



## Cure kinetics and thermal properties of novel bismaleimide containing phthalide cardo structure

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### ABSTRACT

A novel bismaleimide containing phthalide cardo structure (BMIP) was mixed with 2,2'-diallyl bisphenol A (DABPA), and the cure behavior of the mixture was studied by Fourier transform infrared (FTIR) spectroscopy and differential scanning calorimetry (DSC). The FTIR results demonstrated the cure reaction below 200 °C progressed preferentially via alternating copolymerization of maleimide and allyl groups. The DSC thermogram of the prepolymer showed three different cure regimes in the temperature range of 100–350 °C and the 2nd exothermic peak was predominant. The kinetic parameters of the 2nd curing process were evaluated using various kinetic models: Kissinger and Ozawa–Flynn–Wall, and the apparent activation energies obtained from two methods were consistent with each other. Thermal properties of the cured network were characterized by thermogravimetric analysis (TGA) and dynamic mechanical analysis (DMA). Experimental results exhibited that the onset decomposition temperature ( $T_{5\%}$ ) was ~431 °C and char yield at 600 °C was ~39.1%. In addition, the glass-transition temperature ( $T_g$ ) reached 274 °C based on the  $\tan \delta$  peak temperature.

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### 1. Introduction

Bismaleimide (BMI) resins are a promising and relatively young class of thermosetting polymers [1]. They play an increasingly important role in high-tech industries due to the fact that their cured products have good electrical properties, lower coefficient of thermal expansion, excellent fire and moisture resistance, superior thermal and thermal-oxidative stability, and high glass transition temperature and mechanical strength [2–9]. However, the inherent brittleness, limited durability and poor impact resistance of the pure resins, resulting from high crosslink density and rigid molecular skeleton, hamper the further application in the aerospace and electronic industries [10]. Hence, many modification methods have been developed to overcome the above-mentioned drawbacks [11–13]. It was reported that the most successful modification method was the copolymerization of BMIs with allyl-substituted aromatic compounds, which not only could be able to enhance the toughness of BMIs but also endowed the resultant resins with better process flexibility and lower cost [14–16]. Based on the 4,4'-bismaleimidodiphenyl methane (BMPM) and 2,2'-diallyl bisphenol A (DABPA), numerous high performance modified BMI resins were developed, such as QY8911, Matrimid 5292 and BASF 5260 [17].

Despite the 2,2'-diallyl bisphenol A modified BMI resins win great honors for their outstanding properties, there is still not unambiguous information about the mechanism and kinetic feature of their cure reaction. Undoubtedly, aside from dependence on the molecular structure of various ingredients in the system, the properties of polymeric materials such as  $T_g$ , modulus and toughness also depend strongly on the extent of cure and the cure pathway which is controlled by the time of cure and the cure temperature [16,18,19]. Therefore, the optimization of polymer properties calls for reliable curing kinetic parameters and a clear picture of the chemical transformations which occur during curing. In fact, many efforts have been made to investigate the curing pathways and kinetics of BMPM/DABPA systems. Mijovic and Andjolic studied the isothermal cure of BMPM/DABPA using remote in situ real time fiber optic near-infrared spectroscopy in the 140–250 °C range [2]. They reported the principal reaction was alternating copolymerization involving maleimide and allyl double bonds, and maleimide homopolymerization occurred only in the initial stages of reaction at temperatures above 200 °C. Phelan and Sung characterized the cure behavior by FT-IR, fluorescence, and UV-reflectance spectroscopy and discussed various reaction pathways [16]. Rozenberg et al. reported the cure kinetics and mechanism of equifunctional BMPM/DABPA revealed by a combination of many analytical techniques [20]. In addition, isothermal and nonisothermal DSC methods were often employed for kinetic analysis of BMPM/DABPA cure [4,5,14,17]. According to these studies, the following reaction types have been proposed to be involved in the curing process: Ene, Diels–Alder, homopolymerization, alter-

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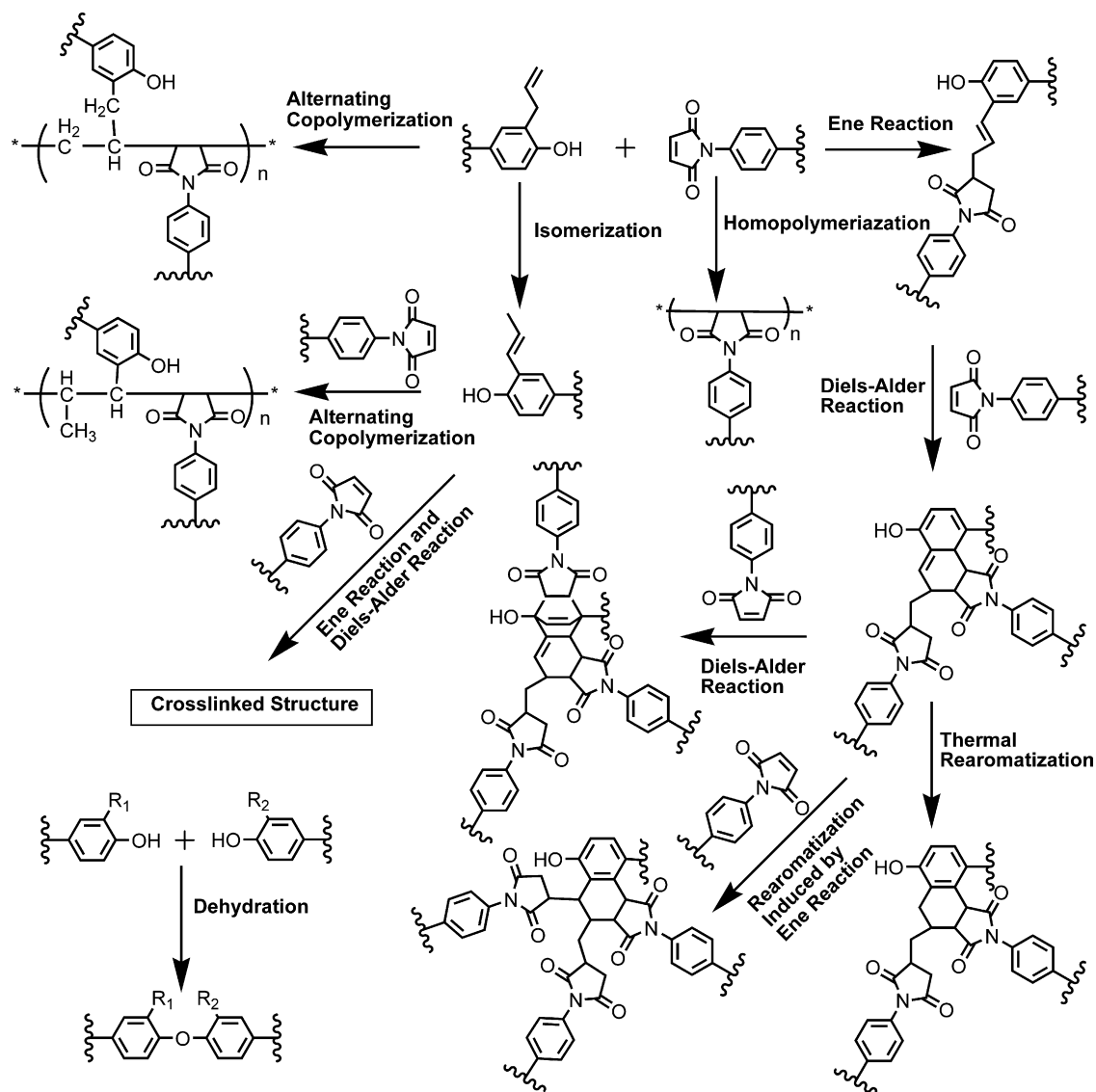


Fig. 1. Proposed curing mechanisms for BMI/DABPA resin.

nating copolymerization and rearomatization. The proposed curing pathways are outlined in Fig. 1.

In the previous research, we designed and synthesized a chain-extended BMI monomer containing phthalide cardo structure (BMIP) [21]. The monomer shows an advantageous combination of properties, such as good solubility, lower melting point and favorable cost. Nevertheless, its high melt viscosity and high cure temperature disfavor preparation of good-quality products. To solve these manufacturing limitations, DABPA was chosen to copolymerize with BMIP. The objective of this study was to provide the information about the mechanism and kinetics of curing for equimolar BMIP/DABPA resin investigated by FTIR and nonisothermal DSC. Furthermore, the thermal properties of the blend resin were characterized by DMA and TGA.

## 2. Experimental

### 2.1. Materials

Commercially available 2,2'-diallyl bisphenol A (DABPA) was provided by Laizhou City Laiyu Chemical Co., Ltd. (Shandong, China). BMIP was synthesized according to the reported method [21].

### 2.2. Preparation of BMIP–DABPA blend

The structures of BMIP and DABPA are shown in Fig. 2. The prepolymer BMIP/DABPA was prepared by mixing an equimolar amount of crushed BMIP and DABPA at 150 °C under vigorous mechanical stirring for about 10 min, and then a homogeneous,

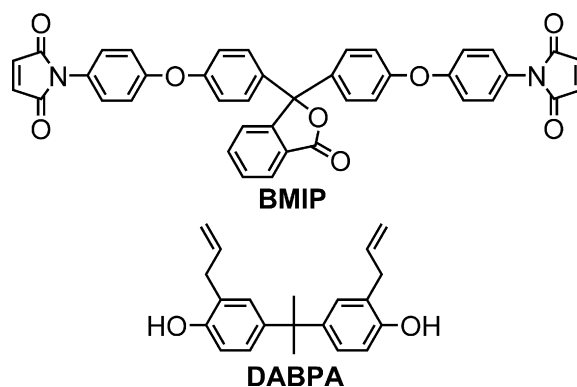


Fig. 2. Chemical structures of BMIP and DABPA.

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