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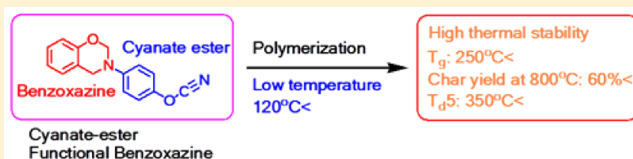
Synthesis and Characterization of Cyanate Ester Functional Benzoxazine and Its Polymer

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ABSTRACT: The first benzoxazine incorporating cyanate ester group in its structure has been synthesized. The polymerization process investigated by differential scanning calorimetry (DSC) exhibits two clearly separated exotherm maxima, corresponding to cyanate ester trimerization and benzoxazine, respectively. The nature of each exotherm is studied by Fourier transform infrared spectroscopy (FT-IR).

The activation energies for cyanate ester trimerization and benzoxazine ring-opening polymerization are determined by both Kissinger's and Ozawa's methods. Furthermore, both exothermic temperatures observed are lower than those of the published values of benzoxazine and dicyanate ester blends. Thermal properties such as glass transition temperature and char yield are studied by thermogravimetric analysis (TGA) and dynamic mechanical analysis (DMA). Those properties are found to be outstanding compared to the reported properties of general benzoxazine resins and polymerized blends of benzoxazine and dicyanate ester, offering a polymeric matrix for composite satisfying many requirements for such a material.



1. INTRODUCTION

Benzoxazine polymer is a recently developed class of thermoset which is receiving strong attention in recent years because they possess significant advantages compared with other typical thermosetting resins, such as excellent mechanical and thermal properties, near-zero shrinkage upon polymerization, remarkable molecular design flexibility, high char yield, and surface energy lower than polytetrafluoroethylene.^{1–3} Among those benzoxazine resins, benzoxazines functionalized with maleimide,⁴ amide,⁵ and acetylene⁶ were synthesized and found to exhibit very high thermal resistance. Incorporation of functional group with benzoxazine structure is not only simple to prepare but also compatibility to other compounds to improve their properties. Furthermore, good processability is expected due to their structural simplicity. Additionally, functional groups other than benzoxazine structure will add new polymerization mechanism in addition to the cationic ring-opening polymerization of benzoxazine group, allowing adding more flexibility in processing conditions and wider property ranges.

Cyanate ester resin is also known as a high performance polymer whose properties favorably compare with polyimide, bismaleimide, and high performance epoxy resins for the electronic and aerospace applications^{7,8} since it possesses excellent properties, including high thermal resistance, low dielectric constant, and radiation resistance.⁹ The cyanate ester group undergoes thermal cyclotrimerization to form a stable triazine network under proper reaction conditions. Unfortunately, elevated temperature is needed to trimerize cyanate ester groups,¹⁰ and it is the main drawback of cyanate ester resins to consume high energy in addition to the sensitivity of the cyanate ester group to moisture. In order to solve this issue, the blend of cyanate ester with other polymers, such as epoxy resins, has been studied, and the trimerization temperature was

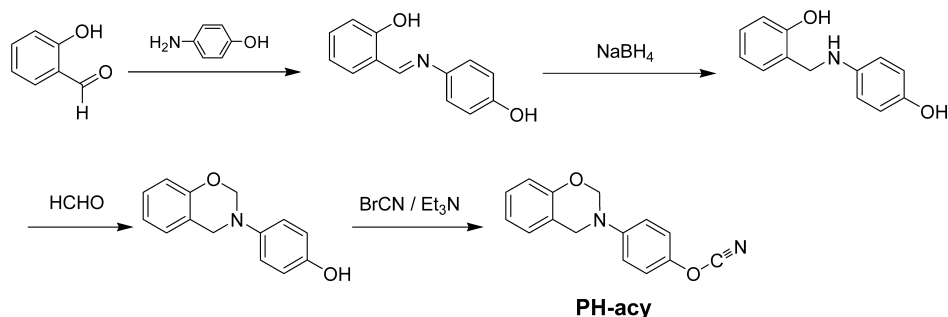
lowered.¹¹ The blend of benzoxazine with cyanate ester is an active research subject in the polybenzoxazine field^{12–16} after a report that showed significant synergism for polymerization of benzoxazine in the presence of cyanate ester groups. Their synergetic effects in thermal and mechanical properties were reported while its reaction mechanism is still not fully understood and is continuously discussed. Nair¹² and Kimura et al.¹³ proposed that the network of benzoxazine and cyanate ester group with iminocarbonate intermediate is produced by the reaction of cyanate ester group with the phenolic hydroxyl group that resulted from the benzoxazine ring-opening. This iminocarbonate intermediate is proposed to further induce polymerization reaction of more molecules of cyanate ester to form polycyanurate. Gu et al.¹⁴ proposed that hydroxyl group of ring-opened benzoxazine catalyzes cyclotrimerization of cyanate ester groups and the ring-opened benzoxazine inserted into triazine structures, resulting in the coexistence of cyanurate and isocyanurate. On the other hand, Lin et al. proposed the benzoxazine ring itself, rather than the phenolic hydroxyl group as a result of oxazine ring-opening, catalyzes cyanate ester trimerization and cyanurate can be converted into isocyanurate with benzoxazine as it is being heated.¹⁶ However, no benzoxazine containing cyanate ester group on the same molecule has yet been prepared and reported to date.

For a high performance matrix used in composite materials, a number of required properties must simultaneously be satisfied. For example, the polymerization temperature is desired to be rather low in order to save energy and reduce expenses for the heating devices. Yet, too low a polymerization temperature

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Scheme 1. *p*-Cyanate Ester Functional Benzoxazine (PH-acy) Synthesis

approaching room temperature often results in poor shelf life and requires cryogenic storage, which adds extra cost. Typically a trade-off exists between polymerization temperature and shelf life. Another desired property is the high thermal properties, such as high glass transition and degradation temperatures and high char yield. In general, precursors for high performance polymers possessing these properties are expensive and difficult to process. Thus, rather inexpensive raw material cost and low monomer or precursor viscosity are rare but highly desirable. It is a goal of the current project to develop a material that exhibits as many these seemingly conflicting properties as possible.

In this paper, a novel, anilinic cyanate-ester-functional benzoxazine (hereinafter abbreviated as PH-acy) was synthesized, and the structure was studied by ^1H NMR, ^{13}C NMR, differential scanning calorimetry (DSC), and Fourier transform infrared spectroscopy (FT-IR). Its polymer was characterized by thermogravimetric analysis (TGA) and dynamic mechanical analysis (DMA). It is further the interest of this paper to compare the reaction of benzoxazine/cyanate ester blends and the benzoxazine that contains cyanate ester in itself.

2. EXPERIMENTAL SECTION

2.1. Materials. Salicylaldehyde (98%), 4-aminophenol (97.5%), sodium borohydride (98%), paraformaldehyde (96%), cyanogen bromide (98%), and triethylamine (99%) were used as purchased from Sigma-Aldrich. Dimethylacetamide (99%), 1,4-dioxane (99%), and anhydrous acetone (99%) were from Fisher Scientific.

2.2. Monomer Synthesis. **2.2.1. Synthesis of 2-((4-Hydroxyphenylamino)methyl)phenol.** 2-((4-Hydroxyphenylamino)methyl)phenol adopted the basic approach used by Ronda¹⁷ and Lin¹⁸ et al. but modified to suit the special nature of bisphenolic structure where one of the phenolic group is intramolecularly hydrogen bonded and the other intermolecularly hydrogen bonded. Salicylaldehyde (4.76 g, 0.04 mmol), 4-aminophenol (4.26 g, 0.04 mmol), and dimethylacetamide (DMAc, 50 mL) were added into a flask and stirred at ambient temperature for 24 h. Sodium borohydride (0.775 g, 0.02 mmol) was added in the solution every 1 h three times and continuously stirred at ambient temperature for more than 12 h. After the reaction, the resulting solution was poured into 500 mL of water. The precipitate was washed several times with water and dried overnight under vacuum at 50 °C. Yield: 4.79 g, white powder, 39%. ^1H NMR (300 MHz, DMSO- d_6 , ppm): δ 4.08 (d, 2H, ArCH₂NH), 5.36 (s, 1H, ArCH₂NH), 6.44 (q, 4H, ArH), 6.69 (t, 1H, ArH), 6.76 (d, 1H, ArH), 7.00 (t, 1H, ArH), 7.15 (d, 1H, ArH), 8.38 (s, 1H, OH), 9.46 (s, 1H, OH).

2.2.2. Synthesis of 3-(4-Cyanatophenyl)-3,4-dihydro-2H-benzoxazine [PH-acy]. 2-((4-Hydroxyphenylamino)methyl)phenol (0.95 g, 4.40 mmol) and paraformaldehyde (0.14 g, 4.80 mmol) in 1,4-dioxane (25 mL) were stirred at 100 °C for 18 h. After the reaction, the solvent was dried under vacuum, and cyanogen bromide (0.46 g, 4.40 mmol) and anhydrous acetone (25 mL) were added. The solution

was cooled to 0 °C under a nitrogen atmosphere, and 5 mL of acetone solution of triethylamine (0.45 g, 4.40 mmol) was added dropwise into the solution and stirred at 0 °C for 30 min. The precipitates were filtered, and the filtrate was dried at room temperature. The resulting compound was redissolved in ethyl acetate and washed with water three times. The solution was dried under vacuum to afford white crystal. Yield: 0.60 g, 54%; mp 77 °C. ^1H NMR (300 MHz, DMSO- d_6 , ppm): δ 4.66 (s, 6H, C-CH₂-NPh), 5.44 (s, 6H, O-CH₂-NPh), 6.72 (d, 1H, ArH), 6.86 (t, 1H, ArH), 7.09 (m, 2H, ArH), 7.27 (q, 4H, ArH). ^{13}C NMR (600 MHz, DMSO- d_6 , ppm): δ 79.1, 109.9, 116.9, 117.1, 119.5, 121.3, 121.6, 127.9, 128.4, 147.1, 147.4, 154.4. FTIR (KBr), cm^{-1} : 2271 (CN stretching of cyanate ester), 2237 (CN stretching of cyanate ester), 1498 (stretching of substituted benzene ring), 1226 (asymmetric stretching of C-O-C), 1165 (asymmetric stretching of C-N-C), and 950 (out-of-plane C-H of benzene ring of benzoxazine). Anal. Calcd for C₁₅H₁₂N₂O₂: C, 71.42; H, 4.79; N, 11.10. Found: C, 70.44; H, 4.64; N, 11.10.

2.3. Preparation of Poly(PH-acy). The molten PH-acy was cast over a glass plate at 80 °C. The resulting film was placed in convection oven and polymerized at 220 °C for 2 h. It was cooled to room temperature, and the dark brown film was obtained.

2.4. Characterization. ^1H NMR spectra were acquired in deuterated dimethyl sulfoxide (DMSO- d_6) with tetramethylsilane as an internal standard on a Varian Oxford AS300 at a proton frequency of 300 MHz. The ^{13}C NMR spectrum was acquired in deuterated dimethyl sulfoxide (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 ^1H and ^{13}C NMR was 16 and 1024, respectively. A relaxation time of 10 s was used for the integrated intensity determination of ^1H NMR spectra for quantitative analysis. Support to molecular studies by NMR was done by Fourier transform infrared spectroscopy (FT-IR) using a 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 for analysis and compressed into a 13 mm pellet or coated on a 25 mm KBr circular disk. A TA Instruments DSC model 2920 was used with a heating rate of 10 °C/min and a nitrogen flow rate of 60 mL/min for the tests of differential scanning calorimetric (DSC) study. Thermogravimetric analysis (TGA) was carried out on a TA Instruments Q500 TGA with a heating rate of 10 °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

The synthesis of cyanate ester functional benzoxazine is shown in Scheme 1. Incorporation of cyanate ester onto a benzoxazine molecule was achieved first by closing the oxazine ring while maintaining one of the two phenolic hydroxyl groups unreacted. Phenolic hydroxyl group-containing benzoxazine cannot be simply synthesized with one-pot Mannich reaction of

phenol, 4-aminophenol, and formaldehyde due to the presence of two different hydroxyl groups. However, synthesis of a phenolic hydroxyl group-containing benzoxazine was reported by Andreu and Ronda¹⁷ and Lin¹⁸ et al. using the approach to close the intramolecularly hydrogen-bonded phenolic hydroxyl group and 2-hydroxybenzylamine into a benzoxazine moiety. This 2-hydroxybenzylamine was prepared from the reduction of the Schiff base that was obtained from the reaction of salicylaldehyde and 4-aminophenol. The cyanate ester functional benzoxazine, abbreviated as PH-acy, was prepared from cyanogen bromide in the presence of triethylamine. The structure of PH-acy was verified by ¹H NMR and ¹³C NMR

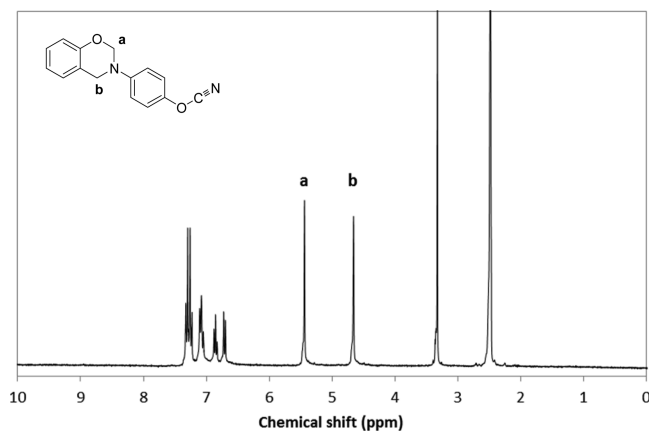


Figure 1. ¹H NMR spectrum of PH-acy in DMSO-*d*₆.

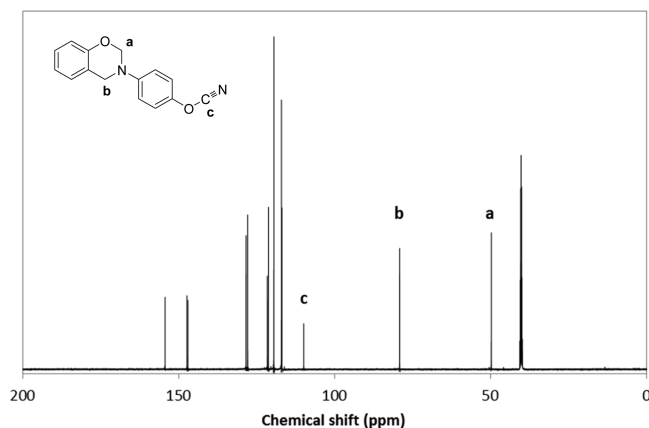


Figure 2. ¹³C NMR spectrum of PH-acy in DMSO-*d*₆.

spectra which are shown in Figures 1 and 2, respectively. In the ¹H NMR spectrum, there are two characteristic resonances at 4.66 and 5.44 ppm, which are assigned to Ar-CH₂*-N- and -O-CH₂*-N- protons, confirming the formation of the benzoxazine group. The separation of these two resonances, 0.78 ppm, is within the typical range of many benzoxazine compounds.¹⁹ The further evidence of benzoxazine ring formation was confirmed by the resonances at 49.8 and 79.2 ppm in ¹³C NMR. The characteristic carbon signal of the cyanate ester -OC*N was also observed at 109.9 ppm.

The cross-linking process was studied by DSC as shown in Figure 3. There are two exothermic maxima at 213 and 229 °C, and the onset of the first peak is around 160 °C in PH-acy. These multiple exotherms can be considered as two different cross-linking processes, namely, cyclotrimerization of cyanate

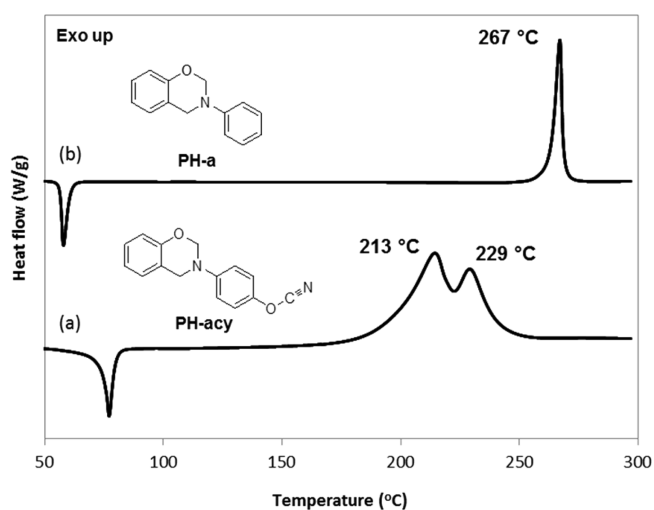


Figure 3. DSC thermograms of (a) PH-acy and (b) PH-a.

ester and ring-opening polymerization of benzoxazine, which occur separately. It is noteworthy that both exotherms of PH-acy appeared in lower temperature ranges than those of the benzoxazine/cyanate ester blends reported in the literature while similar multiple exothermic events were reported in the blend of dicyanate ester and diamine-based benzoxazine.^{12–16} This significant reduction of the polymerization temperature is not due to the phenolic impurities caused by the presence of oligomers as the PH-acy studied was quite pure and sharp crystal melting was also observed. Therefore, it is very likely that cyanate ester reaction promotes benzoxazine cationic ring-opening polymerization as proposed by the studies on benzoxazine/cyanate ester blends but more efficiently in the case where cyanate ester is part of the benzoxazine molecule.

The molecular structure was also confirmed by FT-IR spectra. The characteristic bands at 2271 and 2237 cm⁻¹ are typical OCN stretches. The band at 1226 cm⁻¹ corresponds to the antisymmetric C-O-C stretch of benzoxazine ring, whereas the 950 cm⁻¹ band is assigned to the out-of-plane mode of benzene to which oxazine ring is attached. These spectral features are all consistent with the published benzoxazine and cyanate ester frequencies. In the isothermal FT-IR studies at various temperatures, multiple polymerization processes which are observed by the DSC thermogram in Figure 3 can be simultaneously and independently followed on the molecular level. Heating at 120 °C without added initiator and/or catalyst, cyanate ester stretch mostly disappeared after 2 h, and triazine absorption derived from trimerization of cyanate esters appeared at 1368 cm⁻¹. Additionally, a significant absorption band at 1683 cm⁻¹ due to isocyanurate, which is probably formed by the rearrangement of alkyl group substituted triazine ring, was also observed. From this result, it is concluded that cyanate esters can trimerize at first at 120 °C while benzoxazine ring subsequently opens as signified by the reduction of the band located at 950 cm⁻¹. Spectrum b also provides important information on the order of these two events happening. While the signature of cyanate ester almost completely disappeared at 120 °C after 2 h, the intensity of the 950 cm⁻¹ band that represents unreacted benzoxazine group mostly remains albeit some reduction in intensity. Thus, this clearly establishes the order of these two events, namely cyanate ester trimerizes first. After heating at 170 °C for 2 h, both bands of cyanate ester at 2271 and 2237 cm⁻¹ and benzoxazine at 950

cm^{-1} disappeared. As increasing temperature for further cross-linking, there are almost no significant changes in the FT-IR spectra, and triazine and isocyanurate bands still coexist even heating at 220 °C for 2 h. There are various hypotheses^{13–15} reported on the polymerization mechanism of the blend of benzoxazine and cyanate ester. However, none of them can completely explain the polymerization behavior of this cyanate ester incorporated benzoxazine. A further detailed study on the cyanate ester functional benzoxazine will be discussed to clarify the polymerization mechanism. However, important consequence of the current study is that this novel benzoxazine offers possibility of polymerizing at significantly lower temperature than the majority of benzoxazines reported in the literature. As lowering the polymerization temperature of benzoxazine resins is one of few very strong interests in the benzoxazine research community, the observation reported in this paper contributes toward this goal.

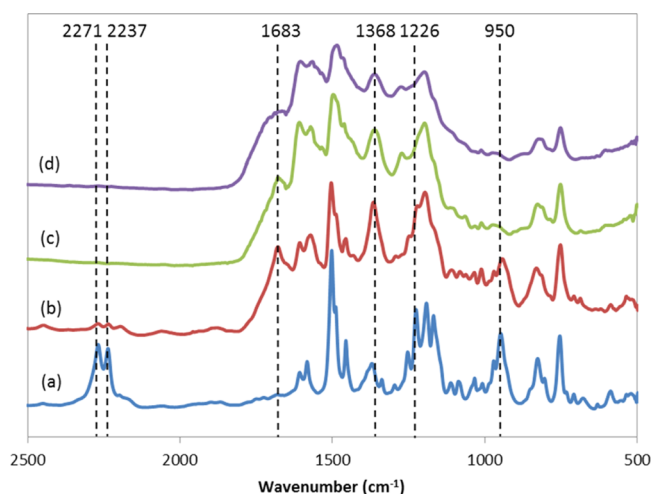


Figure 4. FT-IR spectra of PH-acy (a) monomer, (b) polymerized at 120 °C/2 h, (c) 170 °C/2 h, and (d) 220 °C/2 h.

The polymerization kinetic study of PH-acy can be performed with nonisothermal DSC scans at different heating rates, 5, 10, 15, 20, and 25 °C/min, to determine the apparent activation energy of the polymerization process. The Kissinger²⁰ and Ozawa²¹ methods have been used to determine the activation energy based on these DSC results shown in Figures 5, 6, and 7. The activation energies calculated from the slope of the Kissinger and Ozawa's plots of the first exotherm

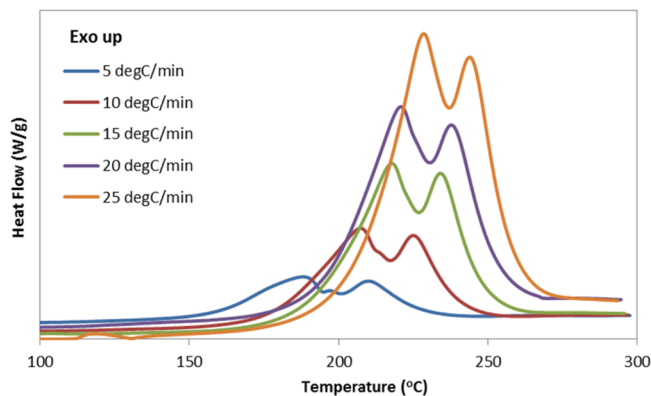


Figure 5. DSC thermograms of PH-acy for several heating rates.

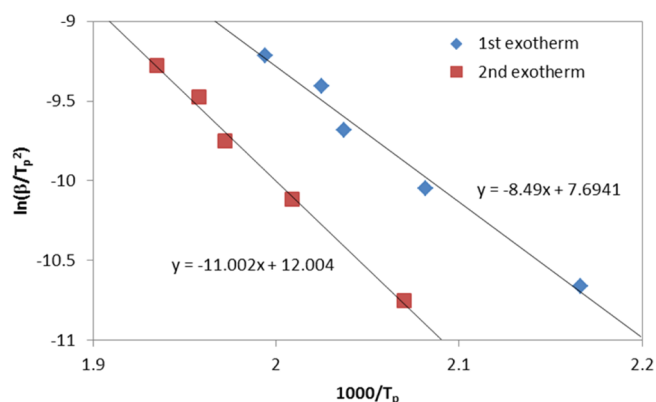


Figure 6. Kissinger plot for determination of the activation energy of PH-acy.

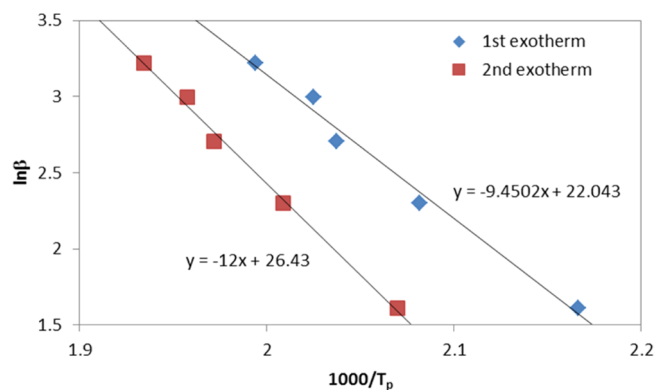


Figure 7. Ozawa plot for determination of the activation energy of PH-acy.

are about 71 and 79 kJ/mol. For the second exotherm are 91 and 100 kJ/mol, respectively, as shown in Table 1. The

Table 1. Activation Energy of PH-acy Calculated by Kissinger's and Ozawa's Methods

	activation energy (E_a , kJ/mol)	
	Kissinger's plot	Ozawa's plot
first exotherm	71	79
second exotherm	91	100

activation energies obtained for the first exotherm agrees with that for the bisphenol A dicyanate, which was reported to be 71 kJ/mol,²² and the second exotherm is also within the range of activation energy for bifunctional benzoxazines, 81–117 kJ/mol.^{23,24} These data strongly support that trimerization of cyanate ester groups occurs first followed by benzoxazine polymerization, which were hypothesized from the FT-IR spectra shown in Figure 4. It is interesting to note that as the heating rate is reduced, the complexity of first exotherm becomes more visible. It appears that overlapped peaks exist in the 170–200 °C range. Broad maxima at approximately 175 and 187 °C are heavily overlapped, whereas a weak but visible small peak also appears around 196 °C. Contrary to these complex cyanate ester exotherms, the peak due to the benzoxazine polymerization seems to show a single process. Therefore, the apparent activation energy for the cyanate ester polymerization reported above is an average value of those processes and thus should be considered only as a guide.

The TGA thermogram of PH-acy polymerized at 220 °C for 2 h is shown in Figure 8. Poly(PH-acy) has 65% char yield at

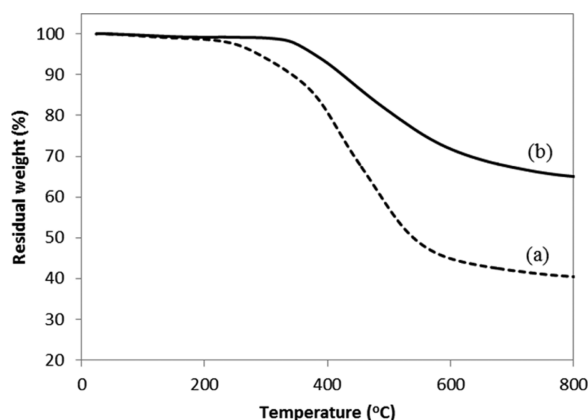


Figure 8. TGA thermogram of poly(PH-a) (a) and poly(PH-acy) (b) polymerized at 220 °C/2 h.

800 °C, which is significantly higher than the polybenzoxazine without cyanate ester, poly(PH-a). This value is higher than that of any blends of benzoxazine and cyanate ester which are thus far reported or typical dicyanate ester polymers which show char yields lower than 60%.²⁵ For thermal degradation of polybenzoxazine, evaporation of amine portion should be considered and is already studied by Ishida²⁶ and Hacıoglu²⁷ et al. The cyanate ester group helps the amine moiety to covalently attach to the cross-linked networks and can prevent from decomposition or evaporation of aniline portion during heating. From the summary of TGA thermogram shown in Table 2, significant enhancement of thermal stability with cyanate ester as much as over 80 °C for both 5 and 10% weight loss temperatures, T_{d5} and T_{d10} , has been observed.

The DMA thermogram of PH-acy polymerized at 220 °C for 2 h is shown in Figure 9. The glass transition temperature, T_g , is determined by the peak temperature of the loss modulus, E'' ; however, the T_g is frequently determined by the peak position of $\tan \delta$ for polybenzoxazine because of difficulty of recognizing the precise peak position in the E'' spectrum. For this polymer, we can observe the T_g on both loss modulus and $\tan \delta$ curves, 284 and 265 °C, respectively. In order to explain these rather high T_g of poly(PH-acy), the following equation for rubbery plateau storage modulus at $T_g + 40$ °C was used to calculate the cross-link density.²⁸

$$d_{\text{cross-link}} = E' / 2(1 + \gamma)RT$$

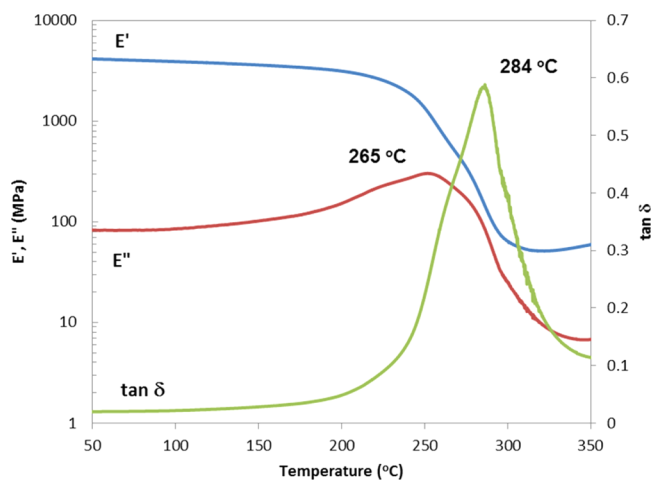


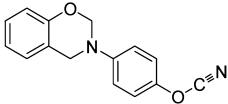
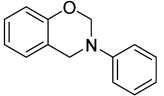
Figure 9. DMA thermogram of poly(PH-acy).

where E' is the storage modulus (dyn/cm^2) of the polymer at temperature T , R is the gas constant, and γ is Poisson's ratio which is assumed to be 0.5 for incompressible networks. $d_{\text{cross-link}}$ is the cross-link density (mol/cm^3) of the polymer. The cross-link density of the poly(PH-acy) can be calculated to be $3.51 \times 10^{-3} \text{ mol}/\text{cm}^3$, which is significantly higher than polybenzoxazine derived from bisphenol A and aniline that is reported to be $1.1 \times 10^{-3} \text{ mol}/\text{cm}^3$.² Thus, its high cross-link density of poly(PH-acy) contributes to its high glass transition temperature. It should be noted that since the rubbery plateau slightly increases because of the small amount of residual reactive groups as the temperature increases beyond the T_g , the cross-link density reported here should only be considered as a guide, although the error is expected to be relatively small.

4. CONCLUSIONS

Monofunctional benzoxazine that incorporates cyanate ester functional group resulted in significant decrease in the polymerization temperature without any added initiator or catalysts. Its polymerization temperature was significantly reduced from the ordinary benzoxazine resins and even lower than the blends of benzoxazine and dicyanate ester while its polymer has high char yield above 60% and glass transition temperature over 250 °C for monofunctional benzoxazine polymer and even the blends of dicyanate ester. Thus, this material is highly attractive for the industrial use, especially for RTM (resin transfer molding) due to its simplicity, high properties, and low-energy consumption because the polymers for RTM often have to sacrifice thermal or/mechanical properties to accomplish their higher processability. Addition-

Table 2. Summary of TGA Thermogram Results

Monomer	Abbreviation	5% Weight Loss (°C)	10% Weight Loss (°C)	Char Yield (%)
	PH-acy	384	428	65
	PH-a	294	347	40

ally, even blends of this benzoxazine with other polymers are promising in terms of reinforcement of processability and properties.

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Notes

The authors declare no competing financial interest.

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