Highly Processible Maleimide and Nitrile Functionalized Benzoxazines for Advanced Composites Applications

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Received 19 March 2009; accepted 29 June 2009
DOI 10.1002/app.31131
Published online 22 April 2010 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Maleimide and 2-aminobenzonitrile (MIan)-based benzoxazine has been synthesized and characterized. MIan contains imide, oxazine, and nitrile functional groups that can react almost simultaneously, leading to complicated reaction mechanisms. For understanding the fundamental polymerization mechanism, the model benzoxazine compound is synthesized. The ortho-nitrile group in the model compound undergoes cyclization reaction, producing the thermally stable six-membered ring species resulting in the excellent thermal properties of the material. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 117: 2559–2565, 2010

Key words: polybenzoxazine; polymerization mechanism; maleimide; nitrile; high performance; high char yield

INTRODUCTION

Recently, the development of the benzoxazine-based family of phenolic resins has received significant attention. Various phenols and primary amines have been used to synthesize benzoxazine resins. For example, polybenzoxazines with mechanical properties comparable to epoxy[1] and polyimide[2] were obtained with the combination of certain phenols and amines. Polybenzoxazines are derived via a thermally activated ring-opening reaction to form a phenolic structure characterized by a Mannich base bridge as shown in Scheme 1, instead of the methylene bridge structure associated with traditional phenolic resins.[3] The attractive characteristics of benzoxazine polymers include low-melt viscosity, no release of volatiles during polymeriztion or need of harsh catalysts, high thermal stability, good mechanical properties, excellent electrical properties, and rich molecular design flexibility.[3–7] These characteristics enable benzoxazine polymers to be excellent candidates for high-performance composites.

By taking advantage of the rich molecular design flexibility of the benzoxazine chemistry, thermal and thermo-oxidative stabilities of polybenzoxazine have been improved by altering the functional group on the amine and/or phenol. Low and Ishida studied the thermal and thermo-oxidative degradation of polybenzoxazines and concluded that there are three stages in the thermal degradation of bisphenol-based polybenzoxazines. Evaporation of amine moiety first occurs below 300°C followed by degradation of the Schiff base between 300°C and 400°C. Finally, above 400°C, the evaporation of phenolic moiety occurs. This observation gives rise to the postulation that if amine evaporation is reduced, the char yield can be greatly increased.[8]

Kim et al. synthesized acetylene-functional benzoxazines, in which acetylene-functionalized side chain could further crosslink upon thermal activation.[9] In a separate study, phthalonitrile-functional polybenzoxazines, which had low flammability due to their high-char yield, were synthesized.[10,11]

Maleimide-based polymers generally have high T_gs and are thermally stable. Recently, Ishida and Ohba synthesized monofunctional benzoxazine with maleimide and aniline to develop low-viscosity benzoxazine monomers with a glass transition temperature above 200°C. Incorporation of the maleimide functionality into the monofunctional benzoxazine resulted in an increased char yield and glass transition temperature.[12]

In our previous work, a monofunctional benzoxazine with maleimide and 2-aminobenzonitrile (MIan) has been developed. This newly synthesized polybenzoxazine exhibits the improvement in thermal and mechanical properties without significantly increasing the viscosity of the monomer. Furthermore, by using Lewis acid catalysts, thermal properties have been improved.[13] However, there has been no report related to the polymerization mechanism

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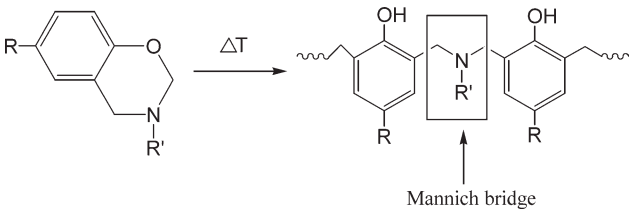
Contract grant sponsors: Air Force Office of Scientific Research, Royal Thai Government.



Scheme 1 Mannich bridge structure formed through benzoxazine ring-opening polymerization.

of this benzoxazine. MIan contains imide, oxazine, and nitrile functional groups that can react almost simultaneously, leading to complicated reaction mechanisms. The goal of this work is to seek further fundamental insight into the subject by using the model benzoxazine compound.

EXPERIMENTAL

Materials

All chemicals were certified A.C.S. grade and used as received. Phenol (99+%), 2,4-dimethylphenol (99.9%), paraformaldehyde (95%), and 2-aminobenzonitrile (98%) were purchased from Aldrich Chemical Company (Milwaukee, WI). Chloroform, diethylether, and methanol were obtained from Fisher Scientific Company (Pittsburgh, PA).

Synthesis

Synthesis of 1-(4-hydroxy-phenyl)-pyrrole-2,5-dione (HPMI)

HPMI (compound **1** in Scheme 2) was synthesized according to Choi et al.[14] Added in a 100-mL round bottom flask were 30 g (360 mmol) maleic anhydride and 30.6 g (280 mmol) *p*-aminophenol in 80 mL dimethylformamide (DMF) at 0°C. A mixture of 15 g (106 mmol) P_2O_5 in 50 mL DMF and 8 g of concentrated H_2SO_4 was added to the flask over 30 min with stirring. The reaction mixture was stirred at 70°C for 3 h in an oil bath. The mixture was then poured into 500 mL of deionized ice water and yellow precipitation was observed. The precipitate was dried under vacuum for $\sim$ 12 h and then purified by recrystalization in isopropanol. The product was in the form of yellow "needle-like" crystals (30.1 g, yields 57%) with a melting point of 176°C. ^{1}H-NMR (200 MHz, DMSO-d_6, 298K) δ: 6.80 (d, 2H), 7.06 (d,2H), 7.13 (d, 2H), and 9.70 (s, 1H).[12]

Synthesis of 2,4-dimethylphenol and 2-aminobenzonitrile-based benzoxazine monomer (24DMPan)

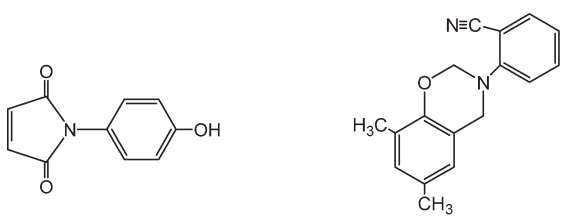
The monomer synthesis was performed by the solventless reaction,[15] where stoichiometric amounts of 2,4-dimethylphenol (0.01 mole), 2-aminobenzonitrile (0.01 mole), and paraformaldehyde (0.02 mole) were continuously stirred at 105°C for 30 min (Compound **2** in Scheme 2). The product was further purified with 0.5*N* solution of sodium hydroxide and recrystalized from methanol. White crystal: mp 126°C (yield: 82%).

Synthesis of 2-(1-(4-hydroxy-11-(2-hydroxy-3,5-dimethylbenzyl)-8-(2-hydroxy-3,5-dimethylphenyl)-3H-pyrazino[1,2-a]quinazolin-3-yl)benzonitrile: model compound

The model compound was prepared by following the benzoxazine dimer synthesis.[16] 24DMPan benzoxazine monomer was mixed with equimolar amount of 2,4-dimethylphenol at 200°C for 60 min. The product was recrystalized from methanol and subsequently purified by column chromatography with silica gel which is treated with *n*-dodecylsilane. The mixture of hexane/ethyl acetate (10 : 1) was used as the eluent. Yellow fine crystal: mp 167°C. ^{1}H-NMR (600 MHz, $CDCl_3$, 298K) (δ: 2.35 (s, 6H), 7.04 (s, 1H), 7.12–7.71 (Ar, 9H), and 8.62 (s, 1H). Anal. Found: C, 77.31; H, 6.56; N, 10.08. Calcd. For $C_{43}H_{35}N_5O_3$: C, 77.13; H, 5.23; N, 10.46.

Measurements

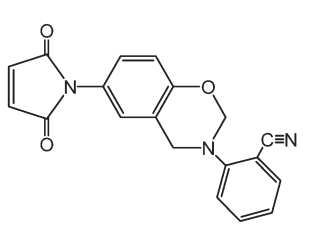
Fourier transform infrared (FTIR) spectra were obtained using a Bomem Michelson MB100 FTIR



HPMI

2,4-Dimethyl Phenol and 2-aminobenzonitrile functionalized benzoxazine (24DMPan)

1 **2**



Maleimide and 2-aminobenzonitrile functionalized benzoxazine (MIan)

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Scheme 2 The name and abbreviation of the compounds used.

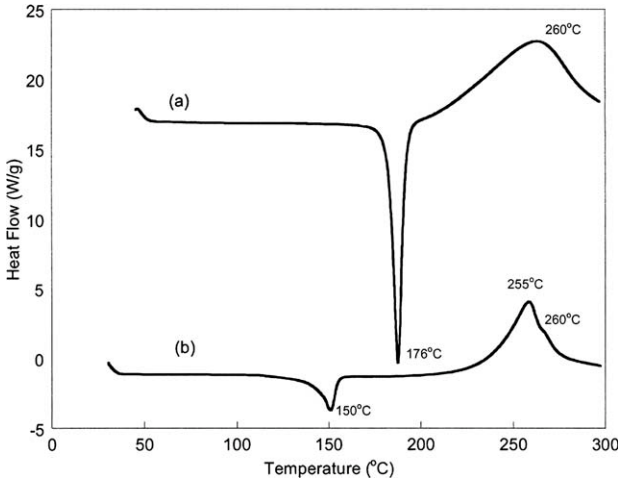


Figure 1 DSC thermograms of HPMI (a) and MIan monomer (b).

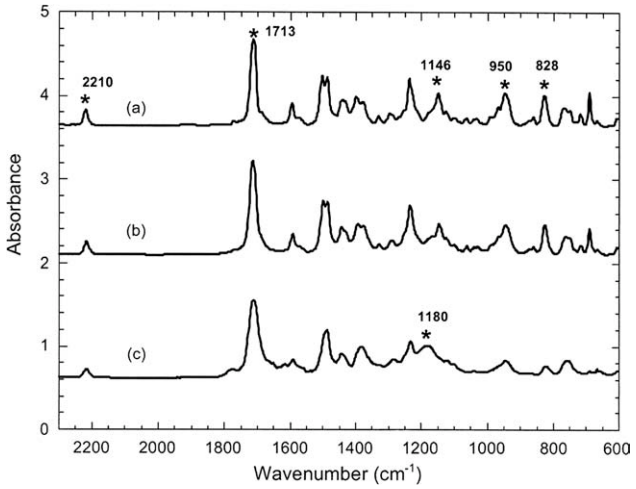


Figure 3 FTIR spectra of MIan monomer (a), after heated isothermally at 150°C for 10 min (b), and 90 min (c).[13]

spectrometer which was equipped with a deuterated triglycine sulfate (DTGS) detector. Coaddition of 16 scans was recorded at a resolution of 4 cm^{-1} after a 20 min purge with dry air. FTIR spectra of the monomers were taken using the KBr powder technique while thin films were cast on a KBr plate for partially cured samples.

Thermal stability and curing behavior were studied by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), respectively. TA Instruments High Resolution 2950 thermogravimetric analyzer was used with nitrogen as a purge gas for all testing. A heating rate of 20°C/min with a nitrogen flow rate of 90 mL/min was used for all tests. TA Instruments DSC model 2910 (equipped with pressure DSC cell) and model 2920 were used with heating rate of 10°C/min and a nitrogen flow rate of 65 mL/min for all tests. Samples were crimped in hermetic aluminum pans with lids.

Mass identification was carried out on a matrix assisted laser desorption ionization time-of-flight mass spectroscopy (MALDI-TOF) (Bruker, Model BIFLEX III). α-Cyano-4-hydroxycinnamic acid was used as the matrix substance. The ratio of the matrix to benzoxazine model compound is ~ 10 : 1. Both matrix and the model compound were dissolved in THF. Sodium iodide (4.3 mg) in 1-mL methanol was added into the sample mixture as an ion source.

Both ^{1}H-NMR and ^{13}C-NMR spectra were recorded using a Varian 600-MHz NMR spectrometer at a proton frequency of 600 MHz and its corresponding carbon frequency. Deuterated chloroform was used as an NMR solvent with 0.05% tetramethylsilane as the internal standard. Relaxation time (D1) of 10 s was used to obtain integration results for the proton spectrum.

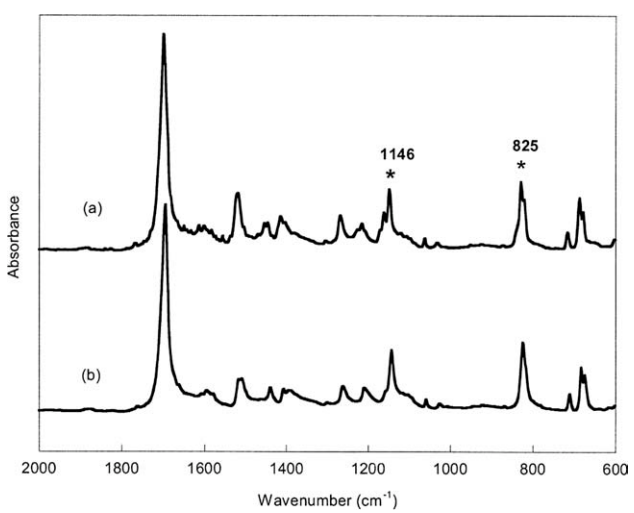


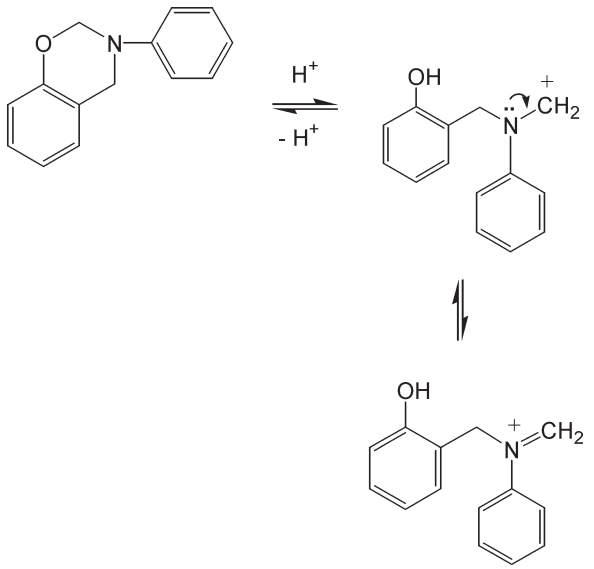
Figure 2 FTIR spectra of HPMI (a) and after heated isothermally at 150°C for 90 min (b).

RESULTS AND DISCUSSION

Model compound study

Maleimide and 2-aminobenzonitrile-based benzoxazine monomer (MIan, compound **3** in Scheme 2) has been synthesized and characterized. This monomer shows good processibility while the polymer derived from this monomer maintains excellent thermal and mechanical properties.[13] However, MIan contains imide, oxazine, and nitrile functional groups that can react almost simultaneously, resulting into the complicated polymerization mechanisms. To better understand the possible reactions between each functional group, several model compounds were synthesized.

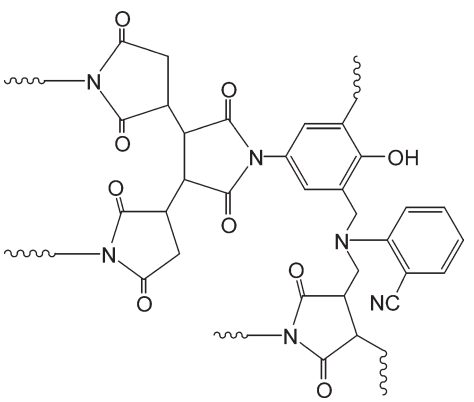
HPMI[1] is used to study the homopolymerization and the reaction of the maleimide functionality.



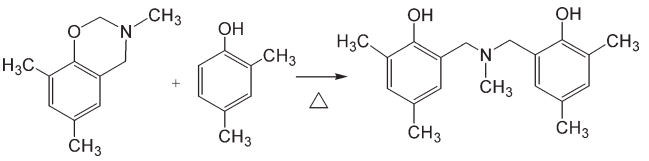
Scheme 3 Formation of Schiff base through benzoxazine ring-opening polymerization

Nonisothermal DSC thermograms of HPMI[1] and MIan benzoxazine monomer[3] (Scheme 2) are shown in Figure 1(a,b), respectively. The melting point of HPMI, which has only the maleimide functional group, is at 176°C. The onset exotherm is around 205°C, and the main exotherm peak is centered at 260°C. By incorporating the benzoxazine functionality, the melting point is reduced to ~ 150°C and the onset of polymerization is observed around 170°C which is attractive from the processibility point of view. Unlike HPMI, MIan shows two exotherm peaks: the first main exotherm peak is centered at 255°C and the second exotherm appears as a shoulder around 260°C.

FTIR spectrum of HPMI and the heated film are shown in Figure 2. The prominent band at 1713 cm^{-1} is attributed to the C=O stretching mode of the maleimide group. The band at 825 cm^{-1} is assigned to the imide CH wagging of the vinylene group. The band at 1146 cm^{-1} corresponds to the



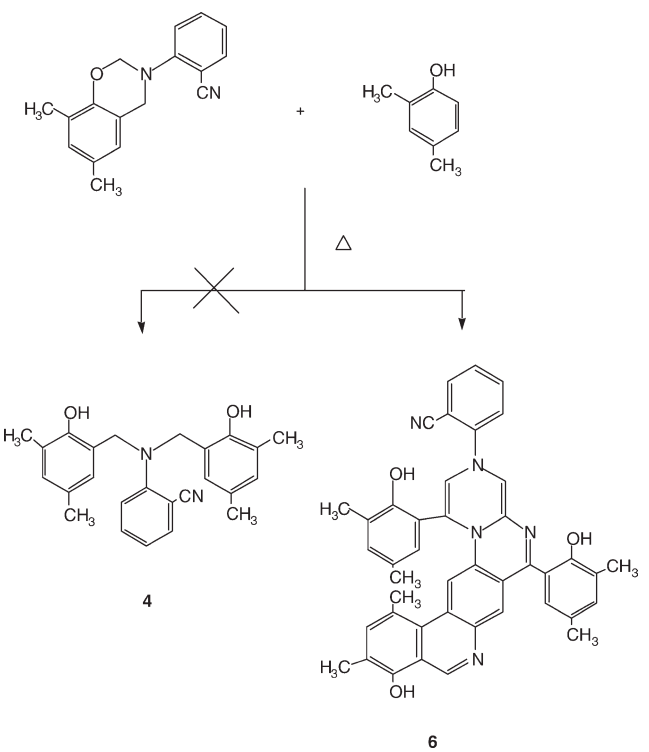
Scheme 4 Possible reactions on maleimide sites.



Scheme 5 General approach for benzoxazine dimer synthesis.

C—N—C bending mode of the imide ring.[17] The band at 825 cm^{-1} is used to follow the homopolymerization of the maleimide functionality.

The FTIR spectra of heated HPMI film at 150°C shows no significant change even after 90 min [Fig. 2(b)]. It suggests that the homopolymerization of maleimide does not take place at this temperature, which supports the DSC result. However, the FTIR study of MIan shows different result. It is interesting to find that, when the oxazine functionality is incorporated, both oxazine ring opening and maleimide polymerization occurred at 150°C as shown in Figure 3. Oxazine ring-opening polymerization can be followed by the band at 950 cm^{-1} which is the vibration of benzene ring to which oxazine ring is attached.[18] The maleimide polymerization is confirmed by the shifting of the band at 1146 cm^{-1}, which is assigned to the C—N—C bending mode of the maleimide ring to 1180 cm^{-1}, which corresponds to the C—N—C bending mode of the succinimide ring. In addition, the intensity of the band at 825 cm^{-1} which is used to follow the



Scheme 6 Synthesis of model compound 6.

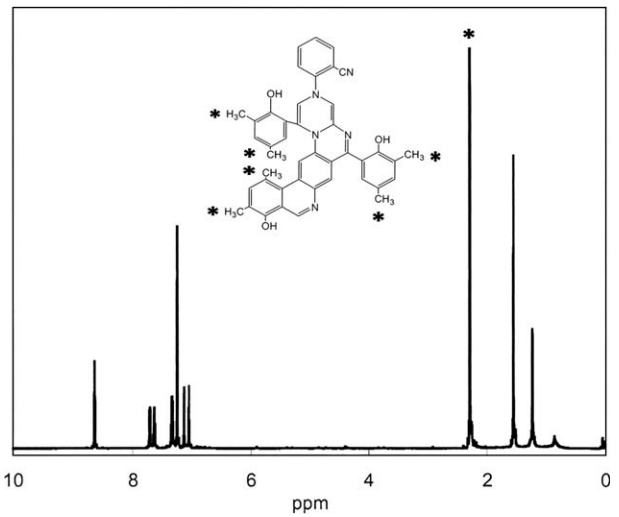


Figure 4 ^{1}H-NMR of model compound **6** in $CDCl_3$.

TABLE I
^{13}C-NMR Assignments for Model Compound 6

	Model compound (ppm)
C1	20.38
C2	29.83
C3	130.59
C4	133.52
C5	126.65
C6	158.02
C7	108.63
C8	126.84
C9	119.09
C10	151.89
C11	126.86
C12	128.05
C13	117.02
C14	133.86
C15	165.67
C16	117.81

homopolymerization of the maleimide functionality as mentioned earlier decreased considerably.

On the basis of the DSC and FTIR studies, it is postulated that the oxazine ring-opening polymerization catalyzes the maleimide polymerization. It has been reported that the ring-opening polymerization of the oxazine ring creates the Schiff base as shown in Scheme 3.[3,19] The Schiff base is a highly reactive specie and very likely to react with the unsaturated groups such as maleimide. A possible reaction of MIan at the maleimide site is shown in Scheme 4. Recently, Liu and Yu studied the cocuring behaviors of benzoxazine and maleimide derivatives and found similar results indicating that the ring-opening polymerization of benzoxazine showed the catalytic effect on the polymerization of maleimide.[20]

To investigate the reactivity of nitrile groups with respect to oxazine ring during the thermally activated polymerization of MIan, 24DMPan benzoxazine monomer and 2,4-dimethyl phenol (1 : 1 mole ratio) were used to synthesize a model compound. The reaction was carried out at 200°C to simulate the thermal polymerization. It has been demonstrated that the preferred reaction site of the benzoxazine polymerization is mainly at the ortho and, to some extent, para positions to the hydroxyl functionality on the aromatic ring (Scheme 1).[21–27] Therefore, 24DMPan benzoxazine monomer was selected since methyl blocking at the ortho and para positions of the reactants should greatly reduce the possibility of side reactions. Our research group has synthesized and studied the model dimers of benzoxazines based on 2,4-dimethyl phenol and aliphatic amines as shown in Scheme 5.[28,29] Hence, the dimer compound **4** was expected to be the main product

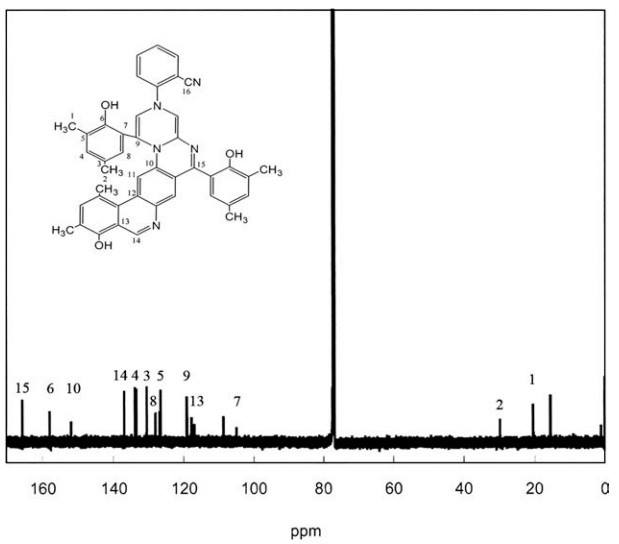


Figure 5 ^{13}C-NMR of model compound **6** in $CDCl_3$.

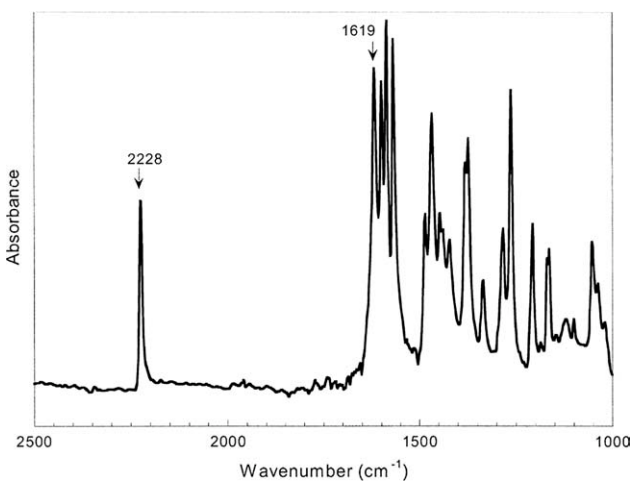


Figure 6 FTIR spectrum of model compound **6**.

(Scheme 6). Surprisingly, the as-synthesized product was found to be mainly the model compound **6**. It is suggesting that by using nitrile-substituted aromatic amine, the mechanism of dimer formation is more complex. The impurities which are the 24DMPan monomer and other small molecules were separated from the model compound **6** by washing with cold methanol. Then the model compound **6** was recrystalized several times in methanol and subsequently purified by column chromatography with silica gel using hexane/ethyl acetate (10 : 1) as the eluent. It is worth mentioning that the model compound **6** is highly hydrophilic in nature, therefore silica gel treated with *n*-dodecylsilane had to be used as the column packing agent.

The ^{1}H- and ^{13}C-NMR spectra of the model compound **6** are shown in Figures 4 and 5, respectively, along with the assignments. Using assignment of the ^{1}H- and ^{13}C-NMR resonances in deuterated chloroform reported by Dunkers and Ishida,[18] the spectra of the model compound are assigned. In ^{1}H-NMR, the prominent resonance at 2.3 ppm corresponds to the protons from the methyl groups attached to the aromatic ring. The resonances appearing at 7.2–7.7 ppm are assigned to the protons on the aromatic rings. It is interesting to see that no resonance was recorded either at 3.6 ppm which contributes to the methylene protons in the dimer[29,30] or at 4.5 and 5.5 ppm, which correspond to the methylene protons in the oxazine ring.[18] The chemical shifts from ^{13}C-NMR spectra are summarized in Table I.

FTIR spectrum of the model compound **6** shows two characteristic bands as seen in Figure 6. The band at 2228 cm^{-1} represents the stretching of —C≡N and the band at 1619 cm^{-1} is associated with the —C=N— species. The FTIR result is in agreement with the assignments of the ^{1}H- and ^{13}C-NMR spectra of the model compound discussed earlier. While not shown, the OH band of the phenols was also observed in the range between 3400 cm^{-1} and 3300 cm^{-1}.

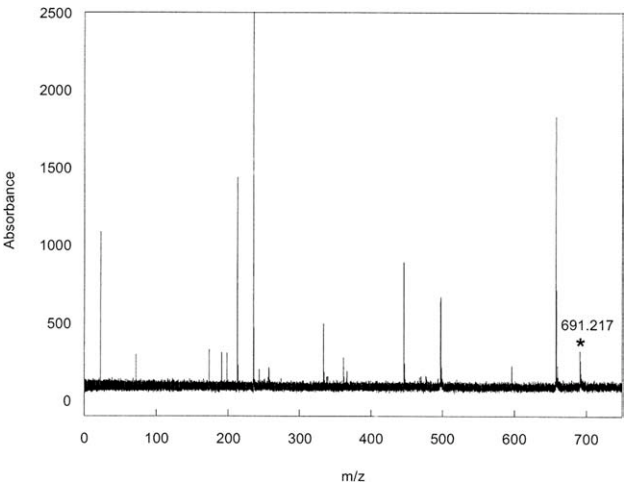
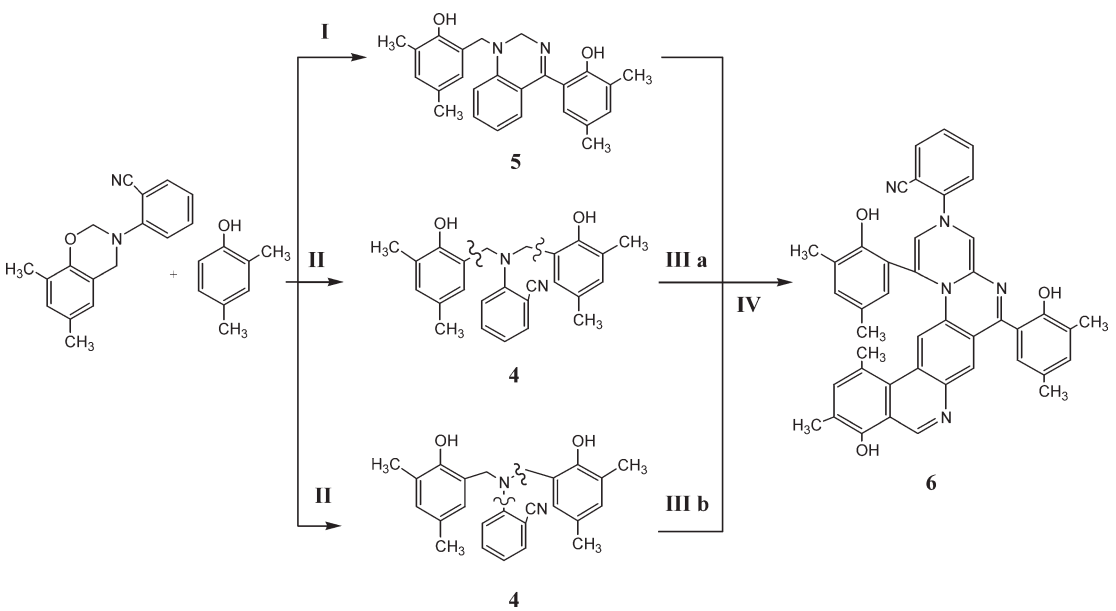


Figure 7 The molecular weight of model compound **6** from MALDI-TOF mass spectroscopy.

From MALDI-TOF mass spectrum shown in Figure 7, the molecular weight of 669 corresponds to the calculated molecular weight of this model substance (this molecular weight was derived from the molecular weight of 691 shown in the spectrum after



Scheme 7 Proposed mechanisms of reactions between nitrile and oxazine functionalities I. Reaction via intramolecular cyclization II. Conventional dimer formation III a. Thermal decomposition—cleavage of C—C bond b. Thermal decomposition—cleavage of C—N bond IV Recombination.

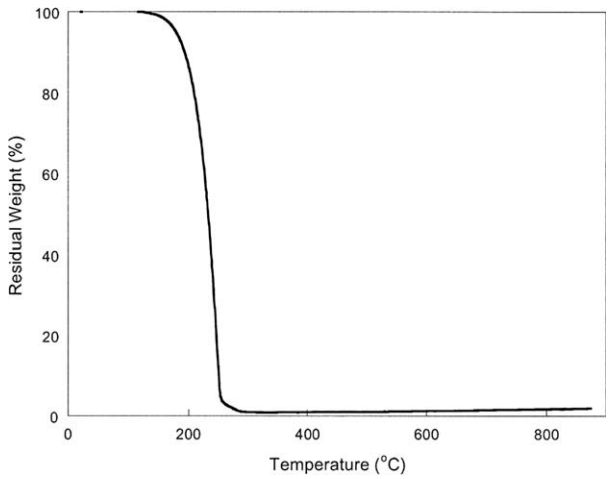


Figure 8 TGA thermogram of 24DMPan monomer.

subtracting the atomic mass of the sodium ion which was used as an ion source).

As a result of the model compound study, the mechanism of nitrile reaction with respect to oxazine functionality is proposed as shown in Scheme 7. During the model compound synthesis, two reaction processes can take place simultaneously. One is the conventional dimer formation. Another possibility is that during the ring-opening polymerization, the nitrile group reacts preferably via intramolecular cyclization with the open Mannich bridge to afford formation of a six-membered ring (compound **5**); resulting in an energetically stable conformation.

Low and Ishida studied the thermal and thermooxidative degradation of polybenzoxazines and concluded that evaporation of amine moiety usually occurs first below 300°C.[27] Helvetian et al. reported the onset of degradation of the 2,4-dimethylphenol-based dimers at about 160°C.[31] They have also proposed the mechanism for thermal decomposition of 2,4-dimethylphenol-based dimers which can be applied to our system.

The TGA thermogram of 24DMPan shows the onset of thermal degradation below 200°C (Fig. 8). We believe that there are two different fragmentation processes which take place simultaneously. One is the cleavage of the C—N bond of the Mannich bridge (III b in Scheme 7), which results in the formation of a Schiff base. The second fragmentation process is the cleavage of the C—C bond (III a in Scheme 7), resulting in the formation of the tertiary amine and 2,4-dimethylphenol. The driving force for the cleavage of C—N and C—C bonds is the product stability caused by resonance delocalization. The Schiff base and tertiary amine stabilized free radicals are then reacted with compound **5**, yielding the model compound **6** (Scheme 7).

CONCLUSIONS

HPMI and model compound has been synthesized to investigate the thermal polymerization of Maleimide and 2-aminobenzonitrile-based (MIan) polybenzoxazine. The stable cyclic compound containing imine functionality is proposed to form during thermal polymerization, yielding polybenzoxazine with excellent thermal properties as reported in our previous study.

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