

Pyridinyl-containing benzoxazine: Unusual curing behaviors with epoxy resins



Ching Hsuan Lin^{a,*}, Yu Sin Shih^a, Meng Wei Wang^a, Chun Yu Tseng^a, Tzu Chun Chen^a, Hou Chien Chang^{a,*}, Tzong Yuan Juang^b

^a Department of Chemical Engineering, National Chung Hsing University, Taichung 402, Taiwan

^b Department of Applied Chemistry, National Chiayi University, Chiayi, Taiwan

ARTICLE INFO

Article history:

Received 1 December 2013

Received in revised form

5 February 2014

Accepted 9 February 2014

Available online 21 February 2014

Keywords:

Pyridinyl

Benzoxazine

Curing behaviors

ABSTRACT

A pyridinyl-containing benzoxazine (**6**) was synthesized from the Mannich condensation of 4-phenyl-2,6-bis(4-aminophenyl) pyridine (**2**), phenol, and paraformaldehyde. For the purpose of properties comparison, a benzoxazine (**7**), which is structurally similar to (**6**) except for the pyridinyl group, was prepared. The solvent effect on the synthesis of (**6**) was discussed, and toluene/ethanol was found to provide (**6**) with the best purity and yield. The pyridinyl group provides solubility and acts as a catalyst for the ring opening of benzoxazine, as supported by the forward curing in the DSC thermograms. When curing with epoxy resins, a carbonyl absorption at 1670 cm^{-1} and 192 ppm was observed in the IR and ^{13}C NMR spectra. It is proposed that the formation of a cyclic amide structure is responsible for the absorption. A reaction mechanism including nucleophilic addition, Diels–Alder reaction, and rearrangement was proposed. The pyridinyl group acts as a crosslinking site, and results in thermosets with good thermal properties.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

Benzoxazines are resins that can be polymerized to thermosets by means of thermally activated ring-opening reactions, and have been reviewed by many authors [1–5]. Thermosets with low water absorption, superior electrical properties [6] and low surface energy [7] can be obtained after curing. There are two types of difunctional benzoxazines, including bisphenol-based benzoxazines, and diamine-based benzoxazines. Bisphenol-based benzoxazines are prepared by the condensation of bisphenol, primary monoamine, and formaldehyde. Diamine-based benzoxazines are prepared by the condensation of diamine, formaldehyde, and monophenol. It has been reported that incorporating pyridinyl groups into polymers can enhance solubility and thermal stability [8–13]. Therefore, we are interested in developing a pyridine-containing benzoxazine. Pyridinyl-containing amines are generally prepared by Chichibabin reaction [14–17] and modified Chichibabin reaction [18]. The diamines, 4-aryl-2,6-bis(4-aminophenyl) pyridines, can be prepared by a modified Chichibabin reaction [8]. In this work, we report the synthesis of a pyridinyl-containing benzoxazine (**6**) from the Mannich condensation of 4-

phenyl-2,6-bis(4-aminophenyl) pyridine (**2**), phenol, and paraformaldehyde. A benzoxazine (**7**), which is structurally similar to (**6**) except for the pyridinyl group, was prepared for properties comparison. When (**6**) acts as an epoxy curing agent, unusual curing behaviors were found. Detailed synthesis of monomers, curing mechanism, and properties of the resulting thermosets are provided in this work.

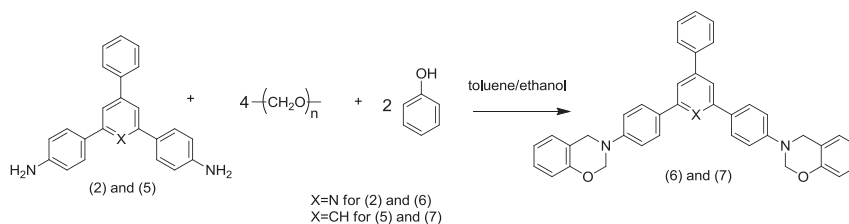
2. Experimental part

2.1. Materials

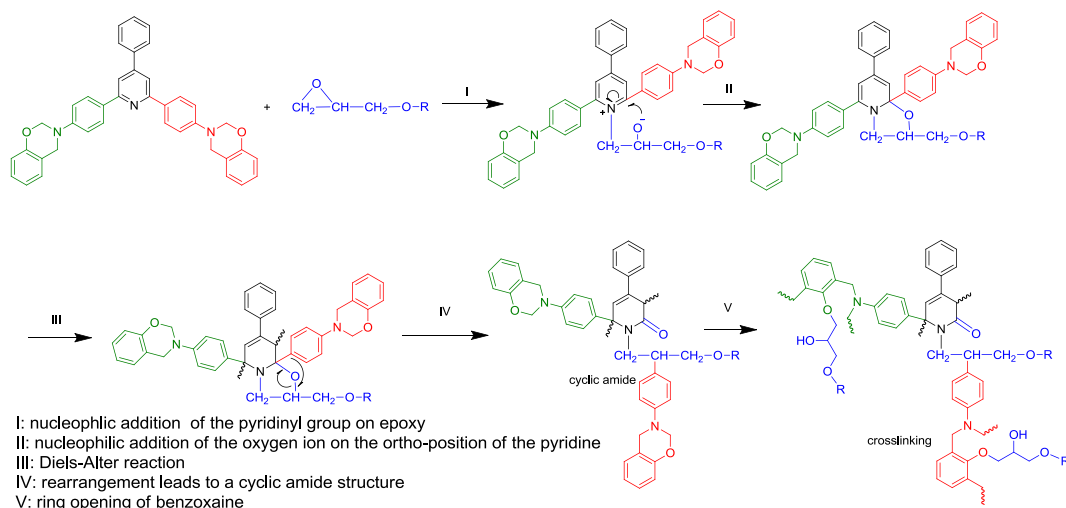
Benzaldehyde, and paraformaldehyde were purchased from TCI. Phenol, ammonium acetate, and hydrazine hydrate 80% were purchased from Showa. Palladium on carbon 10%, p-nitroacetophenone were purchased from Acros. Glacial acetic acid and acetic anhydride were purchased from Scharlau. Boron trifluoride diethyl etherate was purchased from ALFA. Diglycidyl ether of bisphenol A (DGEBA) with an epoxy equivalent weight (EEW) of 187 g/eq and dicyclopentadiene epoxy (DCPDE, commercial name HP-7200) with EEW 269 g/eq were kindly supplied by Chang Chun Plastics, and Dainippon Ink and Chemicals Corporation, respectively. All solvents were HPLC grade and were purchased from Tedia.

* Corresponding authors.

E-mail address: linch@nchu.edu.tw (C.H. Lin).



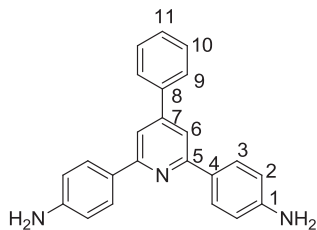
Scheme 1. Synthesis of benzoxazines (6–7).



Scheme 2. The proposed reaction mechanism between (6) and epoxy.

2.2. Preparation of diamine (2)

Diamine (2) was prepared by a modified Chichibabin reaction, followed by reduction (Scheme S1, Supporting Information) [8]. ^1H NMR (ppm, $\text{DMSO-}d_6$), $\delta = 5.42$ (4H, NH_2), 6.72 (4H, H^2), 7.48 (1H, H^{11}), 7.54 (2H, H^{10}), 7.81 (2H, H^6), 7.94 (2H, H^9), 8.04 (4H, H^3). ^{13}C NMR (ppm, $\text{DMSO-}d_6$), $\delta = 112.71$ (C^6), 113.66 (C^2), 126.57 (C^4), 127.04 (C^9), 127.75 (C^3), 128.82 (C^{11}), 128.97 (C^{10}), 138.56 (C^7), 148.62 (C^8), 149.85 (C^1), 156.60 (C^5). Melting point from DSC thermogram: 200.8 °C. Melting enthalpy 88.6 J/g.



2.3. Preparation of diamine (5)

Diamine (5) was prepared by a three-step procedure according to the literature (Scheme S2, Supporting Information) [19]. ^1H NMR (ppm, $\text{DMSO-}d_6$) $\delta = 5.2$ (4H, NH_2), 6.7 (4H, H^2), 7.4–7.5 (7H, $\text{H}^{3,10,11}$), 7.5–7.8 (5H, $\text{H}^6, 9, 12$). Melting point from DSC thermogram: 229.3 °C. Melting enthalpy 77.5 J/g.

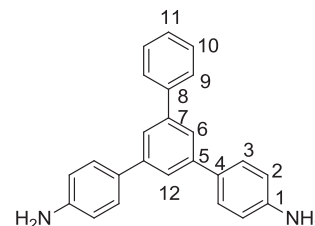


Table 1
Solvent effects on benzoxazine synthesis.

Run	Sample ID	Temp (°C)	Time (h)	Solvent	Reaction status
1	(6)	80	24	1,4-dioxane	A lot of gelation
2	(6)	80	24	xylene	A lot of gelation
3	(6)	80	24	toluene	A lot of gelation
4	(6)	60	24	chloroform	Homogeneous but low yield
5	(6)	80	24	1,4-dioxane/ ethanol (2:1)	Homogeneous but low yield
6	(6)	80	24	xylene/ ethanol (2:1)	Homogeneous but low yield
7	(6)	80	24	toluene/ ethanol (2:1)	Homogeneous with high yield
8	(7)	60	24	chloroform	Powder precipitation during polymerization
9	(7)	80	24	toluene/ ethanol (2:1)	Powder precipitation during polymerization
10	(7)	80	24	toluene/ ethanol (1:1)	Powder precipitation during polymerization

Download English Version:

<https://daneshyari.com/en/article/5181473>

Download Persian Version:

<https://daneshyari.com/article/5181473>

[Daneshyari.com](https://daneshyari.com)