



## Full Length Article

# Mechanisms and kinetics of non-isothermal polymerization of *N,N'*-bismaleimide-4,4'-diphenylmethane with 1,3-dimethylbarbituric acid



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## ABSTRACT

Mechanisms and kinetics of non-isothermal polymerization of *N,N'*-bismaleimide-4,4'-diphenylmethane (BMI) with 1,3-dimethylbarbituric acid (13BTA) were investigated. Competition between free radical polymerization and Michael addition reaction mechanisms for the BMI/13BTA reaction system was characterized by using DSC and <sup>1</sup>H NMR technique. Model-free (isoconversional) method was used to determine triplet kinetic parameters for the polymerization of BMI with 13BTA. Average activation energy ( $E_a$ ) and pre-exponential factor ( $A_0$ ) are ca. 56 kJ mol<sup>-1</sup> and 65.83 × 10<sup>5</sup> min<sup>-1</sup> in the fractional conversion ( $\alpha$ ) range 0.1–0.9, respectively. Particle nucleation involved in the polymerization process was satisfactorily predicted by the nucleation Avrami-Erofeev model  $\{f(\alpha) = n(1 - \alpha)[- \ln(1 - \alpha)]^{(n-1)/n}\}$  with  $n = 1.46$ . The  $z$ -average particle size of microgel particles was measured by dynamic light scattering, which supported the particle nucleation and growth process.

## 1. Introduction

Polyimides synthesized from the reaction of *N,N'*-bismaleimide-4,4'-diphenylmethane (denoted as BMI) with barbituric acid (BTA) [1,2] exhibiting hyper-branched or highly crosslinked network structures offer excellent mechanical properties, chemical resistance, and thermal stability. These unique polymeric materials produced by the polymerization of BMI with BTA or its derivatives (termed as STOBA<sup>®</sup>) have been used as an additive that provides a lithium-ion battery with the multi-protection mechanism to prevent it from thermal runaway and ultimately disastrous explosion [3–6]. With two reactive terminal  $-C=C-$  groups, BMI is capable of undergoing highly crosslinking polymerizations. For example, BTA was shown to initiate free radical polymerization of BMI [1,2,7]. In addition, BTA containing two  $>NH$  groups and one  $>CH_2$  group was also capable of polymerizing with BMI via (aza)-Michael addition reaction mechanisms [2,8]. Thus, competition among free radical, Michael addition and aza-Michael addition polymerization mechanisms was operative in the BMI/BTA system [9].

In our previous study [10], 5,5-dimethylbarbituric acid (55BTA, a derivative of BTA) containing two reactive  $>NH$  groups was illustrated to react with BMI in the presence of triphenylphosphine (Ph<sub>3</sub>P, acting as a base catalyst) via aza-Michael addition reaction mechanism. It is

noteworthy that, in the absence of an adequate catalyst, the reactivity of the  $>NH$  groups of 55BTA toward the  $-C=C-$  groups of BMI was rather weak [9,10]. On the other hand, the  $>CH_2$  group of 1,3-dimethylbarbituric acid (13BTA) not only initiated free radical polymerization of BMI but also effectively induced polymerization of BMI via Michael addition reaction mechanism [9]. However, the kinetics and reaction mechanisms involved in the polymerization of BMI with 13BTA have not been investigated yet and these subjects were the foci of this work. The triplet kinetic parameters of the non-isothermal polymerization including activation energy ( $E$ ), pre-exponential factor ( $A$ ) and reaction model  $f(\alpha)$  were determined by both model-free and model-fitting methods with the kinetics data attained from a differential scanning calorimeter (DSC). The reaction mechanisms were confirmed by electron spin resonance (ESR, used to detect free radicals, if present, for the BMI/13BTA reaction system) and <sup>1</sup>H NMR measurements. The results obtained from this work are of great value in the molecular design and scale-up of these BMI/13BTA based polymers.

## 2. Theory

## 2.1. Single step polymerization kinetics

The rate ( $d\alpha/dt$ ) of a single step polymerization can be described as

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follows:

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

$$\alpha = \frac{\Delta H_T}{\Delta H} \quad (2)$$

where  $t$  is time,  $R$  the gas constant,  $T$  the absolute temperature,  $\alpha$  the fractional conversion and  $f(\alpha)$  the reaction model. The parameter  $\Delta H_T$  is the integral area under the heat flow versus temperature curve from the initial temperature to a specified  $T$  for the polymerization, and  $\Delta H$  the apparent overall heat of reaction.

## 2.2. Determination of activation energy ( $E_\alpha$ ) by the model-free method

For a non-isothermal polymerization process, temperature is varied by a constant heating rate  $\beta$  ( $= dT/dt$ ) and  $\alpha$  can be analyzed according to the following equation.

$$\frac{d\alpha}{dt} = \beta \left( \frac{d\alpha}{dT} \right) = A \left[ \exp\left(-\frac{E}{RT}\right) \right] f(\alpha) \quad (3)$$

The model-free (isoconversional) method is independent of reaction models and, consequently, it can be used to estimate  $E_\alpha$  without resort to any model assumption. The most common isoconversional (Friedman) method in differential form is based on Eq. (4) [11,12].

$$\ln\left(\frac{d\alpha}{dt}\right)_{\alpha,h} = \ln\left(\beta \frac{d\alpha}{dT}\right)_{\alpha,h} = -\frac{E_\alpha}{RT_{\alpha,h}} + \ln[A_\alpha f(\alpha)] \quad (4)$$

where the subscript  $h$  represents the ordinal number of a non-isothermal experiment conducted at a heating rate of  $\beta_h$ , and the subscript  $\alpha$  the quantity evaluated at a specific  $\alpha$  in Eq. (4). According to Eq. (4),  $E_\alpha$  and  $\ln[A_\alpha f(\alpha)]$  at each  $\alpha$  of different  $\beta_h$  values can be obtained from the slope and intercept of the least-squares best-fitted straight line passing through the  $\ln(d\alpha/dt)_{\beta,h}$  versus  $1/T_{\beta,h}$  data points, respectively.

## 2.3. Determination of compensation parameters

The model-fitting method can be used to determine  $E_i$ ,  $A_i$ , and  $f_i(\alpha)$ , and the resultant  $E_i$  and  $A_i$  used to determine the compensation parameters [11]. Eq. (5) defined for the model-fitting method [11] is shown as follows:

$$\ln\left[\frac{(d\alpha/dt)}{f_i(\alpha)}\right] = \ln\left[\frac{\beta(d\alpha/dT)}{f_i(\alpha)}\right] = -\frac{E_i}{RT} + \ln A_i \quad (5)$$

where the subscript  $i$  represents the ordinal number of the triplet kinetic parameters. The triplet kinetic parameters [ $E_i$ ,  $A_i$ , and  $f_i(\alpha)$ ] can be obtained from Eq. (5) by the linear least-squares best-fitting technique with the model [ $f_i(\alpha)$ ] of choice. For example, plotting the  $\ln[(d\alpha/dt)/f_i(\alpha)]$  versus  $1/T$  data should result in a straight line with the model  $f_i(\alpha)$ , in which the best linearity is identified by the very high coefficient of determination ( $R^2$ ). Thus, the slope and intercept of the least-squares best-fitted straight line represent the values of  $-E_i/R$  and  $\ln A_i$ , respectively. Subsequently,  $E_i$  and  $\ln A_i$  can be used to determine the parameters  $a$  and  $b$  associated with the compensation effect as follows [11]:

$$\ln A_i = aE_i + b \quad (6)$$

Based on Eq. (6),  $a$  and  $b$  can be obtained from the slope and intercept of the least-squares best-fitted straight line passing through the  $\ln A_i$  versus  $E_i$  data points, respectively.

## 2.4. Determination of reaction model [ $f(\alpha)$ ]

One prerequisite for determination of the reaction model is that variations in  $E_\alpha$  during the reaction are insignificant. Thus,  $E_\alpha$  can be simply replaced by an average value  $E_0$ . With the knowledge of  $a$  and  $b$ ,

$\ln A_0$  can be determined by substituting  $E_0$  into Eq. (6). In this manner, the reaction model [ $f(\alpha)$ ] can be reconstructed by substituting  $E_0$  and  $A_0$  into Eq. (4) to result in the following equation.

$$f(\alpha) = \left(\frac{d\alpha}{dt}\right)_{\alpha,h} \left[A_0 \exp\left(-\frac{E_0}{RT_{\alpha,h}}\right)\right]^{-1} \quad (7)$$

This is followed by comparing the resulting numerical values of  $f(\alpha)$  with the theoretical results attained from reaction models available in the literature in order to identify the best-fitting model.

Finally, the best-fitting model,  $f(\alpha)$ , can be reconstructed based on Eq. (7). The method that evaluates the difference in the form of residual sum of squares (RSS) [11,13] can be used to identify the reaction model of choice.

$$RSS = \sum (f(\alpha)_{\text{exp}} - f(\alpha)_{\text{calc}})^2 = \min \quad (8)$$

where the subscripts  $\text{exp}$  and  $\text{calc}$  represent the experimental and calculated, respectively.

## 3. Experimental

### 3.1. Materials

The chemicals used in this work include *N,N'*-bismaleimide-4,4'-diphenylmethane (95%, Beil), 1,3-dimethylbarbituric acid (+98%, Sigma-Aldrich), hydroquinone (HQ, 99%, ACROS), dimethylsulfoxide-*d*<sub>6</sub> (DMSO-*d*<sub>6</sub>, +99%, ACROS), and *N*-methyl-2-pyrrolidone (NMP, 99%, ACROS). All chemicals were reagent grade and used as received.

### 3.2. Characterization

Non-isothermal polymerization of BMI/13BTA [1/1 (mol/mol)] was carried out in a Tzero hermetic 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 different heating rates ( $\beta = 2, 3, 4.5$  and  $6^\circ\text{C min}^{-1}$ ). The total solids content of BMI/13BTA in NMP was ca. 20 wt%, and a sample weight of  $12 \pm 0.2$  mg used throughout this work.

ESR (Bruker, Elexsys-II E580) measurements were used to detect free radicals in the BMI/13BTA reaction system. Furthermore, <sup>1</sup>H NMR (Bruker Avance, 600 MHz) was adopted to investigate the relevant reaction mechanisms. In addition, hydrodynamic particle size ( $d$ ,  $z$ -average) of microgel particles (MPs) of BMI/13BTA polymer was measured by dynamic light scattering (DLS, Malvern 1000 HSA). The sample was diluted with NMP to eliminate multiple light scattering. The evolution of MP size for the reaction system of BMI/13BTA [1/1 (mol/mol)] was determined by DLS.

## 4. Results and discussion

### 4.1. Characterization

The ESR technique was used to detect free radicals in the reaction system of BMI/13BTA [1/1 (mol/mol)] or BMI alone in NMP (20 wt% solids content for BMI/13BTA and 14 wt% for BMI) at 25 °C. Fig. 1 shows that the ESR intensity of BMI/13BTA reaction system is much higher than that of BMI in NMP. This indicates that 13BTA can effectively generate free radicals to initiate the propagation reaction of BMI. Furthermore, the two active hydrogen atoms of the  $>CH_2$  group of 13BTA could react with the  $-C=C-$  groups of BMI via the Michael addition mechanism as well [8,9]. Therefore, competition between the simultaneously occurring free radical polymerization and Michael addition reaction mechanisms must be considered in the BMI/13BTA polymerization, as illustrated in Scheme 1.

To simplify such a complicated reaction system, HQ was used to effectively inhibit the free radical polymerization of BMI with BTA in our previous work [8–10,13]. As a result, the sole Michael addition

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