



Understanding of the polymerization mechanism of the phthalonitrile-based resins containing benzoxazine and their thermal stability



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ABSTRACT

As a unique class of high-performance phthalonitrile-based resins, phthalonitrile containing benzoxazine resin has attracted increasing interests in a wider application fields including aerospace, electronic packaging materials and flameresistant materials in marine. In order to reveal the polymerization mechanism of nitrile groups in the presence of benzoxazine, model experiments were designed and performed with three model compounds, which were synthesized according to the structures of the ring-opened benzoxazine rings. Model compounds with phenolic hydroxyl groups, amine structures and both of them were blended with bisphenol A phthalonitrile monomers and their curing behaviors were investigated by DSC and FTIR. Also, the possible polymerization process was proposed and discussed in detail. Results indicated that the polymerization of nitrile was promoted by the synergistic catalysis effects of the amine structures and the active hydrogen generated from the ring-opening of benzoxazine rings. The nitrile groups were firstly triggered by the lone pair electrons in amine structures and then the further polymerizations were promoted by the phenolic hydroxyl groups. Moreover, it was found that the compounds with well-ordered structures of phenol hydroxyl groups and amine structures exhibited relatively weak acceleration on the trigger polymerization of nitrile groups, while higher subsequent polymerization rate, in comparison with the other model compounds, which can be ascribed to their space configuration and the steric hindrance effects. Additionally, the thermal stability of the resulted polymers with various model compounds was studied to confirm the proposed polymerization mechanism and the final polymerization structures.

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1. Introduction

As a unique class of high-performance thermosetting resins, phthalonitrile-based resins have attracted increasing attentions due to their outstanding thermal stability, good mechanical properties, high glass transition temperature and excellent flame resistance [1–3]. These unique characteristics give the phthalonitrile-based resins a wide range of application in marine, aerospace and microelectronic industries. However, polymerization of neat phthalonitrile monomer is extremely difficult, requiring several days at elevated temperature before the gelation process occurs, which limits their wide uses and exaggerates their

cost [1,3–6]. Up to now, a variety of curing additives including metallic, kinds of amine, carboxylic acids, anhydride, phenolic hydroxyl groups and their composite systems are manipulated in the curing reactions of phthalonitrile resins to improve their polymerization. With the assistance of various kinds of catalyst or curing agents, the final phthalonitrile-based polymers exhibited outstanding properties such as excellent thermal stabilities, outstanding mechanical properties and elevated glass transition temperature (T_g). However, the added heterogeneous catalysts in the polymer matrices always brings lots of problems: (1) the dispersion of the catalysts or curing agents; (2) the volatilization and decomposition of the moisture or micromolecular along with the heterogeneous catalysts; (3) the self-decomposition of the catalysts or curing agents at elevated temperatures during the polymerization of phthalonitrile-based resins; (4) the high cost of the process with the heterogeneous catalysts added [7–9]. Thus,

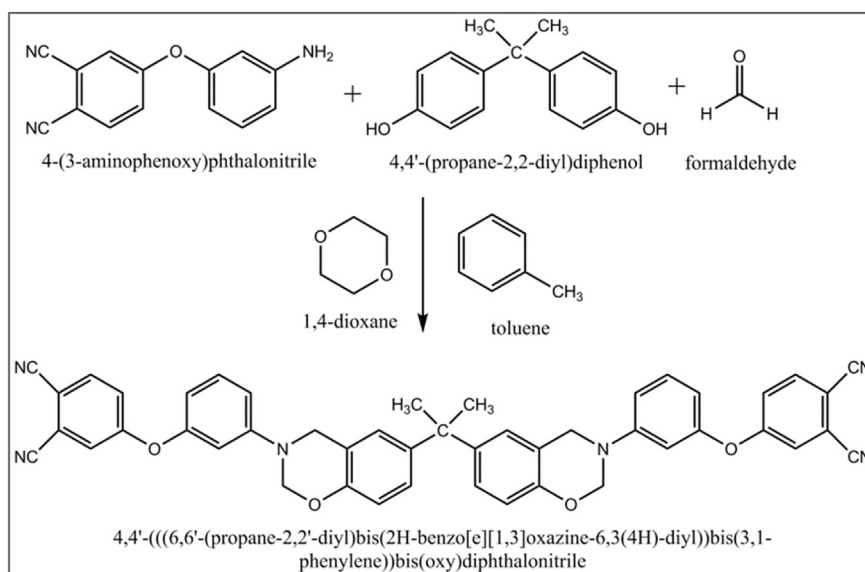
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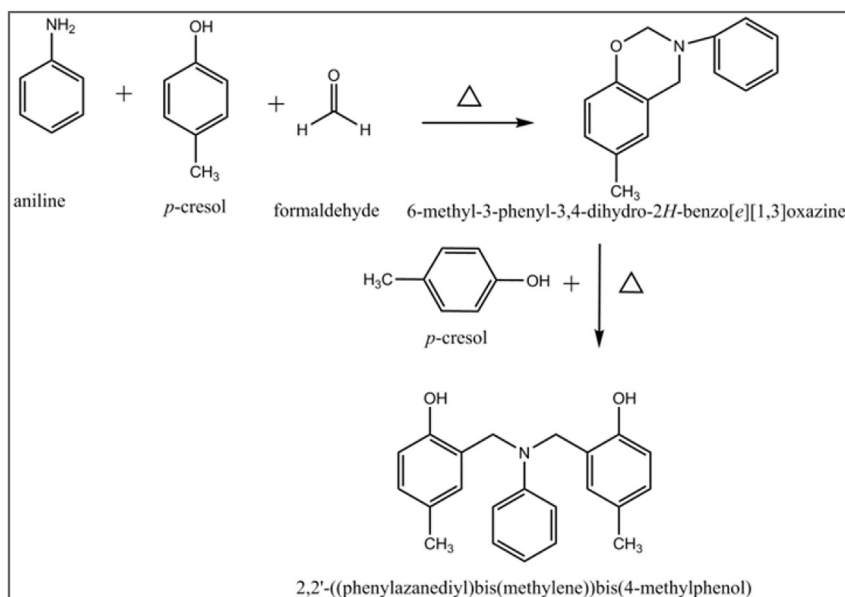
self-polymerization phthalonitrile-based resin has attracted more research interests recently.

As reported, most researchers proposed that phenolic hydroxyl groups and amine unites can promote the polymerization of nitrile groups at about 200 °C [2,7,10]. Thus, the phthalonitrile-based resin with hydroxyl and amino group were designed and prepared via molecular designing, which showed significant self-promoted curing behaviors in the absence of curing additives. In our previous work, various amine-functional phthalonitrile monomers were designed and their polymers were investigated. Results indicated that the introduction of amine unites has significantly decreased their thermal stabilities especially the T_g s and thermal decomposition temperatures. Other researchers also reported the preparation of hydroxyl-functionalized phthalonitrile resins and their final properties, indicating the self-polymerization characteristics and

the decreased thermal stabilities. To maintain the outstanding thermal stabilities of phthalonitrile-based matrices, a phthalonitrile containing benzoxazine (BA-ph) was designed, considering of the outstanding properties of benzoxazine itself [11–13]. Also, the flexible structure-designing enable the preparation of phthalonitrile containing benzoxazine easy and convenient. It was found that the self-promoted curing behavior of BA-ph is evident, in comparison with that of another self-promoted phthalonitrile containing hydroxyl groups [12]. It was reported that the ring-opening polymerization of benzoxazine rings would subsequent occur under the condition of heat, and phenolic hydroxyl groups and amine structures would generate during the formation of Mannich bridge structures [14–18]. Although, various ring-opening processes have been proposed [19], the process provided the product of Mannich base phenol-type structures has gained extensive approvals in the



Scheme 1. Synthetic route of phthalonitrile containing benzoxazine (BA-ph).



Scheme 2. Synthetic route of benzoxazine dimer (Dimer).

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