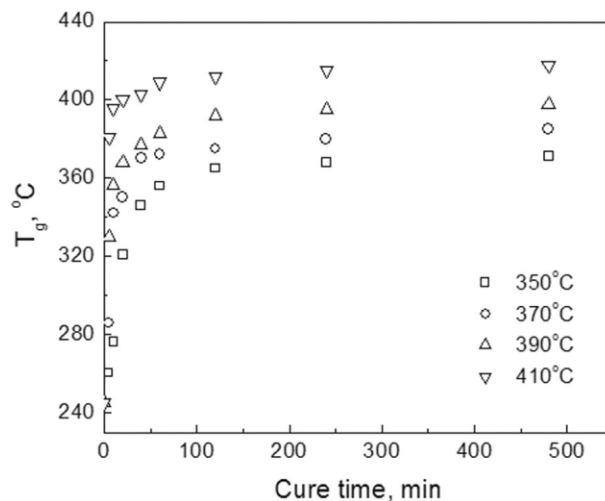
**Figure 6**  $T_g$  versus cure time of AFR-PEPA-4 oligomer cured at 350°C.

Figure 8. The  $T_g$  of the cured oligomer increases with the increase of cure time and cure temperature. The cure temperature 410°C gave the highest cure reaction rate at the beginning of the curing, at which the sample's  $T_g$  went to 381°C, with only 5 min curing. The cure reaction rate tends to be stable after the curing reaches a certain extent because of the diffusion control. The  $T_g$ s of cured oligomers after 8 h curing at 350, 370, 390, and 410°C are 371, 385, 398, and 418°C, respectively.

Since FTIR cannot detect the absorption of residue phenylethynyl group in the highly crosslinked AFR-PEPA-4 polyimide, in our study, the reaction conversion of AFR-PEPA-4 oligomer cured at various temperatures can be calculated from the  $T_g$  of cured samples by using modified DiBenedetto equation obtained earlier.  $T_g$ s as a function of reaction conversion are shown in Figure 9.



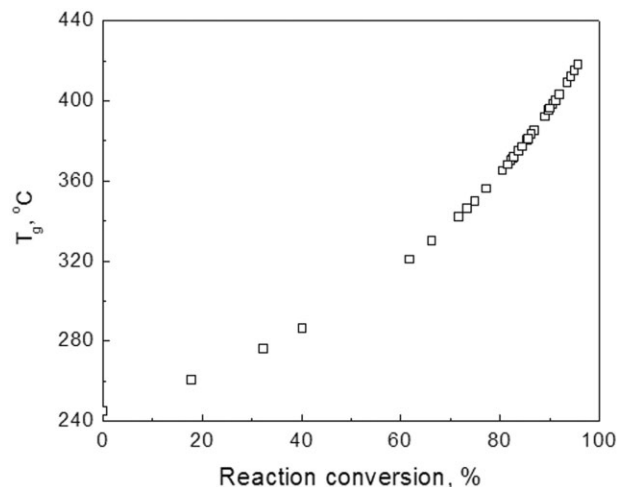
**Figure 7**  $T_g$  as a function of reaction conversion of AFR-PEPA-4 oligomer cured at 350°C.



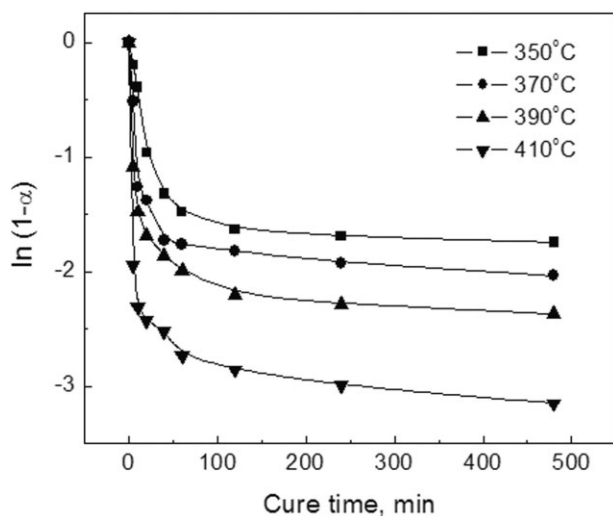
**Figure 8**  $T_g$  versus cure time of AFR-PEPA-4 oligomer cured at various temperatures.

A plot of the  $\ln(1 - \alpha)$  versus cure time (Fig. 10) for a first-order reaction shows significant deviation from linearity once the reaction conversion  $\alpha$  exceeds 80%. If only the experimental points below 80% cure are selected, first order kinetics better simulates the kinetic data (Table II). Thus, the activation energy  $E_{act}$  can be obtained by plot  $\ln k$  versus  $1/T$  (Fig. 11), which is  $34.1 \pm 2.4$  kcal/mol with a regression coefficient of 0.995.

Fang et al.<sup>12</sup> investigated the cure reaction of PETI-5 and found that it followed first order kinetics yielding an activation energy of 37.2 kcal/mol when the cure process was below 90%. It is close to our result for curing of AFR-PEPA-4 oligomer. Studies on solid-state <sup>13</sup>C NMR showed that the primary thermal cure reaction (~70%) of acetylene-terminated imide oligomers is ethynyl to ethynyl addition that forms poly-



**Figure 9**  $T_g$  as a function of reaction conversion of cured AFR-PEPA-4 oligomer.



**Figure 10** Kinetic plots of  $\ln(1-\alpha)$  versus time from DSC  $T_g$  data.

ene structures.<sup>13</sup> Although Diels-Alder cycloaddition between two phenylethynyl groups was expected to be the most probable crosslink mechanism for imide oligomers containing internal acetylene units,<sup>15</sup> phenylethynyl-terminated imide oligomers may not follow this mechanism, because the molecular motion at the internal acetylene groups is more restricted than at the termini. Fang et al.<sup>12</sup> also described a 1.5th order kinetics for whole cure reaction of PETI-5, with an activation energy of 33.8 kcal/mol. However, in our study, this reaction order failed to describe the data over the whole range of conversion values for complete cure. Since 6FDA gives the backbone of AFR-PEPA-4 imide oligomer a higher degree of rotation,<sup>15</sup> the further reaction of polyenes may be more complicated. The heats of reaction do not adequately define the reaction for complete cure.

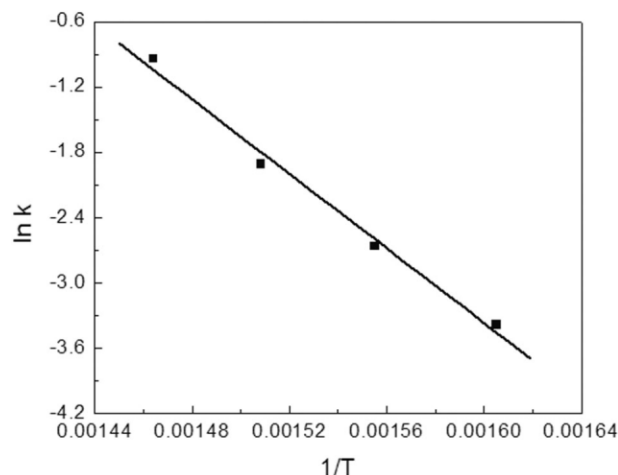
#### Thermal reaction of *N*-phenyl-[4-(phenylethynyl) phthalimide]

Compared with AFR-PEPA-4 imide oligomer, the model compound *N*-phenyl-[4-(phenylethynyl) phthal-

**TABLE II**  
Kinetic Analysis of the Thermal cure of AFR-PEPA-4 by DSC (First Order Below 80% Cure)

Temperature (°C)	Rate constant (min <sup>-1</sup> )	Regression coefficient
350	0.0339	0.973
350 <sup>a</sup>	0.02967	0.988
370	0.06952	0.911
390	0.14797	0.965
410	0.3893	1

<sup>a</sup> Analysis by reaction conversion data from FTIR.



**Figure 11** Kinetic plot of  $\ln k$  versus  $1/T$  of the cure reaction of AFR-PEPA-4 oligomer for first order (below 80% cure).

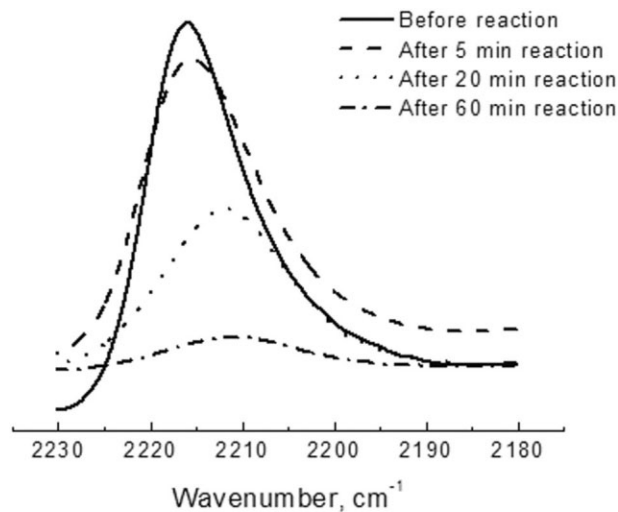
imide] has much more concentrated phenylethynyl groups in its chemical structure, which allows us to easily monitor the consumption of  $C\equiv C$  in phenylethynyl during the cure reaction by IR study.

DSC data of *N*-phenyl-[4-(phenylethynyl) phthalimide] showed a sharp peak for the melting at 210°C. The reaction started from 320°C and reached the peak at 397°C. Thermal reactions of this model compound at various temperatures 330, 350, 370, and 390°C were monitored by FTIR, using the procedure similar to that for AFR-PEPA-4 oligomer. From the IR spectra shown in Figure 12(a), the absorption peak of 2216  $cm^{-1}$  decreases with the increase of cure time, indicating the consumption of  $C\equiv C$  triple bonds during thermal reaction. Moreover, it was found that the intensity of another absorption band around 1611  $cm^{-1}$ , which could be attributed to stretching vibrations of  $C=C$  conjugated with ethynyl group,<sup>18</sup> also decreased during the reaction [Fig. 12(b)]. It was observed that the absorption band of phenylethynyl group switches to lower wavenumbers and that of conjugated bonds switches to higher wavenumbers during the thermal reaction. However, in IR spectra of phenylethynyl-terminated imide oligomers, the absorption at 1611  $cm^{-1}$  always overlaps with 1580  $cm^{-1}$ , which is attributed to aromatic structure itself.

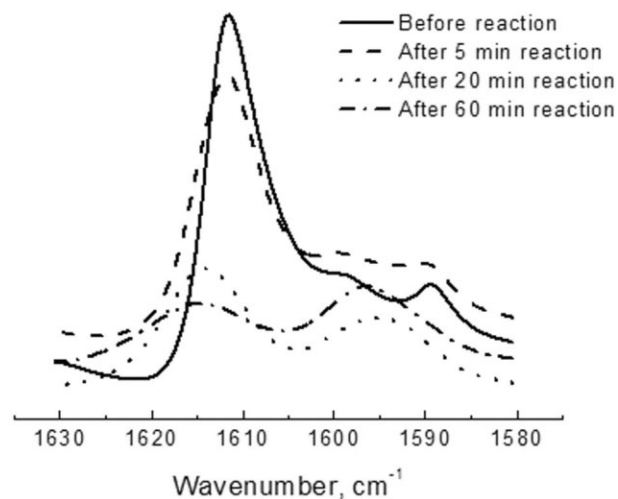
The quantitative results are shown in Figure 13. The reaction conversion of *N*-phenyl-[4-(phenylethynyl) phthalimide] increased with the increase of cure time. Assuming that the cure reaction follows  $n$ th order kinetics, the rate equation can be written as

$$-\frac{d[A]}{dt} = k[A]^n \quad (3)$$

By simulating the cure reactions as  $n$ th order kinetics from reaction conversion data, the kinetics order of



(a)

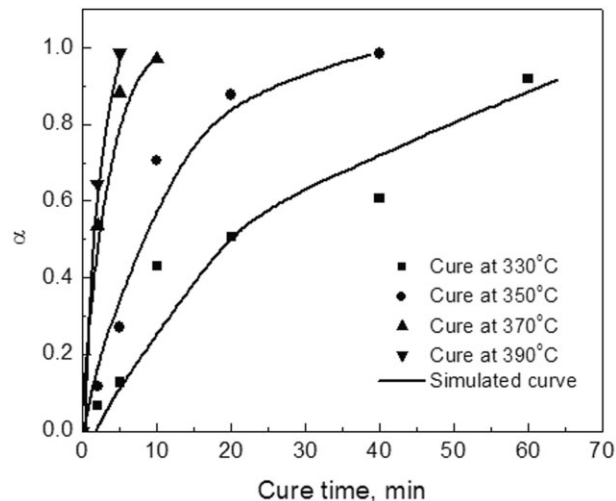


(b)

**Figure 12** Changes of IR absorption during the thermal reaction of *N*-phenyl-[4-(phenylethynyl)phthalimide] at 330°C in air (a) C≡C at 2216 cm<sup>-1</sup>; (b) conjugate bonds at 1611 cm<sup>-1</sup>.

0.95 fits the reaction best. The rate constant for thermal reactions at 330, 350, 370, and 390°C is 0.03, 375, 0.09, 557, 0.3303, and 0.8110 min<sup>-1</sup>, respectively. Thus, the activation energy  $E_{\text{act}}$  can be obtained by plot  $\ln k$  versus  $1/T$  (Fig. 14), which is  $41.5 \pm 2.0$  kcal/mol with a regression coefficient of 0.998.

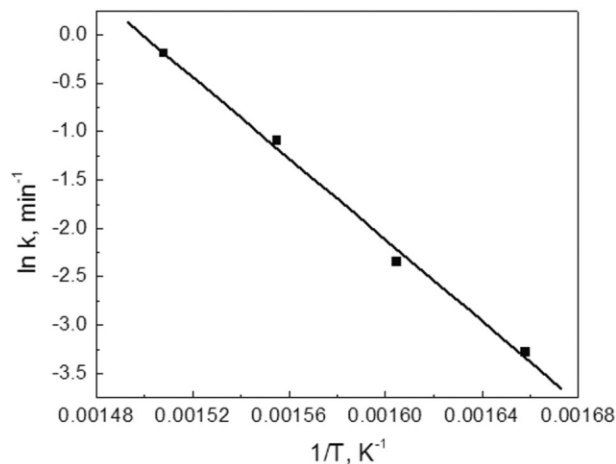
Takekoshi and Terry<sup>11</sup> reported that the thermal reaction of *N*-phenyl-[4-(phenylethynyl) phthalimide] closely followed the first order with an activation energy of 36.5 kcal/mol, which was obtained from HPLC study. Fang et al.<sup>12</sup> utilized IR to monitor the cure kinetics of a phenylethynyl end-capped model compound 3,4'-bis[4-(phenylethynyl)phthalimido]diphenyl ether (PEPA-3,4'-ODA). First order kinetics with an activation energy of 40.7 kcal/mol was re-



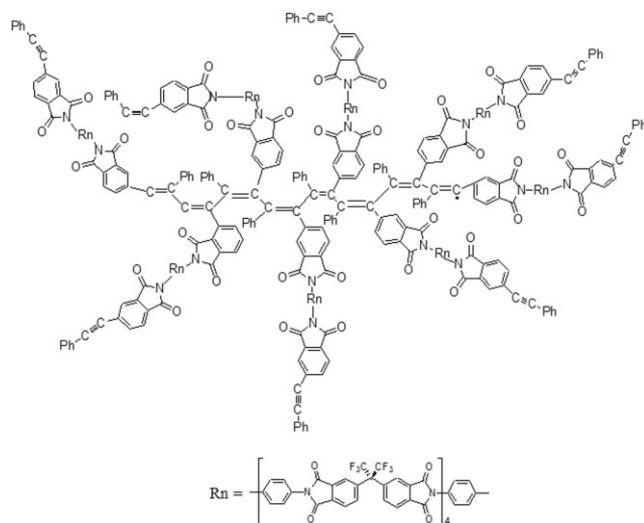
**Figure 13** Reaction conversion  $\alpha$  versus cure time of *N*-phenyl-[4-(phenylethynyl) phthalimide] cured at various temperatures.

vealed for the whole thermal reaction of PEPA-3,4'-ODA, indicating that ethynyl to ethynyl addition mainly occurred, though carbon-carbon saturated bonds were also formed from polyene structures.<sup>14</sup> Unlike PEPA-3,4'-ODA or other imide oligomers, the model compound *N*-phenyl-[4-(phenylethynyl) phthalimide] has a much smaller molecule structure, so that other addition reactions such as Diels-Alder cycloaddition or cyclotrimerization can also take place without much steric hindrance and form polycyclic aromatic structures. Therefore, the whole thermal reaction of *N*-phenyl-[4-(phenylethynyl) phthalimide] cannot be simply described with first order kinetics.

Fang et al.<sup>12</sup> proposed a two-stage kinetic/diffusion model for thermal curing of PETI-5 oligomer, which may also be valid for AFR-PEPA-4 system. On a fast



**Figure 14** Kinetics plot of  $\ln k$  versus  $1/T$  of the cure reaction of *N*-phenyl-[4-(phenylethynyl) phthalimide].



**Figure 15** Proposed chemical structure of partially cured AFR-PEPA-4 polyimide.

stage, the cure reaction takes place mainly by simple ethynyl to ethynyl addition reactions to form a partial cured polyene structure (Fig. 15), which follows first-order kinetics. On a slow second stage, crosslinking reaction is kinetically controlled by diffusion. The double bond addition reactions mainly occur in this stage. A series of reactions such as Diel-Alder, Friedel-Crafts, Straus and Glaser coupling reactions have been suggested.<sup>12</sup> The formation of polycyclic aromatic structures derived from polyene causes the significant deviation from linearity of first order reaction, once the reaction conversion of the triple bond in phenylethynyl groups exceeds 80%.

## CONCLUSIONS

Thermal cure of phenylethynyl terminated imide oligomer AFR-PEPA-4 and model compound *N*-phenyl-[4-(phenylethynyl) phthalimide] were characterized. The changes in IR absorbance of phenylethynyl triple bonds at  $2216\text{ cm}^{-1}$  and that of conjugated bonds at  $1611\text{ cm}^{-1}$  of *N*-phenyl-[4-(phenylethynyl) phthalim-

ide] were detected. Thermal reaction of the model compound followed the kinetics with an order of 0.95. DSC was used in determining the cure kinetics of AFR-PEPA-4 oligomer by following the increase in  $T_g$  as a function of cure. The activation energy of thermal cure reaction of AFR-PEPA-4 oligomer is  $34.1 \pm 2.4$  kcal/mol with the kinetic order of one, when the reaction conversion is less than 80%. The cure process of imide oligomer can be described as a fast first order reaction stage forming polyene structures, followed by a slow diffusion-controlled crosslinking reaction stage.

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