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Synthesis and characterization of maleimide and norbornene functionalized benzoxazines

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Abstract

Two types of monofunctional benzoxazines with imide functionalities have been synthesized for improved thermal properties. These materials achieve char yields above 55% and exhibit glass transition temperatures above 250 °C. The new benzoxazines have maleimide and norbornene functionalities that can further polymerize with mechanisms different from benzoxazine. The multiple polymerization mechanisms of the maleimide based benzoxazine monomer with different free radical initiators are monitored by Fourier transform infrared spectroscopy (FTIR) and differential scanning calorimetry (DSC). The extent and type of polymerization, which affect the final network structure of the benzoxazine polymer, are characterized.

Keywords: Polybenzoxazine; Maleimide; Norbornene

1. Introduction

In recent years, the performance requirements have risen for polymeric materials as their electronic and structural applications have gone through technological advances. Consequently, high performance thermosets such as bismaleimides, bisnadimides, advanced epoxy resins, and others have been engineered to meet the demands of the industry. Although these resins have improved thermal and thermo-oxidative resistance, chemical resistance, and high mechanical strength, they face numerous processibility issues due to their high viscosity and low solubility in organic solvents.

Holly and Cope discovered the chemistry for the aromatic oxazines in 1944 using phenols, formaldehyde, and amines via Mannich reaction [1]. The chemistry of benzoxazines and their oligomers were further studied by Burke and other groups [2–8] through the 1950 to 1960s; however, only recently has there been a thorough investigation into the polymerization of benzoxazine monomers. During polymerization, benzoxazines undergo thermally activated ring-opening reaction to form a Mannich base bridge [9–11]. A number of benzoxazine polymers have been developed to have excellent mechanical and thermal properties [12–15]. The attractive characteristics of benzoxazine polymers include low melt viscosity, no release of volatiles during cure and no need for harsh catalysts, high thermal stability, good mechanical properties, excellent electrical properties and, molecular design flexibility [16–18]. These characteristics make this class of polymers a promising candidate for high performance composites.

By taking advantage of the molecular design flexibility of benzoxazine chemistry, thermal and thermo-oxidative stability of polybenzoxazines has been improved by adding functional groups on the amine and/or phenol. Shen and Ishida [14,19] developed polyfunctional naphthoxazines and benzophenone-based benzoxazines to improve thermal stability by increasing the number of aromatic groups per repeat unit. This resulted in glass transition temperatures above 300 °C and char yield of 67% for some of the compounds.

Low and Ishida [20] studied the thermal and thermo-oxidative degradation of polybenxozazines, using thermogravimeteric analysis–Fourier transform infrared spectroscopy (TGA–FTIR), and gas chromatography–mass spectrometry (GC–MS), and concluded that there are three stages in the thermal degradation of bisphenol-based polybenzoxazines. Evaporation of amine moiety first occurs

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below 300 °C and between 300 and 400 °C, the degradation of the Schiff base occurs. Finally above 400 °C, the evaporation of phenolic moiety was observed. This observation gave rise to the postulation that if amine evaporation was reduced, the char yield can be greatly increased. Thus, Kim et al. [21] synthesized acetylene-functional benzoxazines, in which acetylene-functionalized amine side chain could further crosslink upon thermal activation. In a separate study, phthalonitrile functional polybenzoxazines, which show low flammability due to its high char yield, was synthesized [22,23]. Recently, Choi et al. [24] included phenyl phosphine oxide in the main chain of benzoxazines and that resulted in high char yields of 50–60%.

In other groups, Caulifield [25] synthesized a series of *N*-hydroxyphenyl succimides to be reacted with an imide and hexamethylenetetramine (HMTA) system in which both benzoxazines and benzylamine type intermediates were identified. Although polymerization was successful, no thermal or mechanical properties were reported. Recently, Ishida and Twite [26] and Agag and Takeichi [27] incorporated imides into benzoxazine to improve heat resistance. In the studies by Agag and Takeichi, they synthesized hydroxyphenylmaleimide (HPMI) and/or amine terminated butadiene acrylonitrile modified polybenzoxazine by mixing bisphenol A and aniline-based benzoxazine monomer (BA-a) with HPMI.

Our current research includes synthesis and characterization of monofunctional benzoxazines with maleimide and norbornene functionality. The curing effects using different free radical initiators for the vinylene group and thermally activated polymerization of benzoxazine ring were studied. It is also the purpose of this research to develop low viscosity benxozazine monomers that lead to high performance polymers with glass transition temperatures above 200 °C.

2. Experimental

2.1. Materials

All chemicals were used as received. 4-Aminophenol (98%), maleic anhydride (96%), phosphorous pentoxide (98%), paraformaldehyde (95%), and aniline (99%) were obtained from Aldrich chemical company. Sulfuric acid, *N*,*N*-dimethylformamide (DMF), chloroform, isopropanol, and dichloromethane were obtained from Fisher scientific company. All solvents used were certified A.C.S. grade and used as received.

2.2. Synthesis

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

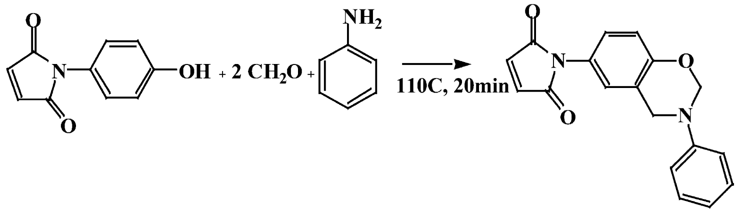
The HPMI was synthesized according to Choi et al. [28]. In a 100 ml round bottom flask were added 30 g (360 mmol) maleic anhydride and 30.6 g (280 mmol) *p*-aminophenol and 80 ml DMF at 0 °C. A mixture of 15 g (106 mmol) P_2O_5 in 50 ml DMF and 8 g of concentrated H_2SO_4 was added over 30 min to a round bottom flask while the flask was being stirred by a magnetic stirrer. The reaction mixture was then stirred at 70 °C for 3 h in an oil bath. The mixture was then poured into 500 ml of de-ionized ice water and yellow precipitation was observed. The precipitate was dried under a vacuum chamber for approximately 12 h and was purified by recrystalization in isopropanol. The product was in the form of yellow 'needle like' crystals (30.1 g, yield: 57%). The melting point was 176 °C. ^1H NMR (200 MHz, DMSO-d_6, 298 K) δ: 6.80 (d, 2H), 7.06 (d,2H) 7.13 (d, 2H), and 9.70 (s, 1H).

2.2.2. Synthesis of *p*-hydroxyphenylnadimide (HPNI)

The HPNI was synthesized according to Lyle et al. [29]. In a 50 ml round bottom flask, 1.0 g (6.09 mmol) norbornene and 0.7 g (6.09 mmol) *p*-aminophenol were dissolved in 20 ml of glacial acetic acid and stirred with a magnetic stirrer for 12 h. The mixture was then poured into 500 ml of deionized ice water and was allowed to precipitate and left to dry in a vacuum oven for about 10–12 h. The final product was white crystals and the yield was 85%. The melting point was 242 °C. ^1H NMR (200 MHz, $(CD_3)_2CO$, 298 K) (δ: 1.66 (s, 2H), 3.35 (s, 2H), 3.46(s, 2H), 6.21 (s, 2H), 6.82–6.96 (Ar, 4H), and 8.56 (s, OH).

2.3. Synthesis of 1-(3-phenyl-2H, 4H, benzo[3,4-e] 1, 3-oxazaperhydroin-6-yl)azoline-2,3-dione (MIB) (Scheme 1)

A mixture of HPMI, *p*-formaldehyde, and aniline with a mole ratio of 1:2:1 was added to a flask and stirred at 110 °C for 20 min [30]. The product was then dissolved in dichloromethane, filtered, and washed with de-ionized



Scheme 1. Maleimide-functionalized benxozazine (MIB) monomer synthesis.

water. The solvent was evaporated using a rotary evaporator and product was vacuum dried. The product was a yellow powder (yield 80%), and the melting point was 147 °C. ^{1}H NMR (200 MHz, $(CD_3)_2CO$, 298 K) (δ: 4.73 (s, 2H), 5.49 (s, 2H), and 6.80– 7.28 (Ar, 8H).

Anal. Calcd. for $C_{18}H_{14}N_2O_3$: C, 70.58%; H, 4.61%; N, 9.15. Found: C, 70.60%; H, 4.81%; N, 9.00.

2.4. Synthesis of 4-aza-4-(3-phenyl(2H, 4H-benzo[2,4-3] 1,3 - oxazaperhydroin-6yl))tricycle[5.2.1.0〈2,6〉]dec-8-ene-3,5 dione (NOB) (Scheme 2)

A mixture of HPNI, *p*-formaldehyde, and aniline with a mole ratio of 1:2:1 and DMF were added to a flask and stirred at 90 °C for 36 h. The product was then precipitated into water and collected. The precipitate was dried, dissolved in chloroform, and washed with 1 N NaOH solution and de-ionized water. The solvent was evaporated using a rotary evaporator and the product was vacuum dried. The product was a white powder (yield 82%) with a melting point of 200 °C. ^{1}H NMR (200 MHz, $(CD_3)_2CO$, 298 K) (δ: 1.66 (s, 2H), 3.35 (s, 2H) 3.45 (s, 2H), 4.69 (s, 2H), 5.47 (s, 2H), 6.21 (s, 2H) and 6.74–7.26 (Ar, 8H).

Anal. Calcd. for $C_{23}H_{20}N_2O_3$: C, 74.18%; H, 5.41%; N, 7.52. Found: C, 74.04%; H, 5.46%; N, 7.47.

2.5. Measurements

Fourier transform infrared (FTIR) spectra were obtained using a Bomem Michelson MB100 FTIR spectrometer which was equipped with a liquid nitrogen cooled, mercury cadmium-telluride (MCT) detector with a specific detectivity, D^*, of 1×10^{10} cm/Hz$^{0.5}$/W^1. Co-addition of 128 scans was recorded at a resolution of 4 cm^{-1} after a 20 min purge with dry nitrogen. FTIR spectra of the monomers were taken using the KBr powder technique while the thin film was cast on a KBr plate for partially cured samples.

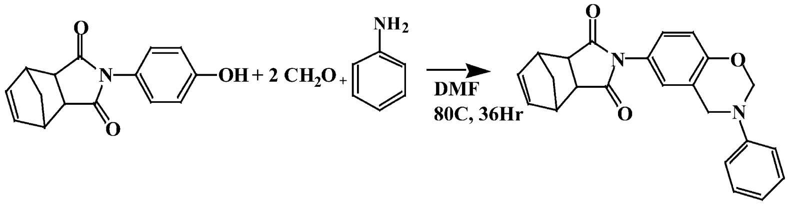
Both ^{1}H NMR and ^{13}C NMR spectra were recorded using a Varian XL 200 nuclear magnetic resonance (NMR) spectrometer at a proton frequency of 200 MHz and the corresponding carbon frequency. Deuterated chloroform, acetone, and dimethyl sulfoxide were used as NMR solvents with 0.05% tetramethylsilane as the internal standard. Co-addition of 128 transients yielded a good signal-to-noise ratio spectrum for ^{1}H NMR spectrum while 2000 transients were used for ^{13}C NMR spectrum. Relaxation time ($D1$) of 10 s was used to obtain integration results for the proton spectrum.

The thermal stability and curing behavior were investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), respectively. TA Instruments High Resolution 2950 thermogravimetric analyzer was used with nitrogen as a purging 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 2920 was used with heating rate of 10 °C/min and a nitrogen flow rate of 65 ml/min for all tests. All samples were crimped in hermetic aluminum pans with lids.

Viscosity of the as-synthesized material was determined using a Rheometrics dynamic mechanical spectrometer (RMS-800) equipped with a 200 g cm force rebalance transducer. A steady share was applied using a parallel plate configuration at a shear rate of 1 s^{-1}. The sample was transferred onto a 50 mm parallel plate fixture and set to a gap of approximately 0.5 mm. The temperature for the viscosity measurement was varied and waited for at least 5 min to stabilize the sample temperature after the instrument indicated the desired temperature.

3. Results and discussion

The structure of MIB and NOB as shown in Fig. 1 were verified by ^{1}H NMR and ^{13}C NMR spectroscopy and the corresponding spectra are shown in Figs. 2 and 3. In ^{1}H NMR, resonances appearing at 4.73 and 5.49 ppm are assigned to the methylene protons in the oxazine ring of MIB. Column chromatography was used to separate the impurities, which were identified as unreacted phenols, amines, and benzoxazine oligomers, eluting with ethyl acetate–hexane (3:1) gradually increasing the ethyl acetate ratio. No resonance was recorded at 5.0–5.3 ppm, which corresponds to the methylene protons in the triazine intermediate [23]. The prominent resonance at 6.98 ppm in the aromatic frequency corresponds to the protons attached to the vinylene group. NOB has proton resonances at 4.69 and 5.47 ppm which correspond to the methylene protons in the oxazine ring. The protons attached to the vinylene group of NOB appear at 6.21 ppm. Furthermore, the structures of both MIB and NOB monomers are confirmed by using ^{13}C NMR and the corresponding chemical shifts are shown in Table 1. Along with the excellent agreement between the calculated and observed



Scheme 2. Norbonene-functionalized benzoxazine (NOB) monomer synthesis.

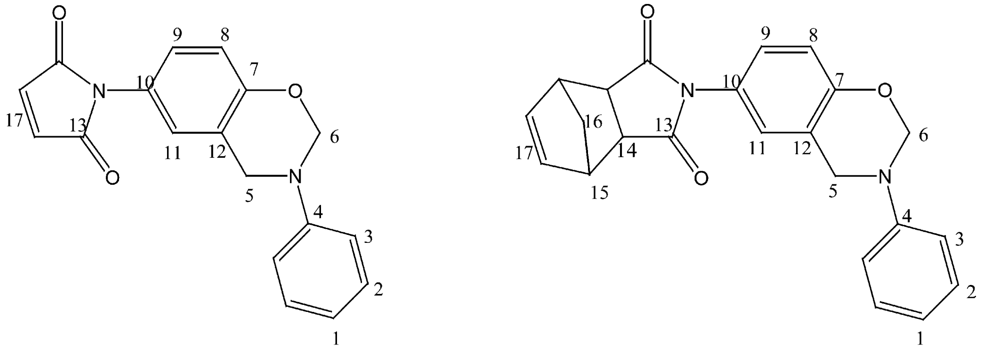


Fig. 1. Structure of MIB and NOB monomers and designation of carbon number for the ^{13}C NMR assignments.

Table 1
^{13}C NMR assgiments for MIB and NOB monomers

	MAM (ppm)	NOB (ppm)
C1	125.47	122.76
C2	130.33	130.32
C3	122.22	119.43
C4	154.05	149.13
C5	49.19	53.18
C6	80.50	80.48
C7	160.42	155.41
C8	121.29	118.66
C9	127.85	127.28
C10	133.86	132.36
C11	125.76	125.36
C12	128.92	125.96
C13	177.23	176.90
C14	–	46.63
C15	–	46.41
C16	–	51.42
C17	138.99	122.76

data of the elemental analysis for the purified sample, it shows that the targeted compounds were obtained in high purity.

Thermal properties of both MIB and NOB which were polymerized according to the cure schedule described in the previous section were examined by TGA (Figs. 4 and 5). The polymers from MIB and NOB exhibit thermal stability up to 375 and 365 °C, respectively. The char yields at 800 °C for MIB and NOB under nitrogen were 56 and 58%, respectively, when heated at 20 °C/min. In Table 2, the thermal properties of MIB and NOB are summarized and compared to other benzoxazines. It is observed that there is a significant improvement of 20% higher char yield than regular monofunctional benzoxazines. Previous studies have shown that degradation occurs in the sequence of evaporation of the amine, and then breakage of phenolic linkage which occurs simultaneously with degradation of the Mannich base [31]. In case of MIB, due to the incorporation of the imide group, which has partial conjugation with the benzene ring, the rotation of the imide residues is hindered. This phenomenon resulted in the increased stiffness and thermal stability of the material. It is also important to note that the incorporation of the imide group increased the viscosity compared to monofunctional benzoxazines but did not increase above typical difunctional benzoxazines [32], which would allow reasonable processibility. While MIB had steady-state shear viscosity of 2.0 Pa s at 100 °C, bisphenol-A-based benzoxazines had similar viscosity of 3.0 Pa s at the same temperature (Fig. 6).

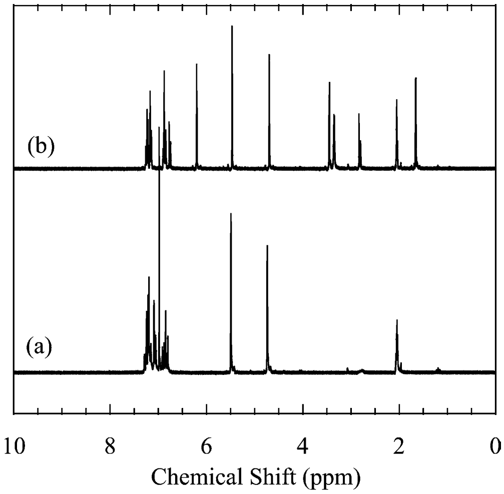


Fig. 2. ^{1}H NMR spectra of (a) MIB and (b) NOB monomers in $(CD_3)_2CO$.

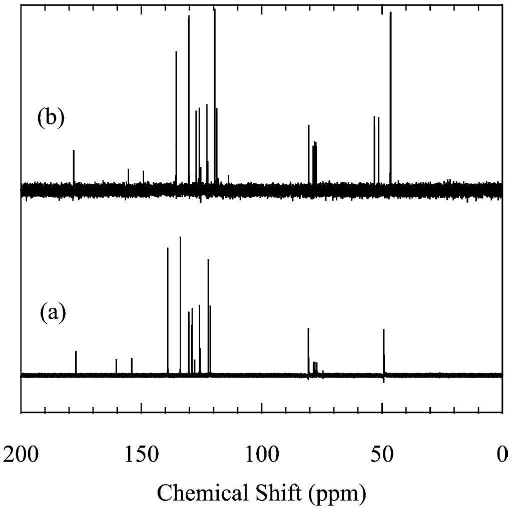


Fig. 3. ^{13}C NMR spectra of (a) MIB and (b) NOB monomers in $CDCl_3$.

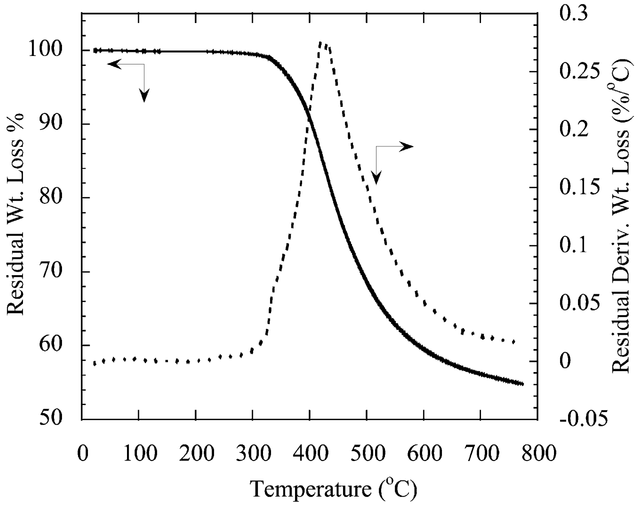


Fig. 4. TGA thermogram of MIB polymer cured at 150 °C (2 h), 170 °C (2 h), and 190 °C (1 h).

The polymerization reactions were studied by DSC as shown in Figs. 7 and 8. MIB and NOB show benzoxazine polymerization exotherms at 213 and 261 °C, respectively. Since, MIB has a maleimide group, it can be further polymerized by free radical mechanism either by thermal activation or with an initiator. Different free radical initiators were dry mixed into the monomer with a concentration of 5 mol% to determine the extent and temperature at which vinyl polymerization occurs (Table 3).

Three initiators, 2,2′-azobisisobutyronitrile (AIBN), benzoyl peroxide (BPO), and dicumyl peroxide (DICUP), were chosen so that the vinyl polymerization can be initiated at three different temperatures. When MIB is polymerized in the presence of AIBN and BPO, it has distinct polymerization peaks for vinyl polymerization from the benzoxazine polymerization. In addition, the heat of reaction of the benzoxazine polymerization is much greater than the maleimide polymerization. However, when DICUP was added to the system, the benzoxazine polymerization peak around 210 °C is significantly lower in intensity than the maleimide polymerization peak. This may explain why the T_g of the MIB with DICUP is approximately 20 °C lower than the T_g observed in the other systems. In case of DICUP, a more extensive rigid succinimide chain backbone is formed which can hinder the benzoxazine polymerization, causing the T_g to decrease.

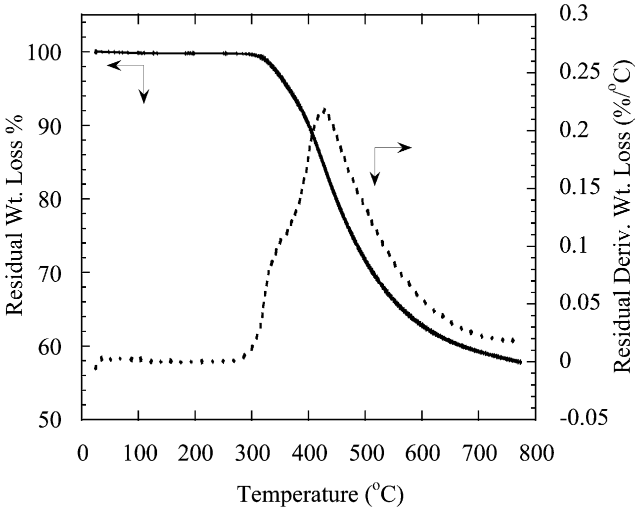


Fig. 5. TGA thermogram of NOB polymer cured at 150 °C (1 h) 180 °C (2 h) and 220 °C (1 h).

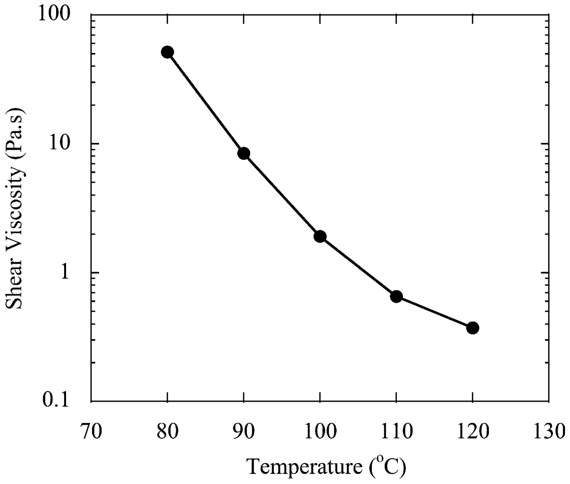


Fig. 6. Shear viscosity of MIB at various temperatures.

We found that AIBN was a more effective free radical initiator than BPO at temperatures below 100 °C. Therefore, for the FTIR studies, AIBN was chosen to confirm each of the exotherm peaks which will be discussed later. In all three thermograms, it is conceived that the first exotherm is attributed to free radical polymerization, the second exotherm between 200 and 230 °C is the benzoxazine polymerization reaction, and the third exotherm above 230 °C is due to thermally activated polymerization of the maleimide group.

NOB can undergo crosslinking reaction at the nadimide

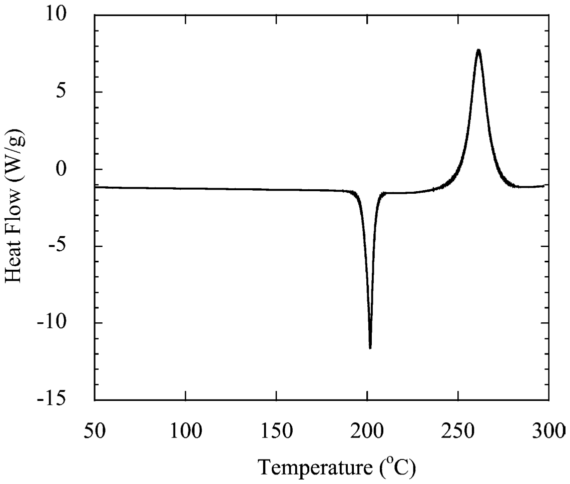
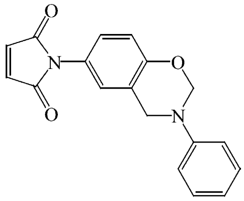
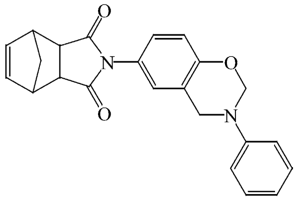
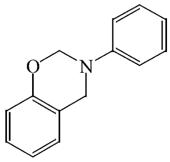
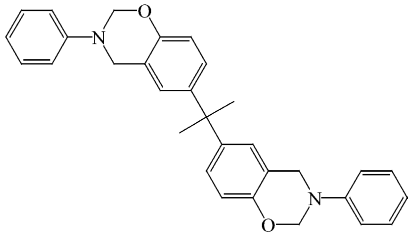


Fig. 7. DSC thermograms of NOB polymerization.

Table 2
Summary of TGA results

Monomer	Abbreviation	Char yield (%)	5 wt% Loss (°C)	10 wt% Loss (°C)	Reference
	MIB	56	375	392	This work
	NOB	58	365	383	This work
	Ph-a	35	326	353	[36]
	BA-a	30	339	348	[36]

group via reverse Diels–Alder reaction at temperatures higher than 271 °C [33]. During this reaction, the nadimide group produces cyclopentadiene and maleic anhydride or their radicals act as monomers for chain polymerization. Due to the high temperature required for the polymerization of the norbornenyl group that overlaps with the degradation temperature, we could not differentiate the thermal degradation process of the benzoxazine from the cross-linking reaction.

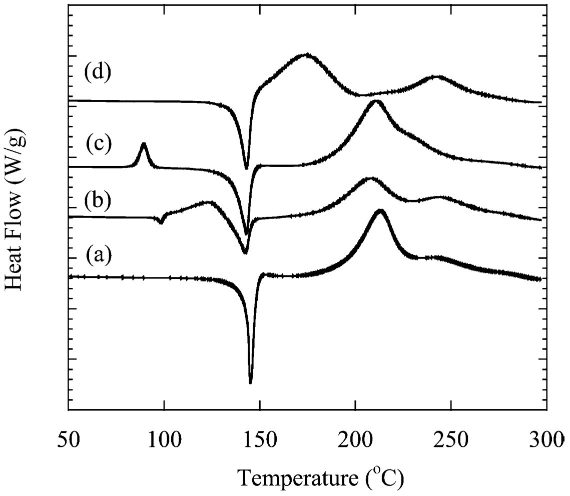


Fig. 8. DSC thermogram of MIB polymerization (a) and its polymerization with different initiators; (b) AIBN (c) BPO and (d) DICUP.

The FTIR spectra of the MIB and NOB monomers and polymers are shown in Figs. 9 and 10. IR band assignments were made for MIB and NOB based on the assignments of monofunctional benzoxazines previously reported by Dunkers and Ishida [34]. The benzoxazine ring modes were determined by comparing the spectra of the monomer and polymer of the MIB polymerized at 170 °C, since we do not expect thermal polymerization of the maleimide group at this temperature. Absorption bands at 1500 and 935 cm^{-1} are due to tri-substituted benzene ring. The band at 1236 cm^{-1} was assigned to the C–O–C antisymmetric stretch, while the band at 1032 cm^{-1} was assigned to the

Table 3
Summary of DSC results and glass transition temperatures

Material	Peak exotherms (°C)	Total heat of reaction (J/g)	T_g (°C)
MIB	213, 244	295	252
MIB w/AIBN[a]	123, 207, 244	318	260
MIB w/BPO[a]	90, 210	337	246
MIB w/DICUP[a]	174, 243	310	232

[a] 5 mol% free radical initiators were dry mixed into the monomer at room temperature before polymerization.

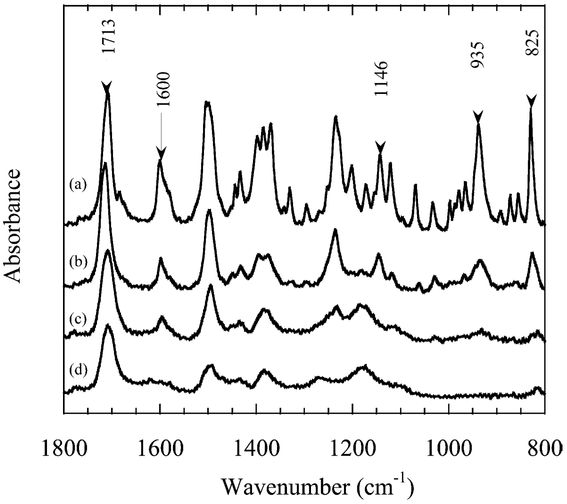


Fig. 9. FTIR spectra of MIB monomer (a) and partially cured monomer at 140 °C (b), 180 °C (c), and 220 °C (d).

C–O–C symmetric stretch. As polymerization proceeds, the appearance of the C–O stretch of the phenolic group can be seen by the appearance of the band at 1272 cm^{-1}. The tetra-substituted benzene mode at 1494 cm^{-1} was also observed, suggesting benzoxazine polymerization via ring opening.

The prominent band at 1713 cm^{-1} is attributed to imide I, and other imide bands can be found at 1397 cm^{-1}, imide II, and at 695 cm^{-1}, imide IV [37]. The band at 828 cm^{-1} is assigned to the CH wag of the vinylene group and the 1600 cm^{-1} is assigned to the C=C stretch. At temperatures of 180 °C and above, the bands attributed to the CH wag and C=C stretch of the vinylene group start to disappear. The band at 1146 cm^{-1}, assigned to the C–N–C bending mode, imide III, of the maleimide ring, shifted to 1180 cm^{-1}, which corresponds to the C–N–C bending mode of the succinimide ring, increased with maleimide polymerization.

In Fig. 11, FTIR spectra obtained during the polymerization of MIB monomer with 5 mol% AIBN are shown. By monitoring the bands at 1600 and 825 cm^{-1} which correspond to the vinylene group, we can determine the reaction temperatures at which the free radical and thermal polymerization of the maleimide group and thermally activated polymerization of the benzoxazine ring occur. According to the spectra, at 140 °C there is a significant decrease of the band at 825 cm^{-1}, before the tri-substituted benzene mode at 935 cm^{-1} disappears. This indicates that, with the addition of a free-radical initiator, the maleimide polymerization takes place before the benzoxazine polymerization as previously concluded from the DSC results. On the other hand, without the free-radical initiator, the benzoxazine polymerization takes place before the maleimide thermal polymerization.

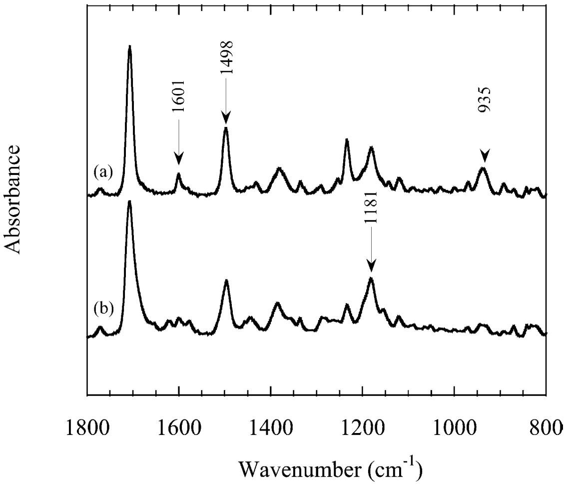


Fig. 10. FTIR spectra of NOB monomer (a) and partially cured monomer at 170 °C (b).

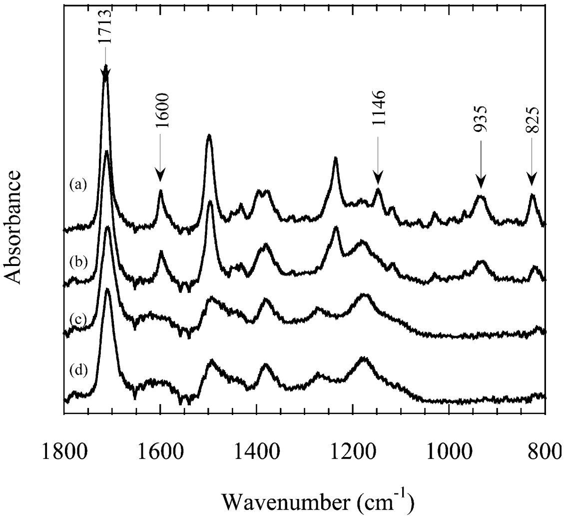


Fig. 11. FTIR spectra of MIB monomer with 5 mol% AIBN (a) and partially cured monomer at 140 °C (b), 180 °C (c), and 220 °C (d).

The order and extent of each polymerization mechanisms have a considerable effect on the resulting glass transition temperatures (Table 3). The T_g of the pure MIB polymer was 252 °C, but when AIBN was added to the system, the T_g increased to 260 °C. It is interesting to observe that when DICUP was added, in which case the largest heat of reaction was observed for vinyl polymerization before benzoxazine polymerization, the T_g was decreased to 232 °C. It can be concluded that a modest vinyl polymerization before benzoxazine polymerization improves the network structure and thermal properties of the final polymer compared to polymerization without any free radical initiator. However, a more extensive vinyl polymerization experienced when adding DICUP will hinder benzoxazine polymerization due to the formation of a rigid backbone structure.

4. Conclusions

Incorporation of the maleimide and norbonene functionality into monofunctional benzoxazine resulted in increase of char yield and glass transition temperature without significantly increasing the viscosity of the monomer. Char yields above 55% and T_g above 250 °C have been observed for both polymers from maleimide and norbornene functional benzoxazine monomers. Furthermore, multiple polymerization processes were observed by using various free radical initiators for vinyl polymerization at different temperatures. By adding AIBN and having extent of maleimide polymerization before benzoxazine polymerization, the glass transition temperature of the resulting MIB polymer was improved by almost 10 °C compared to the homopolymer. However, large extent of maleimide polymerization before benzoxazine polymerization experienced by DICUP resulted in decrease of benzoxazine polymerization and decrease in T_g.

5. Note

During the publication and patenting process, we noticed that a similar paper was published in J Polym Sci Part A: Polym Chem, 42, 5954 (2004). However, the authors indicated in their paper that they obtained the idea of maleimide-functional benzoxazine from our website.

Acknowledgements

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