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Simple and Low Energy Consuming Synthesis of Cyanate Ester Functional Naphthoxazines and Their Properties

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Abstract

The naphthoxazines functionalized with cyanate ester group are synthesized with high yield in the moderate condition, including room temperature synthesis, compared with general benzoxazine synthesis. Additionally, this synthesis can shorten reaction pathways for another cyanate ester functional benzoxazine whose polymer exhibits higher thermal properties than general polybenzoxazines. The catalytic polymerization evaluated by differential scanning calometry (DSC) indicates multiple exotherm maxima, seemingly including cyanate ester trimerization and polymerization of naphthoxazine. The nature of each exotherm is studied by Fourier transform infrared spectroscopy (FT-IR).

Furthermore, their observed exothermic temperatures are lower than those of the reported normal benzoxazines, dicyanate ester blends and cyanate ester functional benzoxazine. Thermal properties collected by thermogravimetric analysis (TGA) and dynamic mechanical analysis (DMA), such as char yield and glass transition temperature, are relatively high compared to those of ordinary polybenzoxazines, polymerized blends of benzoxazine and dicyanate ester.

1. Introduction

Polymeric material development involves synthesizing new materials or modifying existing materials to overcome the shortcomings of the conventional polymers. Polybenzoxazines possess unusual features, such as near-zero shrinkage, low water up-take, some of the polybenzoxazine based materials' T_g much higher than polymerization temperature, high char yield, release of no by-products during polymerization thus avoiding the formation of voids in cross-linked resin, and no strong acid catalysts required for polymerization in contrary to the requirement of a strong acid for polymerization of conventional phenolic resins.[1-5] As is the case for all thermosets, polybenzoxazine too has the inherent disadvantage of being brittle if the polymer is derived from a monomeric precursor: however, if the polymer is derived from a main-chain-type polybenzoxazine precursor, the material is much less brittle.[6-8] Elevated temperature properties make it applicable in aerospace fields and combination of properties like low dielectric constants and loss factor makes it useful for electronic packaging materials.[9] These thermosets can be attractive for composite material manufacturing and also for non-flammable materials for the transportation industry. Starting materials like phenol, formaldehyde and amine are typically used for benzoxazine synthesis. Thus, various types of benzoxazine monomer can be synthesized using combinations of different kinds of phenols and amines with various substituents attached. This rich molecular design flexibility is useful to obtain polymeric materials with desired properties and application requirements.

Incorporation of condensed polynuclear aromatic, such as naphthalene in a polymer, can make it more thermally stable and thus increase its char yield. For example,

naphthalene ring has been incorporated into polymeric main chain such as epoxy,[10] phenolic resin,[11] maleimides,[12] polyester,[13] polyamide,[14] and polyimide.[15] Earlier, monofuctional naphthoxazines were synthesized by reacting naphthol, formaldehyde and primary amines together.[16, 17, 18] The synthesis of bifunctional naphthoxazines with improved thermomechanical properties has already been reported such as naphthoxazines based on difunctional amines like *p*-phenylenediamine and poly(propyleneoxide)amine when reacted with formaldehyde and 2-naphthol.[17, 19] Dihydroxynaphthalene-based naphthoxazine has also been prepared for the enhancement of thermal properties with 1,5-dihydroxynapthalene, formaldehyde and aniline/alkylamines.[16, 17, 20]

The approach of modifying benzoxazine structure by insertion of another polymerizable group such as acetylene,[21] nitrile,[22] maleimide[23] and epoxy[24] has received much attention as a powerful method to obtain high performance benzoxazines having better thermal and mechanical properties. Aromatic cyanate ester resins have emerged as a new class of thermosets for use in the aerospace and electronics industry.[25, 26] As compared to epoxies, they are thermally more stable, have significantly better electrical properties. Cyanate esters also offer ease of handling and processing similar to that of epoxy resin systems. Cyanate esters polymerize via reaction known as cyclotrimerization to form thermally stable triazine rings. Issues like high temperature requirements for trimerization and moisture sensitivity makes its research more complex yet important. Thus blending of cyanate ester resins with other polymers is an active research topic to obtain improved properties.[27] Several researchers have studied chemistry of benzoxazine/cyanate ester blend.[28-31] Earlier, our group synthesized the first benzoxazine incorporating cyanate ester group in its structure and also reported comparison of

properties between benzoxazine/cyanate ester blend and the benzoxazine that contains cyanate ester in itself.[32] We observed that the thermal properties of the cyanate ester-containing benzoxazine, such as T_g and char yield, are superior to the polybenzoxazine and also benzoxazine/cyanate ester blend.

Despite excellent properties of cyanate ester functional benzoxazines, the synthetic method adopted required four steps due to the difficulty of obtaining first a phenolic functional benzoxazine which is a precursor for the cyanate ester-functional benzoxazine. This approach is not as easy as ordinary Mannich condensation of benzoxazines and showed rather low yield of the final product. Therefore, this synthetic approach is not economically attractive. However, taking advantage of the high reactivity of the phenolic functionality on naphthol in comparison to the phenolic group of the aminophenol, preferential formation of a benzoxazine group without consuming the phenolic group of the aminophenol can be envisioned and studied in this paper. The resultant material is a naphthoxazine rather than a benzoxazine. Four kinds of cyanate ester-functional naphthoxazines were synthesized and were analyzed by ^{1}H-NMR, differential scanning calorimetry (DSC) and Fourier transform-infrared spectroscopy (FT-IR). Their polymers were characterized by thermogravimetric analysis (TGA) and dynamical mechanical analysis (DMA) to evaluate thermal stability and thermorheological properties, respectively. It is further the interest of this paper to select the most attractive cyanate ester naphthoxazine among the four synthesized.

2. Experimental

2.1. Materials

1-Naphthol (99+ %, abbreviated as 1NP), 2-naphthol (99+ %, abbreviated as 2NP), 2-aminophenol (99%), 4-aminophenol (97%) and cyanogen bromide (97%) were obtained from Acros Organics. Triethylamine (99.5%) and Formaldehyde (37% in water) were used as received from Sigma-Aldrich. Basic alumina, formic acid (88%), dichloromethane, acetonitrile, hexane, acetone and diethyl ether were purchased from Fisher Scientific. All chemicals were used as received.

2.2. Preparation of Monomers

2.2.1 Synthesis of 3-(4-cyanatophenyl)-3,4-dihydro-2*H*-naphtho[2,1-*e*][1,3]oxazine (abbreviated as 1NP-4acy)

Acetonitrile (30 mL) was added in a 100 mL round bottom flask containing 1-naphthol (1.44 g, 0.01 mol) and 4-aminophenol (1.09 g, 0.01 mol). Formaldehyde solution (1.71 mL, 0.021 mol) and 0.1 mL of formic acid were added to the mixture. The whole mixture was magnetically stirred at ambient temperature for 12 hours. The solution was vacuum filtered through basic alumina column to remove formic acid in the solution. The filtrate was dried in a vacuum oven and brown solid, a precursor of **1NP-4acy**, was obtained. The resulting solid and cyanogen bromide (1.38 g, 0.013 mol) were dissolved in anhydrous acetone (30 mL) in a 100 mL round bottom flask under nitrogen atmosphere and cooled to 0^{o}C. Triethylamine (1.8 mL, 0.013 mol) was added dropwise into the solution with stirring. After stirring for 30 min, the solution was filtered to remove triethylamine hydrobromide salt as byproduct. After drying the filtrate, the product was dissolved in hexane, washed with water 4 times and then dried in the vacuum oven to obtain white powder (2.46 g, yield 81%). ^{1}H-NMR (300MHz, DMSO-d_6, ppm):δ 4.77(s, 2H, C-CH_2-NAr), 5.65 (s, 2H, O-CH_2-NAr), 7.23-7.47 (m, 8H, Ar*H*), 7.79-7.82 (m, 1H,

Ar*H*), 7.96-7.99 (m, 1H, Ar*H*). ^{13}C-NMR (600MHz, DMSO-d_6, ppm):δ 49.6, 79.5, 109.6, 115.4, 116.9, 119.4, 120.3, 121.0, 124.5, 125.5, 126.0, 126.5, 128.0, 133.2, 146.9, 147.2, 149.1. FTIR (KBr), cm^{-1}: 2268 (CN stretching of cyanate ester), 2235 (CN stretching of cyanate ester), 1225 (asymmetric stretching of C−O−C), 1169 (asymmetric stretching of C−N−C), and 921 (out-of-plane C−H of naphthalene ring of naphthoxazine). Anal. Calcd for C19H14N2O2: C, 75.48; H, 4.67; N, 9.27. Found: C, 75.08; H, 4.48; N, 9.26.

2.2.1 Synthesis of 2-(4-cyanatophenyl)-2,3-dihydro-1*H*-naphtho[1,2-*e*][1,3]oxazine (abbreviated as 2NP-4acy)

2-Naphthol and 4-aminophenol were added and rest of the procedure adopted was the same as that of **1NP-4acy**. **2NP-4acy** (white powder, yield 75%); ^{1}H-NMR (300MHz, DMSO-d_6, ppm):δ 4.99(s, 2H, C-CH_2-NAr), 5.52 (s, 2H, O-CH_2-NAr), 7.01 (d, 1H, Ar*H*), 7.32-7.34 (m, 4H, Ar*H*), 7.38 (t, 1H, Ar*H*), 7.53 (t, 1H, Ar*H*), 7.71 (d, 1H, Ar*H*), 7.81 (d, 1H, Ar*H*), 7.87 (d, 1H, Ar*H*). ^{13}C-NMR (600MHz, DMSO-d_6, ppm):δ 47.5, 78.9, 109.7, 113.1, 116.8, 116.9, 118.7, 119.3, 121.9, 124.1, 127.2, 128.6, 128.8, 128.9, 131.4, 146.9, 147.3, 152.0. FTIR (KBr), cm^{-1}: 2266 (CN stretching of cyanate ester), 2237 (CN stretching of cyanate ester), 1230 (asymmetric stretching of C−O−C), 1169 (asymmetric stretching of C−N−C), and 949 (out-of-plane C−H of naphthalene ring of naphthoxazine). Anal. Calcd for C19H14N2O2: C, 75.48; H, 4.67; N, 9.27. Found: C, 75.35; H, 4.50; N, 9.24.

2.2.2 Synthesis of 3-(2-cyanatophenyl)-3,4-dihydro-2*H*-naphtho[2,1-*e*][1,3]oxazine (abbreviate as 1NP-2acy)

1-Napthol and 2-aminophenol were added and rest of the synthesis procedure was the same as above. Diethyl ether, instead of hexane, was used to solubilize it for washing in the last process. **1NP-2acy** (pale yellow powder, yield 71%); ^{1}H-NMR (300MHz, DMSO-d_6, ppm):δ 4.67(s, 2H, C-CH_2-NAr), 5.49 (s, 2H, O-CH_2-NAr), 7.18-7.32 (m, 4H, Ar*H*), 7.44-7.57 (m, 4H, Ar*H*), 7.81-7.84 (m, 1H, Ar*H*), 8.01-8.04 (m, 1H, Ar*H*). ^{13}C-NMR (600MHz, DMSO-d_6, ppm):δ 50.6, 80.6, 109.1, 115.1, 116.9, 120.5, 121.0, 122.9, 124.5, 125.1, 125.3, 126.0, 126.5, 128.1, 128.3, 133.3, 138.4, 145.9, 148.8. FTIR (KBr), cm^{-1}: 2262 (CN stretching of cyanate ester), 1230 (asymmetric stretching of C−O−C), 1168 (asymmetric stretching of C−N−C), and 947 (out-of-plane C−H of naphthalene ring of naphthoxazine).

2.2.3 Synthesis of 2-(2-cyanatophenyl)-2,3-dihydro-1*H*-naphtho[1,2-*e*][1,3]oxazine (abbreviated as 2NP-2acy)

2-Napthol and 2-aminophenol were added and rest of the synthesis procedure was the same as that for **1NP-2acy**. **2NP-2acy** (pale yellow powder, yield 70%); ^{1}H-NMR (300MHz, DMSO-d_6, ppm):δ 4.87(s, 2H, C-CH_2-NAr), 5.35 (s, 2H, O-CH_2-NAr), 7.07 (d, 1H, Ar*H*), 7.18-7.24 (m, 3H, Ar*H*), 7.38 (q, 1H, Ar*H*), 7.49-7.56 (m, 2H, Ar*H*), 7.74 (d, 1H, Ar*H*), 7.78 (d, 1H, Ar*H*), 7.84 (d, 1H, Ar*H*). ^{13}C-NMR (600MHz, DMSO-d_6, ppm):δ 48.4, 80.1, 109.2, 112.8, 116.9, 118.8, 122.0, 123.0, 124.2, 125.1, 127.2, 128.3, 128.6, 128.8, 129.0, 131.1, 138.4, 146.0, 151.8. FTIR (KBr), cm^{-1}: 2264 (CN stretching of cyanate ester), 1228 (asymmetric stretching of C−O−C), 1166 (asymmetric stretching of C−N−C), and 923 (out-of-plane C−H of naphthalene ring of naphthoxazine).

2.3 Preparation of 1NP-4acy sample with Cu catalyst for DSC analysis

1NP-4acy with 200 ppm and 400 ppm in mole of copper (II) acetylacetonate abbreviated as $Cu(acac)_2$ for DSC analysis were prepared by dissolving it with the corresponding naphthoxazine in dichloromethane and drying afterward under vacuum at room temperature for 24 h.

2.4 Polymerization of NP-acy monomers

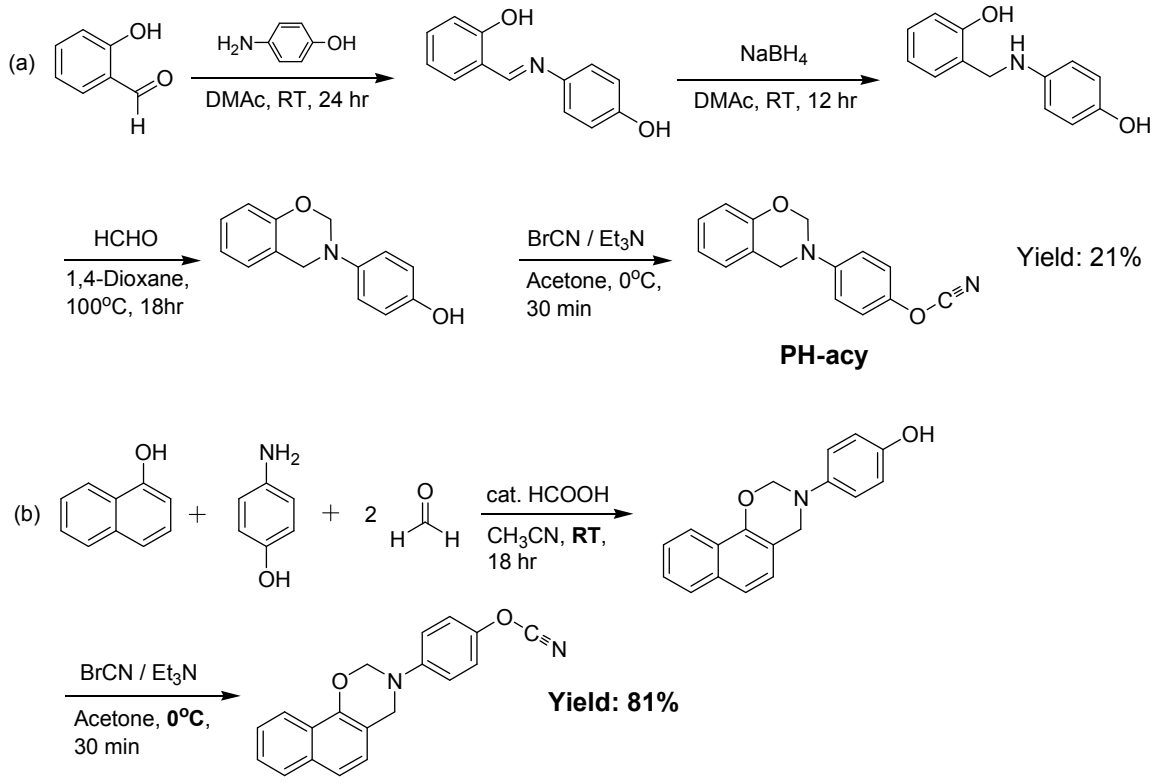
All monomers were polymerized under the same conditions. The monomers cast on a glass plate were placed in a convection oven at 220^{o}C for 2 hours to obtain the polymerized sample with or without the catalyst.

2.5. Characterization

^{1}H-NMR spectra were acquired in deuterated dimethylsulfoxide (DMSO-d_6) with tetramethylsilane as an internal standard on a Varian Oxford AS300 at a proton frequency of 300 MHz. ^{13}C-NMR spectrum was acquired in deuterated dimethylsulfoxide (DMSO-d_6) on a Varian Oxford AS600 at a carbon frequency of 150.864 MHz (proton frequency equivalence of 600 MHz). The average number of transients for ^{1}H and ^{13}C-NMR was 16 and 256, respectively. Support to molecular studies by NMR was done by Fourier transform infrared spectroscopy (FT-IR) using Bomem Michaelson MB 110 spectrophotometer which is equipped with a deuterated triglycine sulfate detector. Thirty two scans were coadded per spectrum at a resolution of 4 cm^{-1} after purging the spectrometer with dry air. Samples were ground with KBr powder and compressed into a 13 mm pellet or coated on a 25 mm KBr circular disk for analysis. TA Instruments DSC model 2920 was used with a heating rate of 10 ^{o}C /min and a nitrogen flow rate of 60 mL/min for the differential scanning calorimetric (DSC) study. Thermogravimetric

analysis (TGA) was carried out on a TA instruments Q500 TGA with a heating rate of 10 ^{o}C /min under nitrogen at a flow rate of 60 mL/min. Dynamic mechanical analyses (DMA) were done on a TA Instruments Q800 DMA, applying a controlled strain tension mode with an amplitude of 10 μm and a temperature ramp rate of 3 °C/min at a frequency of 1.0 Hz.

3. Results and Discussion



Scheme 1. (a) Synthesis of cyanate ester functional benzoxazine (b) Synthesis of cyanate ester functional naphthoxazine

Table 1. Various substitutional cyanate ester functional naphthoxazines

Abbreviation	Naphthol	Aminophenol	Total Yield (%)
1NP-4acy	1-Naphthol	4-Aminophenol	81
2NP-4acy	2-Naphthol	4-Aminophenol	75
1NP-2acy	1-Naphthol	2-Aminophenol	71
2NP-2acy	2-Naphthol	2-Aminophenol	70

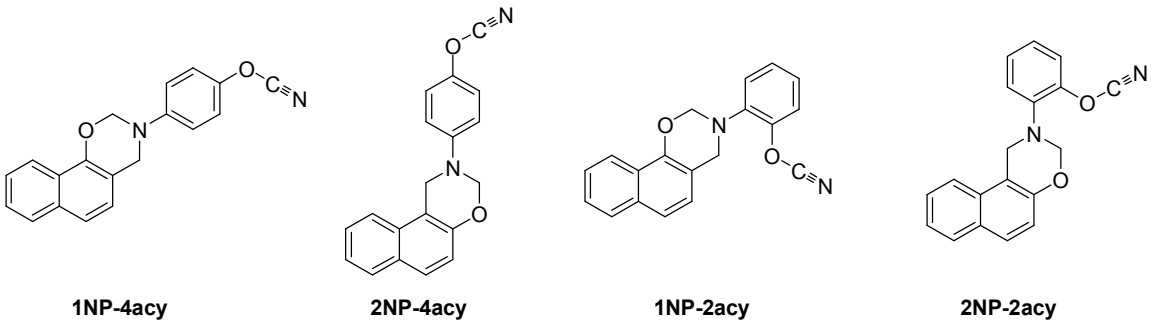
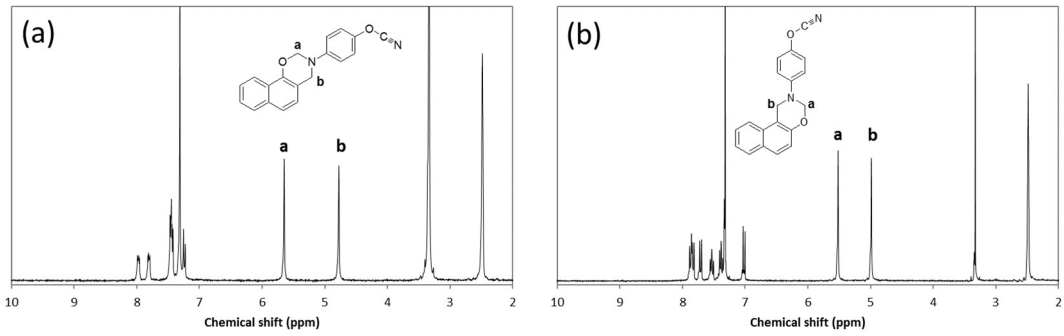


Figure 1. Chemical structures of cyanate ester functional naphthoxazines

In our recent work, incorporation of cyanate ester on benzoxazine, which showed higher reactivity and thermal properties, was reported.[32] Historically, benzoxazine moiety has been made by one-pot Mannich reaction which is carried out by mixing phenol, amine and formaldehyde. However, multiple preparation steps without Mannich reaction were required to prevent from the concerted reaction of two kinds of phenolic hydroxyl groups, phenol and 4-aminophenol as starting materials. As a result, total yield resulted in 21%. Additionally, each reaction needed careful temperature control, especially in the case of benzoxazine ring closure. On the other hand, naphthol has higher reactivity as both nucleophile to formaldehyde and related Mannich base than general phenols due to its extra electron-rich benzene ring. Additionally, there are some reports about the catalytic synthesis of benzoxazines and naphthoxazines to moderate the Mannich reaction condition, which typically use acid catalysts.[33, 34, 35] By using 1-naphthol instead of

phenol, 4-aminophenol, and formaldehyde, the naphthoxazine with hydroxyl group could be synthesized at room temperature with catalytic amount of formic acid via one-pot Mannich reaction. Room temperature one-pot synthesis of oxazine ring has seldom been achieved through Mannich reaction and enables to reduce side reactions or byproduct formation caused by heating process. Cyanate ester functional naphthoxazine abbreviated as **1NP-4acy** was obtained from further reaction with cyanogen bromide/trimethylamine. The resulting total yield was 81%, which was significantly higher than the synthesis of benzoxazine incorporating cyanate ester (**PH-acy**) (Scheme 1). Other cyanate ester functional naphthoxazines which are based on 1,2-naphthol and 2,4-aminopehnol also gained relatively high yield as shown in Table 1. Four kinds of cyanate ester functional naphthoxazines were named as **1NP-4acy**, **2NP-4acy**, **1NP-2acy** and **2NP-2acy** where 1NP and 2NP stand for 1-naphthol and 2-naphthol as the starting materials, and 4acy and 2acy for the cyanate ester functionality derived from 4- and 2-aminophenol (Figure 1).



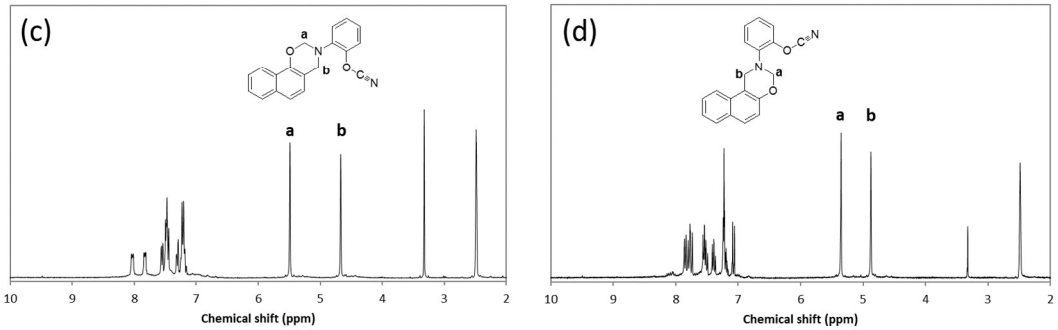


Figure 2. [1]H-NMR spectra of cyanate ester functional naphthoxazines (a) 1NP-4acy, (b) 2NP-4acy, (c) 1NP-4acy, and (d) 2NP-2acy in DMSO-d_6

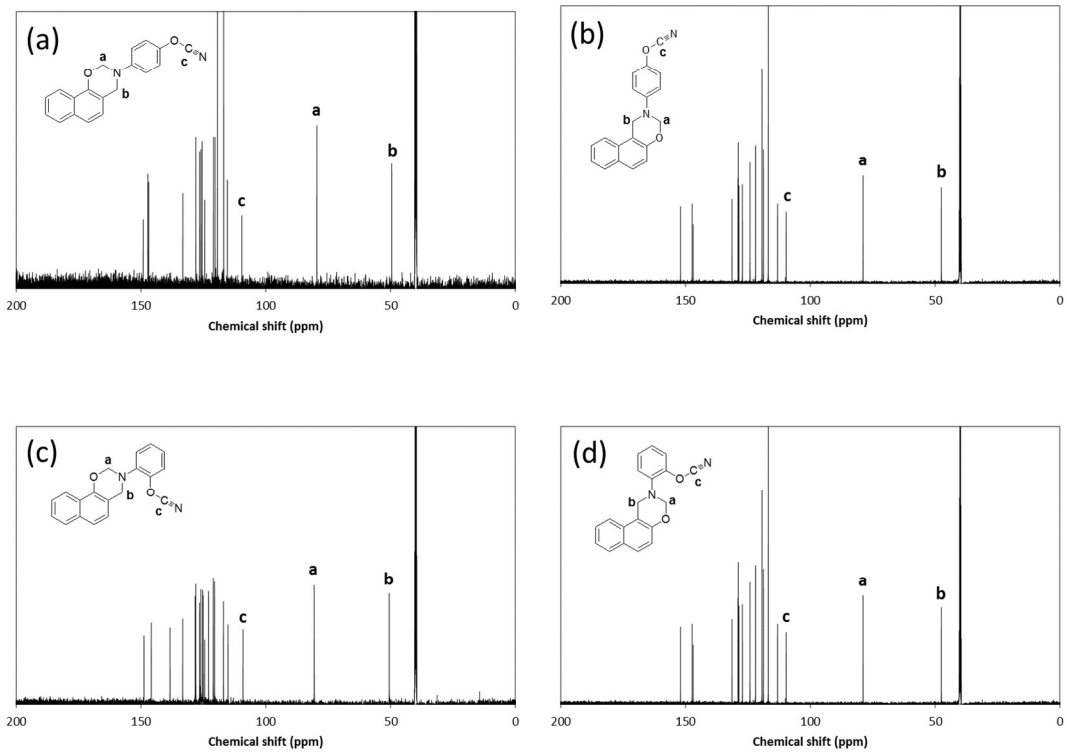


Figure 3. [13]C-NMR spectra of cyanate ester functional naphthoxazines (a) 1NP-4acy, (b) 2NP-4acy, (c) 1NP-4acy, and (d) 2NP-2acy in DMSO-d_6

The chemical structures of synthesized cyanate ester functional naphthoxazine were determined by ^{1}H-NMR (Figure 2). Two singlet resonances located between 4.6-5.0 ppm and 5.2-5.7 ppm were observed, which are attributed to Ar-CH_2-N- and –O-CH_2-N- of oxazine ring, respectively. These specific resonances of naphthoxazine have already been reported in a previous article on naphthoxzine and are very consistent to the formation of naphthoxazine rings.[16, 17] In addition to ^{1}H-NMR, ^{13}C-NMR as shown in Figure 3 is also useful to verify the characteristic signals of naphthoxazine and cyanate ester. The resonances at 47-51 ppm and 78-81 ppm observed in the compounds were consistent with the reported signals attributed to Ar-C*H_2-N and O-C*H_2-N of naphthoxazine ring.[21] The carbon signals of each cyanate esters were also clearly confirmed at 109-110 ppm.

Figure 4 shows DSC thermograms of **1NP-4acy**, **2NP-4acy**, **1NP-2acy** and **2NP-acy**. For **1NP-4acy and 2NP-4acy**, one single exothermic peak was observed unlike the case of **PH-acy** which had two significant exotherms in the previous work.[32] However, the heat of polymerization of each naphthoxazine was almost the same or higher than that of cyanate ester functional benzoxazine (PH-acy), 551 J/g. It is expected that sharp single exothermic peaks on **1NP-4acy** and **2NP-4acy** contains exotherms from multiple origins which are likely due to the simultaneous occurrence of crosslinking of cyanate ester and oxazine-ring opening. On the contrary, *ortho*-substituted cyanate ester, **1NP-2acy** and **2NP-2acy**, showed multiple exothermic peaks and lower exothermic temperature than *para*-substituted cyanate ester functional naphthoxazine. Similar phenomena were already reported in nitrile functional benzoxazine.[22] *Ortho*-nitrile-substituted benzoxazine showed highest reactivity among *ortho*-, *meta*-, and *para*-substituted benzoxazines.

Furthermore, unlike the previously reported naphthoxazine monomers, which showed evaporation of the monomer prior to the polymerization,[16, 36] no obvious evidence was obtained for monomer evaporation for these cyanate ester functional naphthoxazines. Despite showing potentially advantageous properties by difunctional naphthoxazine, such as lower polymerization temperature and higher char yield at 800^{o}C, this evaporation of naphthoxazine monomers prevented from receiving active investigation in the past. Cyanate ester group seems to trimerize at lower temperatures than the evaporation temperature, resulting in higher molecular weight thus minimizing its evaporation and making them a useful class of oxazine resins. Another advantage of cyanate ester incorporated naphthoxazine is its lower polymerization temperature than normal benzoxazine, cyanate ester functional benzoxazine and dicyanate ester.

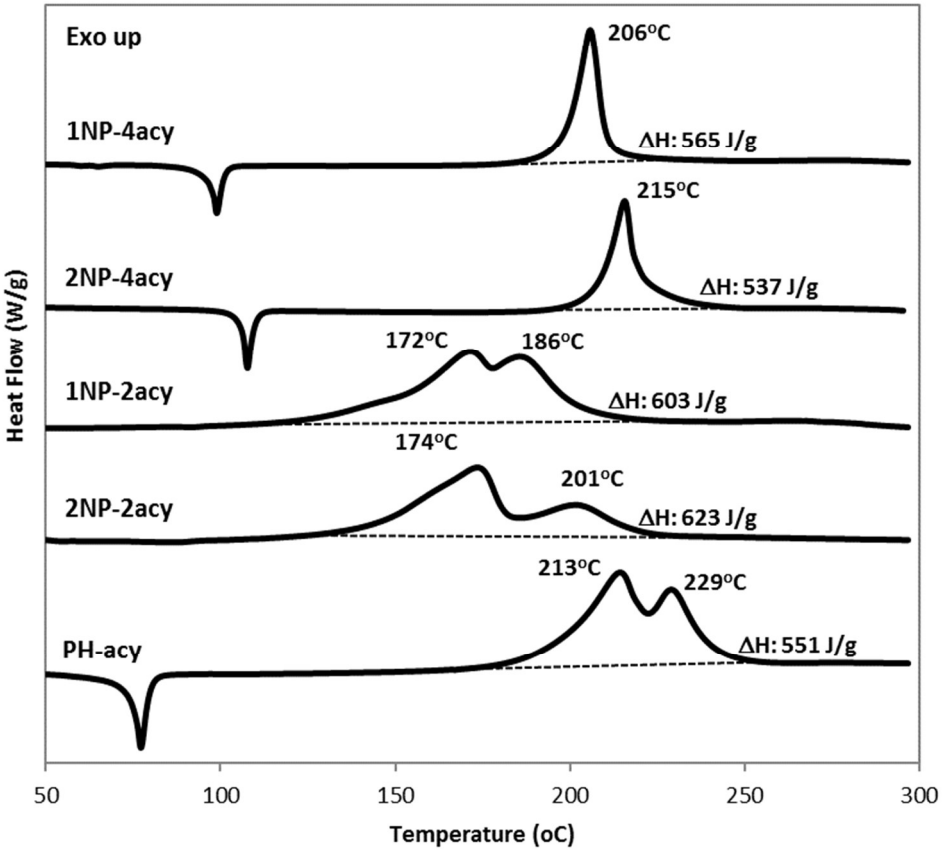


Figure 4. DSC thermograms of cyanate ester functional naphthoxazines

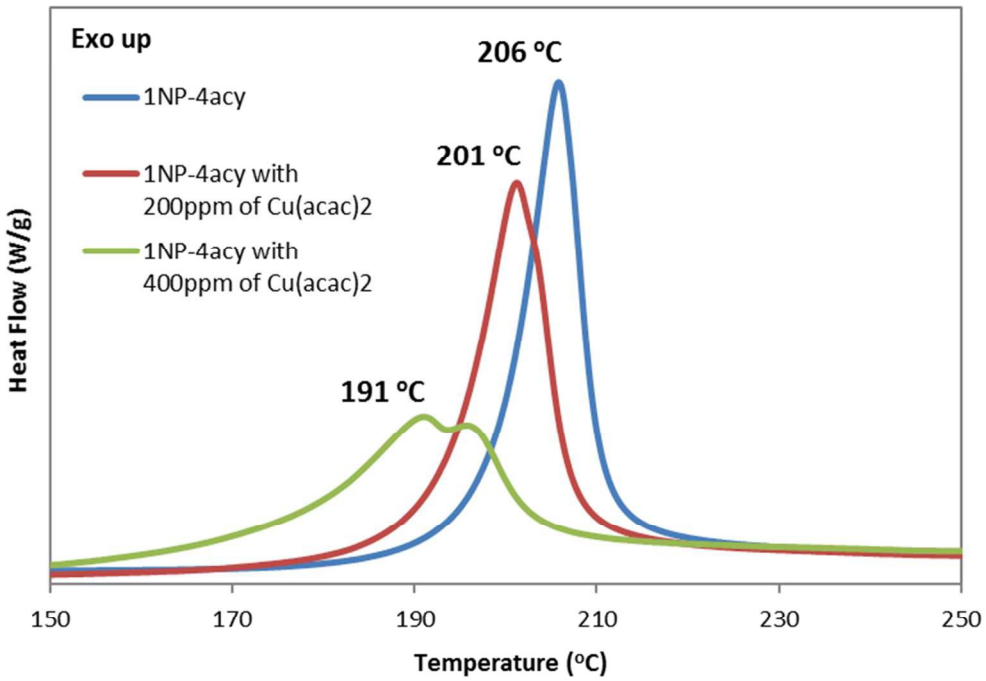


Figure 5. DSC thermograms of **1NP-4acy** catalyzed with $Cu(acac)_2$

It is well-known that cyanate ester trimerization can be catalyzed by copper (II) catalysts. From many papers reported in the literature, copper acetylacetonate ($Cu(acac)_2$) is believed to be one of the most effective catalysts.[37, 38] In this study, 200 and 400 ppm in mole of $Cu(acac)_2$ was added in **1NP-4acy** to selectively accelerate the cyanate ester cyclotrimerization and examine the possible overlap of two distinct polymerization mechanisms. Although a copper catalyst also accelerates the benzoxazine polymerization[39], the effectiveness on the cyclotrimerization and benzoxazine polymerization was assumed to be different. The DSC thermograms with and without the added catalyst are shown in Figure 5. As hypothesized, in the case of the naphthoxazine with 400 ppm of $Cu(acac)_2$, the polymerization exotherm exhibited well-separated two

exothermic peaks. Consequently, it has been demonstrated that single exotherm of **1NP-4acy** consists of accidentally overlapped two different exothermic reactions, cyclotrimerization of cyanate esters and ring-opening polymerization of benzoxazines. As expected, this copper catalyst is very effective in enhancement of the reactivity of both cyanate ester and naphthoxazine polymerization.

The polymerization behavior of **1NP-4acy** could further be evaluated with infrared spectroscopy. Vibrational mode of cyclic C-O-C stretch at 921 cm^{-1} is consistent with the previous study of naphthoxazine whereas the characteristic cyanate ester OCN bands of **1NP-4acy** appear at 2268 cm^{-1} and 2235 cm^{-1}. After heating at 120 ^{o}C for 2 hours without added catalyst, two bands of cyanate ester group mostly disappeared and new sharp bands at 1367 cm^{-1} and 1683 cm^{-1} appeared which are attributed to triazine resulting from trimerization of cyanate ester and isocyanurate seemingly rearranged from triazine ring, respectively. However, the naphthoxazine ring-related mode still exists at 921 cm^{-1}. By further increasing temperature to 170 ^{o}C and, further, 220 ^{o}C, naphthoxazine ring was completely consumed and stable state of this polymer was observed judging from the similarity of the spectra of **1NP-4acy** which were polymerized at 170 ^{o}C and 220 ^{o}C. Similar behavior has also been observed in isothermal FT-IR study in the previous work on cyanate ester functional benzoxazine.[32]

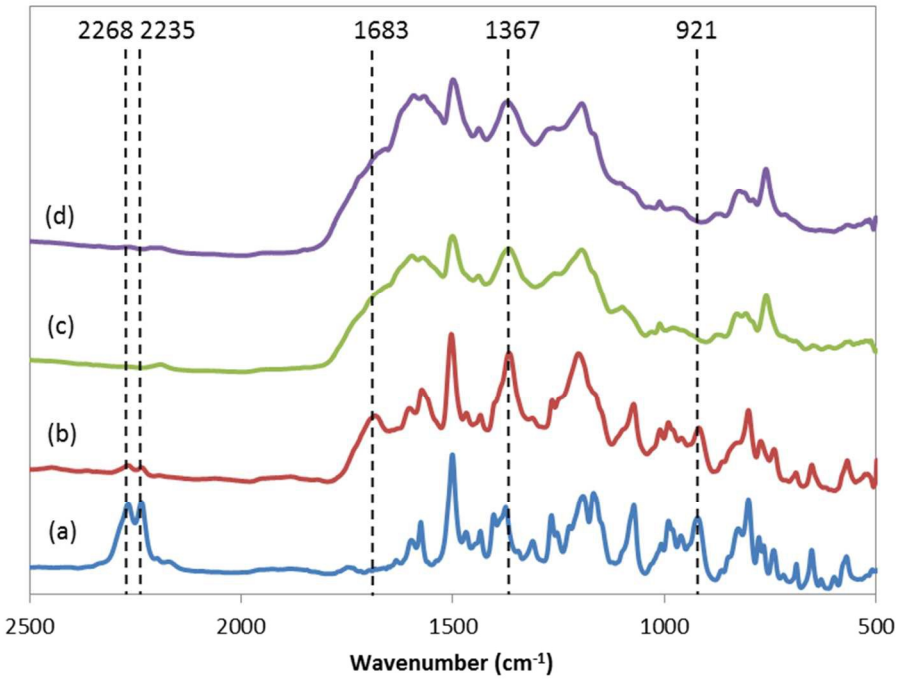


Figure 6. FT-IR spectra of **1NP-4acy** (a) monomer, (b) polymerized at 120 ^{o}C/2 h, (c) 170 ^{o}C/2 h, and (d) 220 ^{o}C/2 h.

Thermal stability of cyanate ester functional naphthoxazines polymerized at 220 ^{o}C for 2 hours was evaluated with TGA as shown in Figure 7. Poly(**1NP-4acy)** obtained 57% as its char yield at 800^{o}C and higher decomposition temperature in comparison with **1NP-a** which is aniline-based naphthoxazine, and **PH-a**. Thermal properties of **2NP-2acy** and **2NP-4acy** derived from 2-naphthol were also drastically improved by incorporation of cyanate ester in the same molecule (Table 2). As observed in the benzoxazine incorporated with cyanate ester group, additional crosslinkage of cyanate ester covalently attached on aniline-based benzene of benzoxazine or naphthoxazine has delayed the evaporation of aniline portion which is initially taken apart from polybenzoxazine during heating. Additionally, the position of cyanate ester group on aniline-based benzene also

slightly influenced in the char yield. Among *ortho*-positioned cyanate esters like **1NP-2acy** and **2NP-2acy**, some steric hindrance can be considered in cyclotrimerization of cyanate ester group leading to less crosslinkage than *para*-positioned ones.

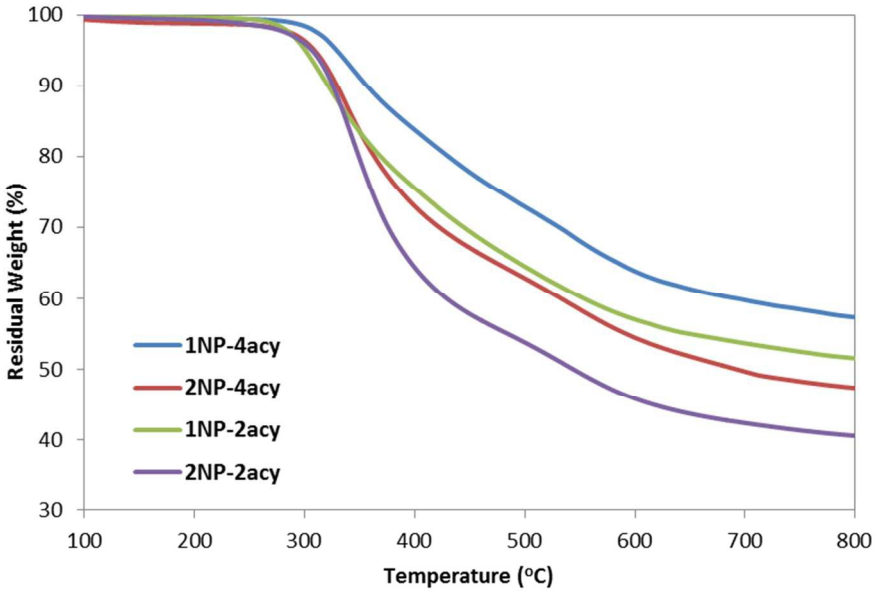
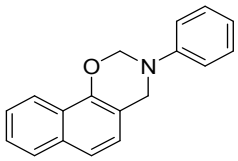


Figure 7. TGA thermogram of cyanate ester naphthoxazines polymerized at 220 °C/2 h

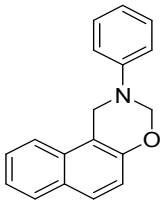
Table 2. Summary of TGA thermogram and comparison with general benzoxazine and naphthoxazine

Monomer	5% Weight Loss (^{o}C)	10% Weight Loss (^{o}C)	Char Yield (%)
1NP-4acy	332	359	57
2NP-4acy	311	330	47
1NP-2acy	302	323	51
2NP-2acy	309	327	41
1NP-a[a)]	310	341	46
2NP-a[a)]	216	236	20
PH-a[b)]	294	347	40

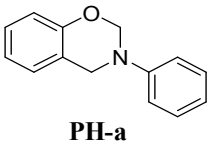
(a) Reference no. 16 (b) Reference no. 32



1NP-a



2NP-a



PH-a

Figure 8 shows DMA thermograms of **1NP-4acy** and **PH-acy** polymerized with a glass fiber reinforcement at 220 ^{o}C for 2 hours. The glass fiber was used to prepare samples that can be used for the DMA study due to the brittleness of poly (**1NP-4acy**). The glass transition temperature, T_g, of each material was determined by the peak of loss modulus (E"). That temperature was significantly higher than the T_g of non-functional polynaphthoxazine, 186 ^{o}C, although there was still residual unreacted group to polymerize in this material judging from the rubbery plateau of storage modulus (E').

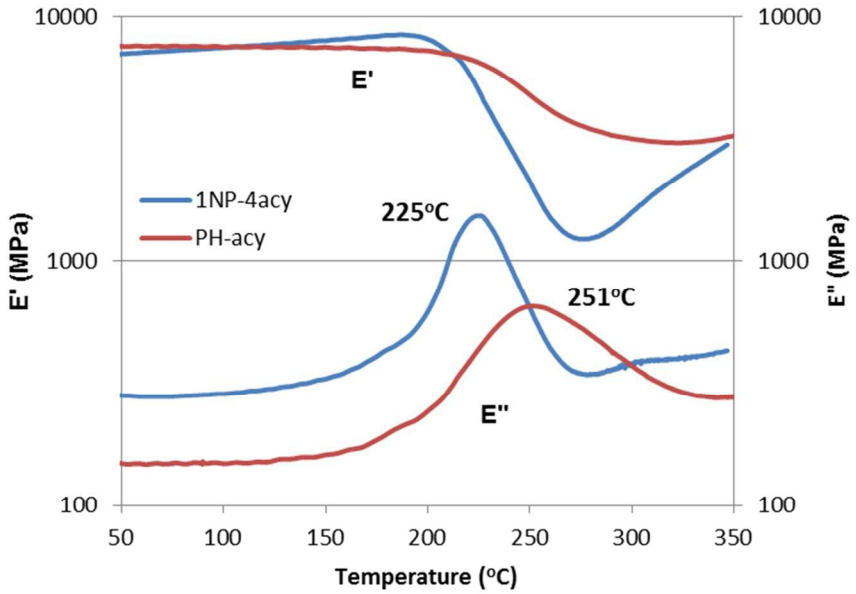


Figure 8. DMA thermogram of poly (**1NP-4acy**) and poly(**PH-acy**) reinforced with glass fiber

5. Conclusions

Cyanate-ester functional naphthoxazines possess significant advantages for actual production and applications, such as low energy consumption because of a short synthetic pathway and room temperature reaction in the entire preparation process. Furthermore, the multiple polymerization mechanism overcame the evaporation of naphthoxazine portion which was considered as a notable disadvantage despite its high thermal properties. The polymerization temperatures of these materials were significantly lower than ordinary polybenzoxazines and the blend of dicyanate ester and benzoxazine while their thermal properties, especially char yield were high enough. Incorporation of cyanate

ester with naphthoxazine units gives us versatile possibilities for enhancement of benzoxazine/polybenzoxazine study many people have ever done.

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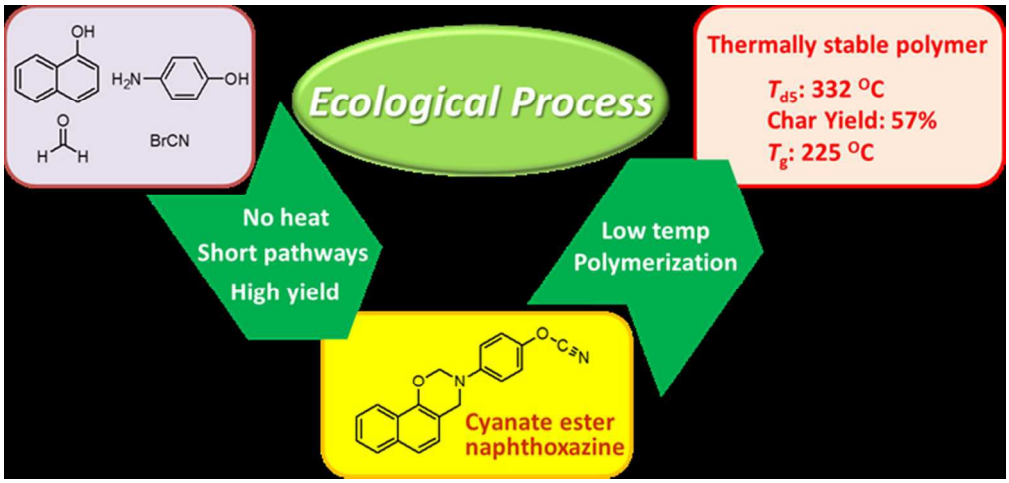

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