

Isothermal Differential Scanning Calorimetry Study of the Cure Kinetics of a Novel Aromatic Maleimide with an Acetylene Terminal

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ABSTRACT: An isothermal differential scanning calorimetry (DSC) study on the cure kinetics was performed on *N*-(3-acetylenophenyl)maleimide (3-APMI) monomer to determine a suitable cure model. The 3-APMI monomer reported in our prior article was a novel aromatic maleimide monomer with an acetylene terminal that would be an ideal candidate for heat-resistant composites. The isothermal DSC study was carried out in the temperature range 150–200°C. Although the cure temperatures were different, the shapes of the conversion curves were similar, and all of the cure reactions could be described by an *n*th-

order kinetic model. In particular, the cure reaction at the initial stage was a first-order kinetic reaction. The cure kinetic parameters of the 3-APMI monomer, including the reaction model, activation energy, and frequency factor, were determined. This information was very useful for defining the process parameters, final properties, and quality control of the cured 3-APMI monomer. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 525–529, 2008

Key words: thermosets; curing of polymers; differential scanning calorimetry (DSC); kinetics

INTRODUCTION

Bismaleimide resins are preferred in a wide range of applications from commodity materials to applications in hi-tech aerospace industries, such as multiplayer printed circuit boards for large-scale computers,^{1,2} advanced composites,^{3,4} structural adhesives, and potting resins,⁵ because of their high thermal stability, hot-wet strength, and fatigue resistance.

Acetylene-terminated monomers are another kind of high-performance resin and are currently being developed to replace, for example, epoxies for use under hot and wet conditions.^{6,7} In addition, the networks formed by acetylene resins are very stable against thermooxidation. It was reported⁸ that acetylene groups can polymerize in the molten state by thermal activation starting at 130°C without the addition of any catalyst, which indicates that they possess good reactivity.

To combine the advantages of the two kind of resins, in our prior study,⁹ we designed and synthesized *N*-(3-acetylenophenyl)maleimide (3-APMI) monomer, which contains both acetylene and maleimide groups in one molecule. The chemical structure

of the monomer is given in Figure 1. The results of dynamic mechanical analysis showed that the cured monomer possessed excellent heat-resistant properties, whose initial decrease in temperature of the storage modulus was about 460°C and whose glass-transition temperature, expressed by $\tan \delta$, was up to 508°C. This makes 3-APMI monomer an ideal resin matrix for high-temperature resistant composites. It is well known the thermal and mechanical properties of thermosets are dependent on the degree of cure (α), and this concept is defined by the reaction kinetics. Therefore, an understanding of the cure kinetics of the 3-APMI monomer becomes essential for defining its final properties, process development, and quality control. The aim of this study was to address the kinetics of the cure reaction of the 3-APMI monomer. The isothermal differential scanning calorimetry (DSC) technique was used to monitor the cure reaction and to obtain the kinetic parameters.

EXPERIMENTAL

Materials

Maleic anhydride (AR, Beijing Chemical Reagent Corp., Beijing, China), 3-aminophenylacetylene (AR, Jiaozhou Chemicals Co., Ltd., Shandong, China), acetone (AR, Beijing Chemical Reagent Corp., Beijing, China), acetic anhydride (AR, Beijing Yili Chemicals

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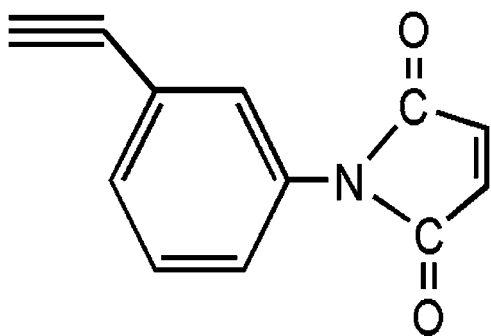


Figure 1 Molecular structure of the 3-APMI monomer.

Corp.), sodium acetate (AR, Beijing Yili Chemicals Corp.), and sodium bicarbonate (AR, Beijing Yili Chemicals Corp.) were used as received.

Synthesis of the 3-APMI monomer

The 3-APMI monomer used in this study was synthesized according to a procedure described elsewhere.⁹ First, maleamic acid was obtained by means of a ring-opening addition reaction between 3-aminophenylacetylene and maleic anhydride. Second, maleamic acid was cyclodehydrated to get the 3-APMI monomer with acetic anhydride and sodium acetate as the dehydrating mixture. The synthesis protocol is given in Figure 2.

The crude product was recrystallized twice in methanol to obtain the monomer with high purity (pale yellow crystal, yield = 51.8%, mp = 134–135°C):

Fourier transform infrared spectroscopy (KBr, cm^{-1}): 3263 ($\equiv\text{C}-\text{H}$), 3110 ($=\text{C}-\text{H}$, maleimide group), 1721 and 1777 ($\text{C}=\text{O}$, maleimide group), 1146 ($\text{C}-\text{N}-\text{C}$), 831 ($\text{C}=\text{C}$, maleimide group). $^1\text{H-NMR}$ (CDCl_3 , δ): 7.3–7.5 (aromatic proton), 6.87 ($\text{C}=\text{C}-\text{H}$, maleimide group), 3.12 ($\equiv\text{C}-\text{H}$). MS (70ev): m/e 197 (M^+). Electron impact (E1) mass spectrum mass-to-charge ratio (m/e) intensity: 197 (100, M^+)

ANAL. Calcd. for $\text{C}_{12}\text{H}_7\text{NO}_2$ (197.19): C, 73.09%; H, 3.58%; N, 7.10%. Found: C, 73.28%; H, 3.57%; N, 7.16%.

Isothermal DSC analyses

The isothermal DSC analyses of the 3-APMI monomer were performed at 150, 160, 170, 180, 190, and 200°C. The heat of cure reaction of 3-APMI was measured with a Mettler-Toledo DSC822^e instrument (Mettler-Toledo Instrument Co., Ltd., Switzerland). Before measurements, the temperature and heat flow calibrations were done by a recommended procedure with pure indium metal (mp = 156.6°C) and with a heat of fusion of 28.45 J/g. Then, the DSC cell was preheated to the selected temperature, and approxi-

mately 8.5 mg of monomer was inserted as quickly as possible. Then, the measurement started. During measurements, nitrogen, at a flow rate of 50 mL/min, was used as purge gas to minimize oxidation of the sample. After measurement, the total area under the exothermic curve, based on the extrapolated baseline at the end of the reaction, was used to calculate the isothermal heat of cure (H_i) at a given temperature. In addition, when the isothermal cure was completed, the sample was cooled rapidly to 25°C and was then heated from 25 to 350°C at 10°C/min to determine the residual heat of reaction (H_r). The sum of H_i and H_r was taken as the total heat of the cure reaction (H_T). The instrument was capable of reaching the designated isothermal temperature at the fastest heating rate (500°C/min) and then equilibrating to the target temperature when the isothermal curing experiment started. Thus, the heat of reaction that was lost (and thus not recorded) during the transient ramping was virtually negligible, which ensured the accuracy of the kinetic analysis. In addition, the samples were weighed again and compared to the initial value before testing. The results show that the weight losses were negligible in all cases.

RESULTS AND DISCUSSION

The thermal polymerization of arylacetylene compounds, in particular, phenylacetylene, has been studied for several years, and mechanism and structures for these system have been proposed in the literature.^{10–19} Polyene structures,^{10–13} benzene and naphthalene structures,^{14–17} diyne,¹⁸ and enyne¹⁹ are possible structures formed during thermal polymerization. Diels–Alder and [2+2] reactions are considered possible reactions that result in the presence of diene, enynes, or diyens in the mixture during the polymerization reaction.^{12,15–17}

The exact cure mechanism, however, is still obscure because of the numerous ways in which polymerization can proceed, combined with the fact that few characterization techniques are available to study these complex thermosets structures. So, in this study, the phenomenological approach, which is only related to the overall reaction and which does

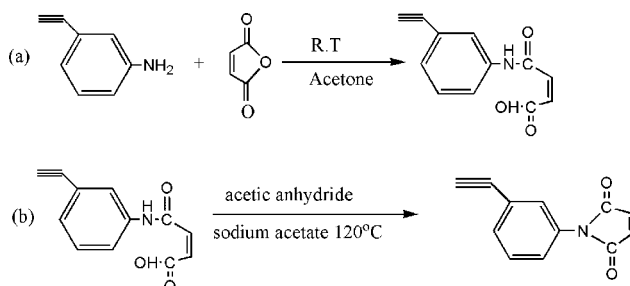


Figure 2 Synthesis protocol for the 3-APMI monomer.

not provide a clear description of the curing process and its chemistry, was used to study the cure reaction of the 3-APMI monomer. The method is based on eq. (1):

$$d\alpha/dt = kf(\alpha) \quad (1)$$

where $d\alpha/dt$ is the reaction rate, α is the conversion or the degree of cure, t is the reaction time, $f(\alpha)$ is a function of the amount of reactant, and k is a rate constant defined by the Arrhenius equation, which is given as follows:

$$k(T) = A \times \exp(-E/RT) \quad (2)$$

where A is the frequency factor, or preexponential factor; E is the activation energy; R is the universal gas constant; and T is the processing temperature expressed in Kelvin. As for the cure kinetics of thermosetting materials, their constitutive modeling equations generally fall into two categories: n th and autocatalytic types. For thermosetting materials that follow n th-order kinetics, the rate of conversion is proportional to the concentration of unreacted material:²⁰

$$f(\alpha) = (1 - \alpha)^n \quad (3)$$

A generalized expression corresponding to an autocatalytic reaction can be given as follows:

$$f(\alpha) = (k_1 + k_2\alpha^m)(1 - \alpha)^n \quad (4)$$

where m and n are the reaction orders, k_1 is a constant, and k_2 is the specific rate constant described by the Arrhenius equation. In this case, the influence of the reaction product on the conversion rate is given by the term $k_2\alpha^m$.

Because the cure of thermosetting resins is an exothermic process, α can be expressed with the enthalpy (heat) released during the reaction of the resin:

$$\alpha = H_t/H_T \quad (5)$$

where H_t is the enthalpy at time t and H_T is the total enthalpy when the cure reaction is complete.

Then, $d\alpha/dt$ can be represented by the equation:

$$d\alpha/dt = 1/H_T \times (dH_t/dt) \quad (6)$$

The heats of polymerization for the APMI monomer at all isothermal temperatures are listed in Table I.

TABLE I
Total Heat of Reaction for 3-APMI Samples Cured at Different Temperatures

Property	Temperature (°C)					
	150	160	170	180	190	200
H_i (J/g)	475.94	518.05	569.42	610.77	631.92	648

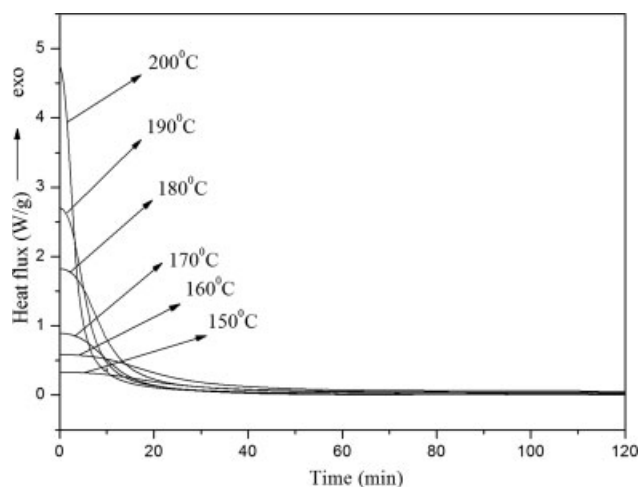


Figure 3 DSC curves from the isothermal mode at different temperatures.

The total heat of polymerization gradually increased from about 476 to 648 J/g with increasing cure temperature from 150 to 200°C; this suggests the increasing extent of the cure reaction.

The DSC curves from the isothermal mode at different temperatures are given in Figure 3. As shown in Figure 3, under isothermal conditions, the heat flow was highest when $t = 0$ and decreased with increasing cure time. The peak value of heat flow increased with increasing temperature, and the time needed to get to the endpoint of the cure reaction shortened with increasing temperature. The area under the isothermal curve up to any time t represents the heat of the reaction at time t (H_t). α and $d\alpha/dt$ can be obtained according to eqs. (5) and (6). The isothermal time–conversion profiles and the cure rate versus time profiles for the 3-APMI monomer at different temperatures are given in Figures 4 and 5, respectively.

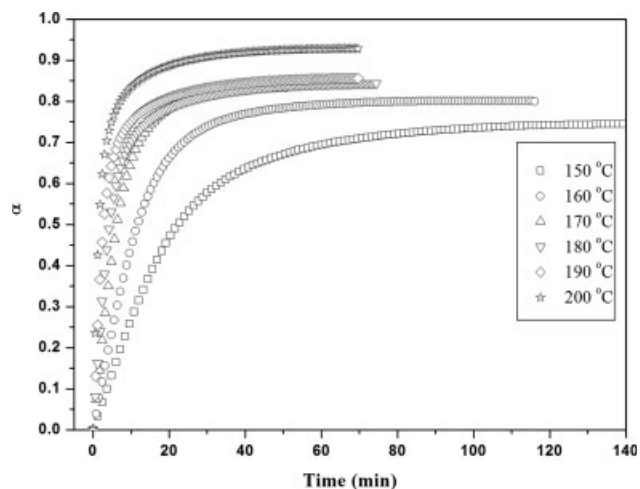


Figure 4 Isothermal time–conversion profiles for the 3-APMI monomer at different temperatures.

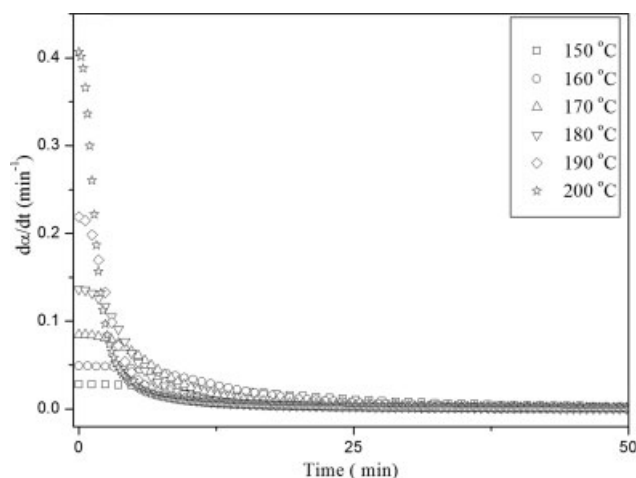


Figure 5 Cure rate/time profiles for the 3-APMI monomer at several temperatures.

As shown in Figure 4, α increased with increasing cure temperatures. It also shows that the time needed to achieve the highest α decreased with increasing temperature. This indicates that a complete cure could be obtained when the reaction temperature was above 200°C and that lower temperatures clearly necessitated longer reaction times to drive the reaction to completion. The initial steep rise in α versus time, followed by a very gradual increase, was suggestive of the kinetic behavior of a diffusion-limited system. At the initial stage of the cure reaction, the viscosity of the medium increased dramatically with the initial reaction of reactive groups of the monomer. When the effects of the decrease in both the concentration of the reactive ends and the ability for diffusive movement of those ends were combined, the rate of the reaction should have begun to diminish once these effects became substantially inhibiting. The effect of the viscosity increase could be minimized and a higher degree of

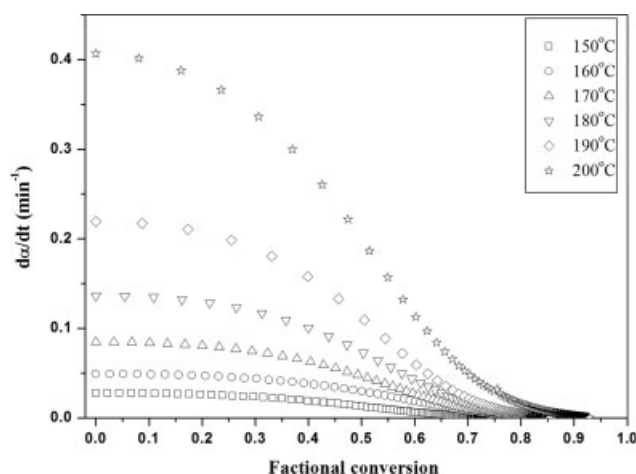


Figure 6 Cure rate/fractional conversion data at several temperatures for the 3-APMI monomer.

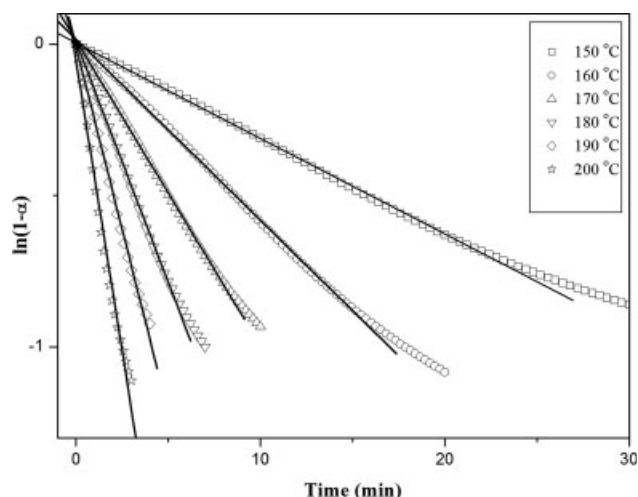


Figure 7 Plot of $\ln(1 - \alpha)$ versus the cure time at several temperatures.

conversion could be achieved as the cure temperature was raised.

The cure rate, represented by $d\alpha/dt$, shown as a function of cure time at different isothermal exposure temperatures from 150 to 200°C for the APMI monomer, is given in Figure 5. As Figure 5 shows, the maximum cure rates appeared about at $t = 0$, which indicated that the cure reaction obeyed the n th-order reaction rule.

Figure 6 shows the plots of the cure rate versus the fractional conversion. As shown, the maximum $d\alpha/dt$ occurred at zero conversion, which is also a characteristic of the n th-order reaction.²¹

Therefore, the cure kinetics of the APMI monomer can be described by the following equation:

$$d\alpha/dt = k(T) \times f(\alpha) = A \times \exp(-E/RT)(1 - \alpha)^n \quad (7)$$

When $n = 1$, after integration, eq. (7) can be written as

$$\ln(1 - \alpha) = kt \quad (8)$$

where k is the rate constant at a specific temperature.

Figure 7 shows the plots of $\ln(1 - \alpha)$ versus time. As shown, the plot of $\ln(1 - \alpha)$ versus time was linear at the initial stage of cure reaction. This means that the cure reaction could be described with the first-order reaction. However, the linear relationship in Figure 7 existed only when α was under 0.6. When α was greater than that value, the relation

TABLE II
 k Values of the Kinetic Parameters at Different Temperatures

Variable	Temperature (°C)					
	150	160	170	180	190	200
k (min ⁻¹)	0.0315	0.0597	0.1008	0.1588	0.2414	0.3835

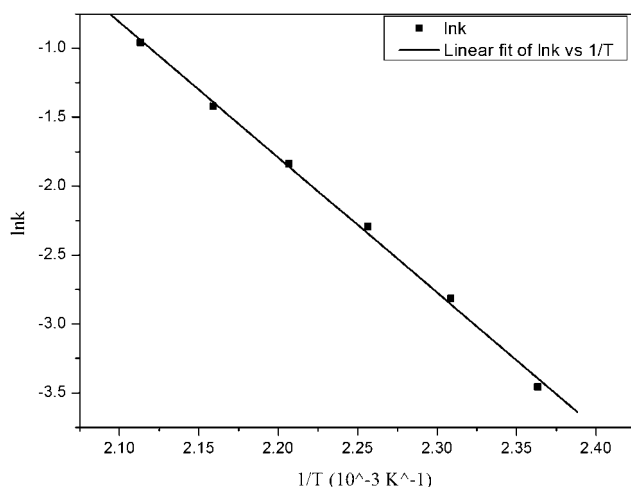


Figure 8 k as a function of the reciprocal cure temperature for the 3-APMI monomer.

between $\ln(1 - \alpha)$ and the cure time obviously deviated from a linear shape, which could be attributed to diffusion control in the late cure stage.

The cure rate constants at different temperatures were calculated from the slope of the line and are given in Table II.

The logarithm of eq. (2) gives

$$\ln k = \ln A - E/RT \quad (9)$$

A plot of $\ln k$ versus $1/T$ is shown in Figure 8. As shown, the data reasonably fit a straight line. From the slope and intercept of the straight line, we obtained values of $\alpha = 4.04 \times 10^8/\text{min}$ and $E = 81.7$ kJ/mol, which were in a close agreement with the values obtained by the dynamic DSC method.⁹ Therefore, the cure kinetics equation for the cure reaction of the 3-APMI monomer can be expressed as follows:

$$d\alpha/dt = 4.04 \times 10^8 \exp(-81,700/RT) \times (1 - \alpha) \quad (10)$$

where t is the cure time, α is the degree of cure, R is the universal gas constant, and T is the cure temperature (K).

CONCLUSIONS

Kinetic characterization with isothermal DSC was performed on the 3-APMI monomer. α was depend-

ent on the cure temperature. With increasing cure temperature, α increased. Lower temperatures needed longer cure times to drive the reaction to completion. The cure reaction of the 3-APMI monomer followed an n th-order reaction. Also, the cure reaction at initial stage could be expressed by the first-order reaction. E and A were determined. At the initial stage of the cure reaction, the cure rate represented a greater value, which indicated that the reaction was chemically controlled. As the cure reaction proceeded, $d\alpha/dt$ gradually decreased and then finally leveled off because of the diffusion-controlled reaction.

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