



# Isothermal polymerization kinetics of *N,N'*-bismaleimide-4,4'-diphenylmethane with cyanuric acid



Quoc-Thai Pham<sup>a</sup>, Jung-Mu Hsu<sup>c</sup>, Fu-Ming Wang<sup>b</sup>, Mei-Ping Chen<sup>a</sup>,  
Chorng-Shyan Chern<sup>a,\*</sup>

<sup>a</sup> Department of Chemical Engineering, National Taiwan University of Science and Technology, Taipei 106, Taiwan

<sup>b</sup> Graduate Institute of Applied Science and Technology, National Taiwan University of Science and Technology, Taipei 106, Taiwan

<sup>c</sup> Materials and Chemical Research Laboratories, Industrial Technology Research Institute, Chutung, Hsinchu 31015, Taiwan

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## ABSTRACT

Kinetics of polymerization of *N,N'*-bismaleimide-4,4'-diphenylmethane (BMI) with cyanuric acid (CA) in *N*-methyl-2-pyrrolidone (NMP) was investigated. Both model-free and model-fitting methods were used to determine the relevant kinetic parameters. For the model-free method, the average activation energy ( $E_a$ ) and pre-exponential factor ( $A_a$ ) are  $23 \pm 1 \text{ kJ mol}^{-1}$  and  $162 \pm 2 \text{ min}^{-1}$  in the  $\alpha$  range 0.1–0.9, respectively. The  $A_a$  value obtained is a result of the model assumption with  $g(\alpha) = -\ln(1 - \alpha)$  [i.e.  $f(\alpha) = (1 - \alpha)$ ], which is based on  $^1\text{H}$  NMR measurements. As to the model-fitting method, the overall activation energy ( $E$ ) and pre-exponential ( $A$ ) are  $23 \text{ kJ mol}^{-1}$  and  $166 \text{ min}^{-1}$  with  $g(\alpha) = [(1 - \alpha)^{0.15} - 1]/0.15$  [i.e.  $f(\alpha) = (1 - \alpha)^{1.15}$ ]. The polymerization kinetics and mechanism of BMI/CA in NMP were characterized by DSC. Furthermore, complementary  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR techniques were used to identify the chemical structure of CA in the reaction medium and, therefore, the reaction mechanism (model) was predicted.

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## 1. Introduction

*N,N'*-bismaleimide-4,4'-diphenylmethane (denoted as BMI) based polymers and composite materials offer excellent mechanical properties, chemical resistance, thermal stability and attractive cost/performance ratio. As a result, these products have been widely used in many applications such as aerospace and electronics industries. With two reactive terminal  $\text{C}=\text{C}$  groups, BMI undergoes highly crosslinked polymerizations. In our previous studies [1–3], barbituric acid (BTA) was shown to initiate free radical polymerizations of BMI or bisphenol A diglycidyl ether diacrylate (EA) [4,5]. Furthermore, BTA containing two  $>\text{NH}$  groups and one  $>\text{CH}_2$  group was capable of reacting with BMI via the Michael addition reaction mechanism [6]. Thus, competition between free radical and Michael addition polymerization mechanisms was operative in the BMI/BTA reaction system. Cyanuric acid (CA) exhibits either an oxo (keto) structure or a hydroxyl (enol) structure. The reaction of CA with electrophiles generally results in derivatives with the keto structure (isocyanurate) [7]. Thus, CA containing three  $>\text{NH}$

groups can react with BMI via the aza-Michael addition reaction mechanism involved in the addition of a nucleophile (CA) to an activated electrophilic olefin (BMI) [6,8].

Lithium-ion battery systems embedded with a relatively low level of BMI/BTA polymer provide the multi-protective mechanism to prevent batteries from thermal run away and ultimate explosion (the key safety issue in this field) [9–12]. The BMI/CA-based polymer represents a potential additive for effectively improving the key performance of lithium-ion batteries. The objective of this work was therefore to investigate the polymerization kinetics of BMI with CA in the presence of triethylamine ( $\text{Et}_3\text{N}$ , as a catalyst for Michael addition reaction). The triplet kinetic parameters of the isothermal polymerization process including activation energy ( $E$ ), pre-exponential factor ( $A$ ) and reaction model  $g(\alpha)$  were determined by a differential scanning calorimeter (DSC). The results obtained from this work are of great value in the molecular design and scale-up of these BMI/CA based polymers.

\* Corresponding author.

E-mail address: [cschern@mail.ntust.edu.tw](mailto:cschern@mail.ntust.edu.tw) (C.-S. Chern).

## 2. Experimental

### 2.1. Materials

The chemicals used include *N,N'*-bismaleimide-4,4'-diphenylmethane (95%, Beil), cyanuric acid (98%, ACROS), triethylamine (99%, ACROS) and *N*-methyl-2-pyrrolidone (NMP, 99%, ACROS). All chemicals were reagent grade, and used as received.

### 2.2. Characterization

Isothermal polymerizations of BMI/CA [1.5/1 (mol/mol)] were carried out in a Tzero pan (sealed by the Tzero hermetic lid) on DSC (TA Instruments Q20) under a nitrogen flow rate of 50 mL min<sup>-1</sup> at 50, 60, 70, and 80 °C, respectively. The total solids content of BMI/CA in NMP solution was kept constant at 20 wt%, and a sample weight of 10 ± 0.2 mg used throughout this work.

<sup>1</sup>H NMR and <sup>13</sup>C NMR (Bruker Avance, 600 MHz) were adopted to investigate the reaction mechanism of active hydrogen atom of the >NH group of CA toward the —C=C— of BMI. DMSO-*d*<sub>6</sub> or NMP was used as the solvent, and tetramethylsilane used as the internal standard for NMP.

### 2.3. Isothermal polymerization kinetics

The rate of polymerization (dα/dt, where α is the fractional conversion and t the reaction time) can be expressed as follows:

$$\frac{d\alpha}{dt} = kf(\alpha) = A \left[ \exp\left(-\frac{E}{RT}\right) \right] f(\alpha) \quad (1)$$

Integration of Eq. (1) leads to Eq. (2), as shown below.

$$g(\alpha) = \int_0^{\alpha} \frac{d\alpha}{f(\alpha)} = k \int_0^t dt = kt = A \exp\left(\frac{E}{RT}\right)t \quad (2)$$

where *f*(α) is the reaction model, *g*(α) the integral reaction model, *k* the reaction rate constant, *R* the gas constant and *T* the absolute temperature. The fractional conversion (α) is calculated according to the following equation.

$$\alpha = \frac{\Delta H_t}{\Delta H} \quad (3)$$

where Δ*H*<sub>*t*</sub> is the integral area under the heat flow versus *t* curve from the initial time *t*<sub>0</sub> to a specified time (*t*) for the polymerization and Δ*H* represents the apparent overall heat of reaction.

There are two common methods available for the analysis of polymerization kinetics, that is, model-free (isoconversional) and model-fitting methods [13–16]. The model-free method is independent of reaction models and, consequently, it can be used to determine *E*<sub>α</sub> without resort to any model assumption. On the other hand, based on the model-fitting technique, kinetic parameters including *E*, *g*(α) and *A* are required to describe the complete polymerization kinetics. Note that Eq. (2), originally defined for the integral model-fitting method, can be rearranged to become Eq. (4) for the integral model-free (isoconversional) method, as shown below.

$$\ln t_{\alpha,i} = \ln \left[ \frac{g(\alpha)}{A_{\alpha}} \right] + \frac{E_{\alpha}}{RT_i} \quad (4)$$

where *t*<sub>α,*i*</sub> is the time to reach a specific α at *T*<sub>*i*</sub> (subscript *i* represents the ordinal number of an isothermal experiment). According to Eq. (4) (the model-free method), *E*<sub>α</sub> and ln[*g*(α)/*A*<sub>α</sub>] at each α of different *T*<sub>*i*</sub> values can be obtained from the least-squares best-fitted slope and intercept of the straight line passing through the ln*t*<sub>α,*i*</sub>

versus 1/*T*<sub>*i*</sub> data, respectively. If the reaction model is accurately predicted, *A*<sub>α</sub> can be obtained from the values of *g*(α)/*A*<sub>α</sub>.

On the other hand, kinetic parameters, *g*(α) and *k* can be obtained from Eq. (2) by the least-squares best-fitting technique provided that very high coefficient of determination (*R*<sup>2</sup> > 0.99) is achieved. For example, plotting the *g*(α) versus *t* data should result in a straight line with the best-fitted model of *g*(α), in which the best linearity can be identified by the maximal *R*<sup>2</sup>. In this manner, the slope of the least-squares best-fitted straight line represents the value of *k*. Finally, the parameter *k* as a function of *T* can be adequately described by Arrhenius equation as follows:

$$\ln k_i = -\frac{E}{RT_i} + \ln A \quad (5)$$

where *k*<sub>*i*</sub> is the reaction rate constant at *T*<sub>*i*</sub>. The slope and intercept of the least-squares best-fitted straight line obtained from the ln *k*<sub>*i*</sub> vs. 1/*T*<sub>*i*</sub> data then represent the values of  $-E/R$  and ln *A*, respectively.

## 3. Results and discussion

### 3.1. Characterization

The polymerization of BMI/CA [1.5/1 (mol/mol)] with 10 wt% Et<sub>3</sub>N (based on the weight of BMI) in NMP was investigated in this work. In order to verify the chemical structure of CA in the reaction medium, <sup>1</sup>H NMR and <sup>13</sup>C NMR of CA and Et<sub>3</sub>N in NMP were performed. In addition, <sup>1</sup>H NMR of CA in DMSO-*d*<sub>6</sub> was also conducted as the reference sample. Fig. 1 illustrates the results of (a) <sup>1</sup>H NMR spectrum of CA in DMSO-*d*<sub>6</sub>, (b) <sup>1</sup>H NMR and (c) <sup>13</sup>C NMR spectra for CA and Et<sub>3</sub>N in NMP. The characteristic peak at the chemical shift (δ) of 11.13 ppm [H, peak a] is attributed to H in >NH of CA in DMSO-*d*<sub>6</sub> (Fig. 1a). By contrast, the characteristic peak at δ = 11.13 ppm disappears in the presence of Et<sub>3</sub>N in NMP (Fig. 1b). It is noteworthy that the characteristic peak at δ = 150.35 ppm is attributed to C (peak a') in >C=O of CA in the presence of Et<sub>3</sub>N in NMP (Fig. 1c). This result suggests that >NH group of CA is deprotonated by basic catalyst (e.g. Et<sub>3</sub>N denoted as:B) to form [>N<sup>-</sup>+BH] species. Aza-Michael addition polymerization mechanism of BMI with CA involves the reaction of the >NH group of CA with the —CH=CH— of BMI is shown in Scheme 1. First, CA is deprotonated by basic catalyst to form [>N<sup>-</sup>+BH] species (Scheme 1a). This is followed by the reaction of [>N<sup>-</sup>+BH] with the —C=C— group of BMI to form >N—BMI<sup>-</sup>. The carbonyl groups of BMI then help stabilize the resultant >N—BMI<sup>-</sup> until the proton transfer process occurs to produce the desired adduct. The reaction rate law can be derived by the rate-limiting step (i.e., the slowest step shown in Scheme 1b) [6,8].

$$R = k_1[>N^{-}BH][BMI] \quad (6)$$

For strong bases, *K*<sub>eq</sub> is quite large and, as a consequence, the forward reaction predominates in the equilibrium reaction shown in Scheme 1a. This will then lead to a relatively constant concentration of [>N<sup>-</sup>+BH]. Under the circumstances, the pseudo-first-order kinetics can be expressed as [8].

$$R = k'[BMI] = k(1 - \alpha) \quad (7)$$

where *R* is the polymerization rate, *k'* the product of *k*<sub>1</sub> and [>N<sup>-</sup>+BH], [BMI] the concentration of BMI monomer, and *k* the reaction rate constant [defined as the product of *k'* and the initial concentration of BMI monomer ([BMI]<sub>0</sub>)]. In this case, the mechanism involved in the Michael addition reaction of >NH of CA with the —CH=CH— of BMI is reaction-controlled with the reaction model *f*(α) = (1 - α).

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