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Study on the co-reaction of benzoxazine and triazine through a triazine-containing benzoxazine

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To study the co-reaction of benzoxazine and triazine structure, a triazine-containing benzoxazine **(P-tta)** was prepared by a nucleophilic substitution of 4-(2H-benzo[e][1,3]oxazin-3(4H)-yl)phenol **(P-ap)** with 2,4,6-trichloro-1,3,5-triazine. DSC thermograms show that the exothermic temperature of **P-tta** is lower than that of the other benzoxazine with a similar structure except for the triazine structure, so we speculate that the forward polymerization is related to the existence of the triazine structure. Through IR monitoring of the curing process, we propose that the curing reactions of **P-tta** include a concerted co-reaction between the triazine and benzoxazine, and a self-polymerization of benzoxazine. A thermoset with a high T_g (279 °C, DMA data), a low thermal expansion coefficient (32 ppm/°C), and high thermal stability ($T_{d5\%}$ 417 °C) can be obtained through the curing of **P-tta.**

Introduction

Fulled cured cyanate esters exhibit high glass transition temperature, high thermal stability, and low dielectric constant.[1-11] They have been used in the electronics, especially in printed circuit board for high frequency communication. Based on the excellent thermal properties of cured cyanate esters, incorporating cyanate ester into benzoxazine is expected to improve properties of polybenzoxazines.

Blends of benzoxazine and cyanate ester have been actively studied by multiple research groups such as Nair et al.,[12] Kimura et al.,[13] Gu et al.,[14] and Lin et al.[15] Different curing reactions have been reported, but they all agreed that the blends are miscible, and the cyclotrimerization of cyanate ester is accelerated in the presence of benzoxazine. To discuss the miscibility, Nair et al. and Kimura et al. proposed that the phenolic OH group resulted from the ring opening reaction of benzoxazine co-reacted with cyanate ester to form polycyanurate as a part of the polybenzoxazine matrix.[12, 13] Gu et al. suggested that the opened oxazine rings could insert into triazine rings, and then, some of the triazine isomerized to isocyanurate.[14] In our previous work, we reported a concerted reaction mechanism for the co-reaction of benzoxazine and triazine that resulted from the cyclotrimerization of cyanate ester.[15] Furthermore, to discuss the origin of rapid cyclotrimerization of cyanate ester, Nair et al. and Kimura et al. indicated that the phenol resulting from the ring-opening polymerization of benzoxazine catalyzes the cyclotrimerization.[12, 13, 16] Gu et al. reported that the fundamental catalyst for the cyclotrimerization of cyanate ester is not the phenolic hydroxyl but the oxygen anion.[17] Recently, we unexpectedly observed that gelation occurred in a methyl ethyl ketone solution of P-oda/BACY (1/1 mol/mol) blend after 24 h at 30 °C, in which P-oda is a 4,4'-oxydianiline/phenol-based benzoxazine and BACY is a dicyanate ester of bisphenol A (Figure 1.). We proposed that the unpaired nitrogen electrons of benzoxazine catalyzed the trimerization of cyanate ester to form a triazine structure.[18] Based on the above literatures, the triazine structure resulting from cyclotrimerization of cyanate ester playss an important role in the co-reaction. To the best of our knowledge, all research has focused on the co-reaction of cyanate ester with benzoxazine but no research has independently discussed the co-reaction of triazine with benzoxazine. In this work, to study the co-reaction of benzoxazine and triazine, we synthesized a triazine-containing benzoxazine (P-tta). An advantage can be achieved in this system, the built-in triazine structure makes analysis of the curing reaction easier since it avoids interference from benzoxazine-catalyzed cyclotrimerization of cyanate ester in the benzoxazine/cyanate ester blend. The ring-opening mechanism of benzoxazine in the presence of the triazine structure could be evaluated clearly. In addition to the curing mechanism, the thermal properties of the resulting thermoset were studied in this work.

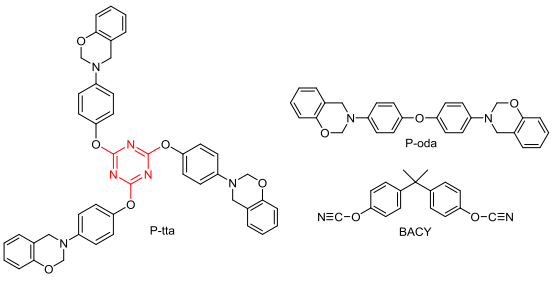

Figure 1. The structures of **P-tta**, P-oda, and BACY.

Experimental

Materials. 2-Hydroxybenzaldehyde, 4-aminophenol, and sodium borohydride ($NaBH_4$) were purchased from Alfa. Paraformaldehyde,

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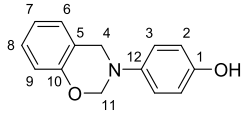
2,4,6-trichloro-1,3,5-triazine, and triethylamine were purchased from Acros. 4,4'-Diamino diphenyl ether/phenol-based benzoxazine (P-oda) was prepared in our lab, according to a previously reported procedure.[19] All solvents (HPLC grade) were purchased from various commercial sources and used without further purification.

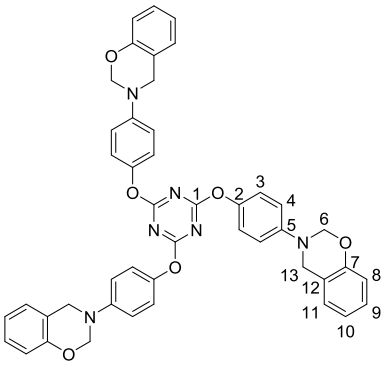
Characterization. Differential scanning calorimetry (DSC) scans were obtained using a Perkin-Elmer DSC 7 in a nitrogen atmosphere at a heating rate of 10 °C/min. Thermogravimetric analysis (TGA) was performed with a Perkin-Elmer Pyris1 at a heating rate of 20 °C/min in an atmosphere of nitrogen or air. Dynamic mechanical analysis (DMA) was performed with a Perkin-Elmer Pyris Diamond DMA with a sample size of 5.0 cm x1.0 cm x0.2 cm. The storage modulus E' and tan δ were determined as the sample was subjected to the temperature scan mode at a programmed heating rate of 5 °C/min at a frequency of 1Hz. The test was performed by a bending mode with an amplitude of 5 μm. Thermomechanical analysis (TMA) was performed with a Perkin-Elmer Pyris Diamond TMA at a heating rate of 5 °C/min from 50 °C to 240 °C. The coefficient of thermal expansion (CTE) in the temperature range of 50-150 °C was recorded. The sample pellet for IR measurement was prepared by blending sample with KBr salt with a weight ratio of 1:100. IR spectra were obtained from at least 32 scans in the standard wavenumber range of 400–4000 cm^{-1} using a Perkin-Elmer RX1 infrared spectrophotometer.

Synthesis of 4-(2H-benzo[e][1,3]oxazin-3(4H)-yl)phenol (**P-ap**). **P-ap** was prepared from 2-hydroxybenzaldehyde and 4-aminophenol by a three-step procedure.[19] 2-hydroxybenzaldehyde 5 g (40.9 mmol), 4-aminophenol 4.468 g (40.9 mmol) and ethanol 50 mL were introduced into a 500 mL round bottom glass flask equipped with a nitrogen inlet and a magnetic stirrer. The reaction mixture was stirred at room temperature for 12 h. $NaBH_4$ 0.52 g (13.7 mmol) was added every hour. After $NaBH_4$ was added three times (13.7 × 3 mmol), the reaction mixture was further stirred at room temperature for 12 h. The mixture was then poured into water (500 mL) and stirred. The yellow precipitate was filtered and dried at 60 °C. 2-(((4-Hydroxyphenyl)amino)methyl)phenol with a melting point of 131 °C (DSC) and a delta enthalpy of 149 J/g was obtained. ^{1}H-NMR (DMSO-d_6), δ=4.11(s, 2H, ph-CH_2-N), 5.33(s, 1H, -NH), 7.20-6.40 (m, 8H), 8.40 (s, 1H, -OH), 9.50 (s, 1H, -OH).

2-(((4-hydroxyphenyl)amino)methyl)phenol 1.0 (4.6 mmol), paraformaldehyde 0.1524 g (5.1 mmol), and 1,4-dioxane 25 mL were introduced into a 100 mL round bottom glass flask equipped with a condenser and a magnetic stirrer. The mixture was stirred at 90 °C for 16 h. After that, 1,4-dioxane was removed using a rotary evaporator. A light red viscous liquid, 4-(2H-benzo[e][1,3]oxazin-3(4H)-yl)phenol (P-ap), was obtained. ^{1}H-NMR (DMSO-d_6), δ=4.50 (2H, H^4), 5.29 (2H, H^{11}), 6.64 (d,2H, H^2), 6.70 (d,1H, H^9), 6.84 (t,1H, H^7), 6.93 (t, 2H, H^3), 7.06 (t, 1H, H^6), 7.07 (t, 1H, H^8), 8.96 (s, 1H, OH) ◦ ^{13}C-NMR (DMSO-d_6), δ=49.80 (C^4), 80.08 (C^{11}), 115.52 (C^2), 116.10 (C^9), 119.80 (C^3), 120.28 (C^7), 121.35 (C^5), 127.07 (C^6), 127.53 (C^8), 140.35 (C^{12}), 151.99 (C^{10}), 154.04 (C^1).



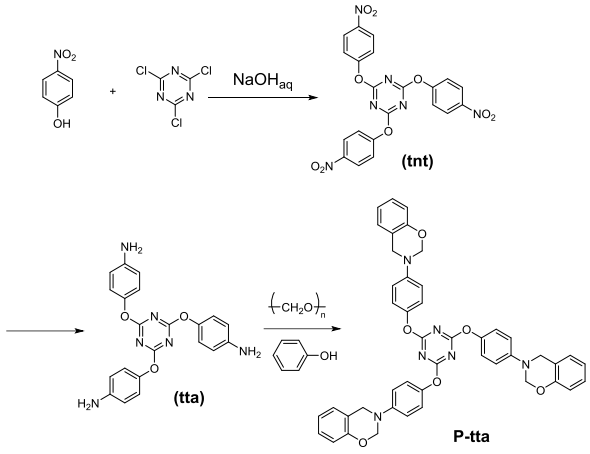
Synthesis of P-tta. P-tta was prepared through a nucleophilic substitution of 4-(2H-benzo[e][1,3]oxazin-3(4H)-yl)phenol (**P-ap**) with 2,4,6-trichloro-1,3,5-triazine. **P-ap** 1.0056 g (4.6 mmol), triethylamine 0.4701 g (4.6 mmol), and acetone 20 mL were introduced into a 100 mL round bottom glass flask equipped with a condenser and a magnetic stirrer. The solution was stirred at 3-5 °C for 1h. Cyanuric chloride 0.2770 g (1.5 mmol) dissolved in 10 mL acetone was added drop-wisely. The solution was stirred at room temperature for 1 h, then refluxed for another 1.5 h. After that, the solution was poured into water. The white precipitate was filtered, washed with acetone, and dried at 60 °C. The yield is 77%. ^{1}H-NMR (DMSO-d_6), δ=4.64 (s, 2H, H^{13}), 5.43 (s, 2H, H^6), 6.72 (d,1H, H^8), 6.86 (t,1H, H^{10}), 7.06 (t, 1H, H^9), 7.08 (d, 2H, H^4), 7.11 (d, 1H, H^{11}), 7.13 (d, 2H, H^3) ◦ ^{13}C-NMR (DMSO-d_6), δ=40.09 (C^{13}), 78.97 (C^6), 116.22 (C^8), 118.26 (C^3), 120.50 (C^{10}), 121.12 (C^{12}), 121.92 (C^4), 127.19 (C^{11}), 127.68 (C^9), 144.99 (C^5), 145.75 (C^7), 153.84 (C^2), 173.26 (C^1).



Sample preparation and curing procedure. P-tta was heated on a hot plate at about 150 °C with continuous stirring, then poured into aluminum modes with dimensions of 5.0 cm x1.0 cm x0.3 cm (for DMA measurement) and 1.0 cm x 1.0 cm x 0.3 cm (for TMA measurement), and cured at 180 °C (2 h), followed by 200 °C (2 h), 220 °C (2 h). A further curing at 240 °C (2 h), or 240 °C (2 h) followed by 260 °C (2 h) was applied for property comparison. After that, the samples were allowed to cool slowly to room temperature to prevent cracking. The thermoset of **P-tta** is named **P(P-tta)-X**, in which X is the final curing temperature. For example, the final curing temperature and period is 240 °C (2 h) for **P(P-tta)-240**.

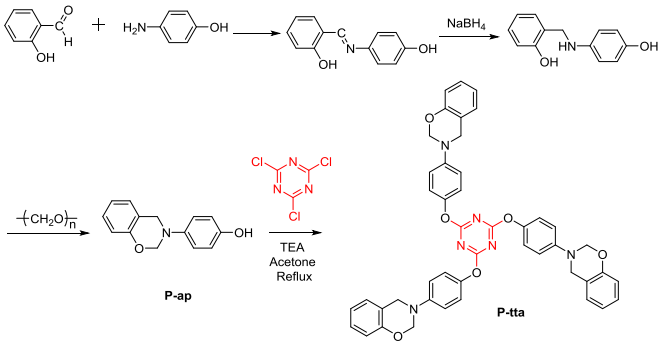
Results and Discussion

Synthesis of benzoxazine P-tta. We initially attempted to synthesize **P-tta** through Mannich condensation of phenol, paraformaldehyde and a triazine-containing triamine, 4,4',4''-((1,3,5-triazine-2,4,6-triyl)tris(oxy))trianiline (**tta**) (Scheme 1). In this strategy, a triazine-containing trinitro (2,4,6-tris(4-nitrophenoxy)-1,3,5-triazine, **tnt**) was first synthesized through a nucleophilic substitution of 4-nitrophenol with 2,4,6-trichloro-1,3,5-triazine in the presence of sodium hydroxide (^{1}H-NMR spectrum, Figure S1). To reduce **tnt** to **tta**, we initially chose hydrazine hydrate as a reducing agent. Figure S2 shows the ^{1}H-NMR spectrum of the reduction product. The characteristic peak of phenolic OH appeared at 8.3 ppm . This result explains that the ether bond of **(tnt)** might be broken in the presence of hydrazine hydrate. To avoid this phenomena, we then used a high pressure procedure using hydrogen as a reducing agent. However, the hydrogenation led to undesired byproducts under various conditions that we have applied, so the synthetic route could not be carried out in this work.



Scheme 1. Attempted synthesis of **P-tta** through Mannich condensation of phenol, paraformaldehyde and a triazine-containing triamine (**tta**).

We then redesigned our strategy and prepared **P-tta** through a nucleophilic substitution of 4-(2H-benzo[e][1,3]oxazin-3(4H)-yl)phenol (**P-ap**) with 2,4,6-trichloro-1,3,5-triazine in the presence of triethylamine (Scheme 2). The precursor, **P-ap**, was prepared by a three-step procedure from 4-aminophenol and 2-hydroxybenzaldehyde.[19] Figure 2 shows the ^{1}H-NMR spectra of **P-ap** and P-tta. The disappearance of the signal for phenolic OH at 8.96 and the shift in the characteristic peaks for benzoxazine from 5.29 to 5.43 ppm, and from 4.50 to 4.64 ppm support the nucleophilic substitution. No signal at around 3.80 ppm corresponding to N-C**H$_2$**-ph (resulting from the ring opening of benzoxazine) was observed,[20] revealing the purity of synthesized benzoxazines. Figure 3 shows the ^{13}C-NMR spectra of **P-ap** and **P-tta**. The characteristic peaks of benzoxazine shift from 80.08 to 78.97 ppm, and from 49.80 to 49.09 ppm, supporting the nucleophilic substitution. The combination of ^{1}H and ^{13}C-NMR spectra confirm the structure of **P-tta**.



Scheme 2. Synthesis of **P-ap** and **P-tta**.

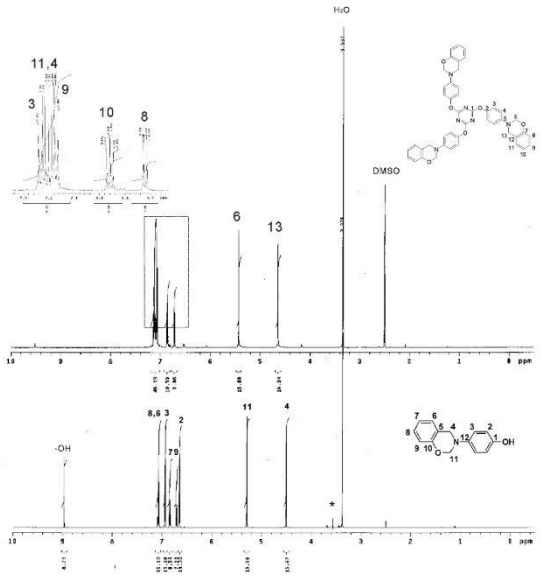


Figure 2. ^{1}H-NMR spectra of **P-ap** and **P-tta**.

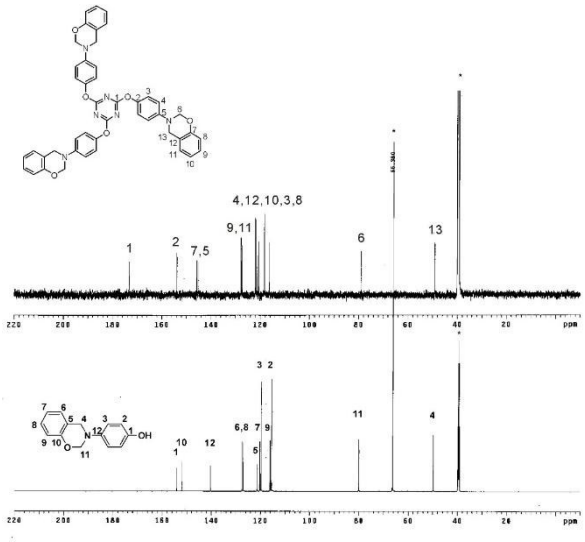


Figure 3. ^{13}C-NMR spectra of **P-ap** and **P-tta**.

Microstructure. Figure 4 shows the DSC thermograms of **P-oda** and **P-tta** at a heating rate of 10 °C/min. The exothermic temperature of **P-tta** is lower than that of **P-oda**, showing a forward polymerization. **P-tta** and **P-oda** have the same structure (O-ph-oxazine, Figure 1) except for the triazine structure, so we speculate that the forward polymerization is related to the existence of the triazine structure. IR was used to monitor the curing reactions, and explain the exothermic peaks.

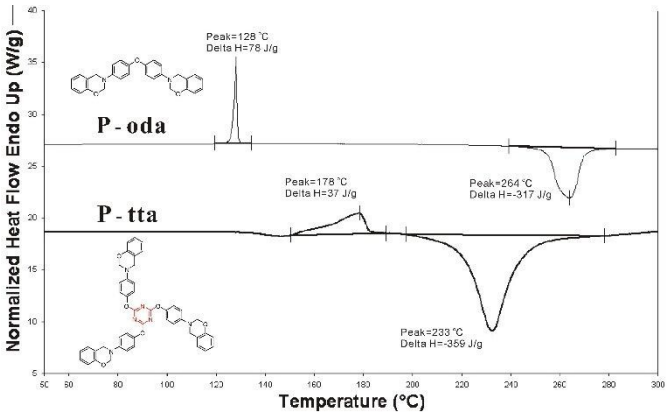


Figure 4. DSC thermograms of **P-oda** and **P-tta** at a heating rate of 10 °C/min.

Figure 5 shows the IR spectra of **P-tta** after accumulative curing at each stage for 20 min. The triazine absorptions at 1570 and 1371 cm^{-1} decrease gradually with the curing temperature. However, from the IR spectra of dicyanate ester of bisphenol A (BACY) after accumulative curing at each stage for 20 min (Figure S3), the intensity of the triazine absorptions (1367 and 1569 cm^{-1}) was maintained even after curing at 240 °C. The spectra suggests that the triazine structure of cured BACY is stable as the curing progressed. Therefore, the instability of triazine in **P-tta** shown in Figure 5 is speculated with the existence of the oxazine structure. As shown in Figure 5, the benzoxazine-related absorptions of N-CH_2-O at 947 and ph-O-C 1222 cm^{-1} decreased with the progress of the curing, and disappeared after curing at 200 °C. It has been reported that triallyl cyanurate can thermally rearrange to triallyl isocyanurate.[21, 22]. Ueda et al. reported the alkyl-aryl cyanurate will rearrange to alkyl-aryl isocyanurate.[23, 24]. Hamerton discussed the reaction between the cyanate ester and epoxy.[25]

The aryl cyanurate (triazine) can react with epoxy, forming alkyl cyanurate, which can rearrange to alkyl isocyanurate. Note that the aryl cyanurate structure is stable, and does not rearrange to aryl isocyanurate. Therefore, the direct rearrangement of aryl cyanurate to aryl isocyanurate in Scheme 3 is speculated not to occurr. The key point is how can we explain the reduction in triazine absorption (at 1371 cm^{-1}) and the formation of isocyanaurate absorption (at 1682 cm^{-1}) in Figure 5. As mentioned in Figure 4, DSC thermograms show that the ring-opening polymerization of benzoxazine in **P-tta** occurs at lower temperature than that in **P-oda,** suggesting the ring-opening polymerization is related with the existence of the triazine structure. In our previous work, we reported a concerted reaction between triazine and oxazine to explain the misbility of benzoxazine/cyanate ester blend, and to explain the reduction in triazine absorption and the formation of isocyanaurate linkage.[15] In that proposed one-step mechanism, the electron-rich oxygen (CH_2-**O**-ph) attacks the aromatic carbon next to oxygen. Then, the C=N double bond opens, and attacks the electron-deficient methylene (O-**C**H_2-N) of benzoxazine, forming isocyanurate. Study on the rearrangement of cyanurate with epoxy, we proposed a modified co-reaction mechanism for benzoxazine and triazine in **P-tta** (Path a of Scheme 4). In the first step, a zwitterion from the break of oxazine was formed at temperature around 180 °C (since the formation of isocyanurate absorption at 180 °C, as shown in Figure 5). The phenolate attacks the aromatic carbon next to oxygen (Note that the carbon is slightly electron-deficient due to the electron-withdrawing character of the oxygen and triazine structure). Then, the Ar-O bond breaks, and the oxygen anion attacks the carbocation of the zwitterion, producing a alkyl substituted cyanurate. This reaction is similar to the insertion of the glycidyl ether into the aryl cyanurate.[25] Furthermore, the alkyl substituted cyanurate rearranged to alkyl isocyanurate in the second step. (Note that the resulting structures are the same as those proposed in our previous work).[15, 26] Theoretically, one triazine structure can react with three oxazine in the concerted reaction, so the stoichiometric ratio of triazine to oxazine is one in **P-tta**. However, self-polymerization of oxazine can occur in the curing process (Path b in Scheme 4), which is supported by the phenolic OH signals at 3389 cm^{-1} in Figure 6. This leads to no stoichiometric benzoxazine to react with triazine, and explains the co-exist absorption of triazine and isocyanurate absorptions in Figure 5. Therefore, the structure of **P(P-tta)** should include isocyanurate, triazine, and ring-opened benzoxazine structures. Since the proposed reaction mechanism cannot be elucidated only by FTIR spectra, we have performed the ^{1}H NMR analysis after accumulative thermal treatment of **P-tta** at 140, 160, and 180 °C for 20 min. As shown in Figure S4, there is no reaction after thermal treatment at 140 °C. Only slight ring-opening polymerization of oxazine of **P-taa** occurred after thermal treatment at 160 °C. However, a further thermal treatment at 180 °C lead the reaction mixture only partially soluble in DMSO-d_6. Therefore, we cannot elucidate the proposed mechanism by NMR spectra. A new design of molecule that contains only one oxazine and triazine linkage and is soluble after thermal treatment is required to prove this mechanism in the future.

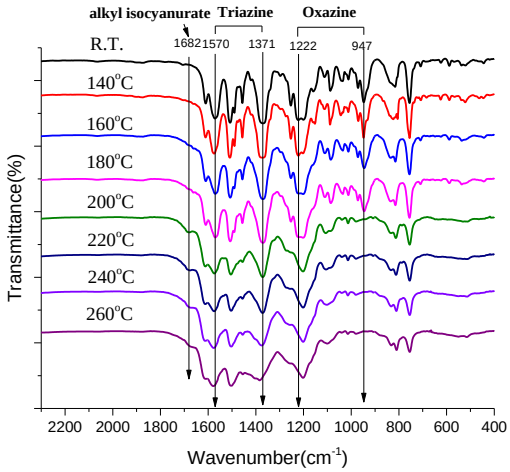


Figure 5. FT-IR spectra of **P-tta** after accumulative curing at each stage for 20 min.

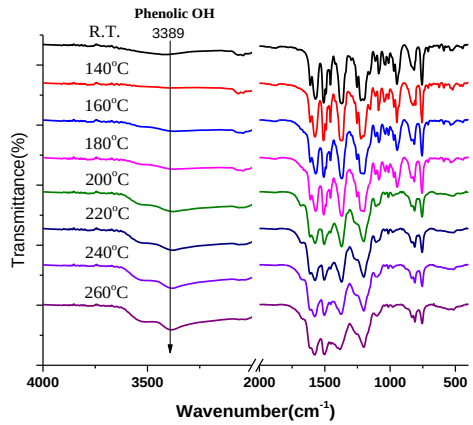
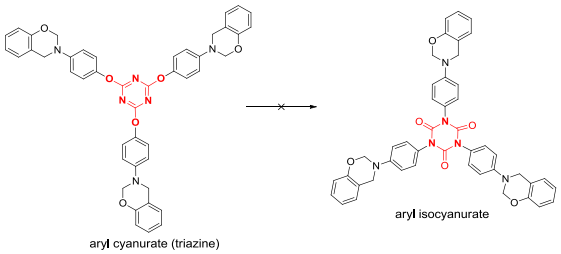
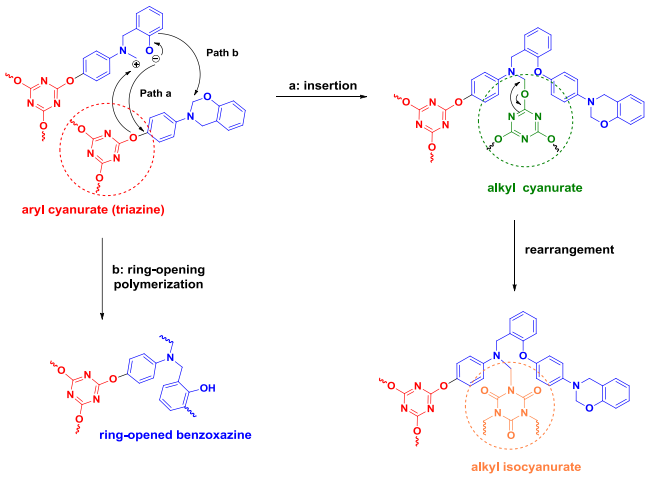


Figure 6. Enlarged FT-IR spectra of **P-tta** after accumulative curing at each stage for 20 min.



Scheme 3. The rearrangement of aryl cyanurate to aryl isocyanurate. Note that the rearrangement is speculated not to occur.



Scheme 4. Proposed curing reactions of **P-tta**.

Storage stability. In our previous work, we observe that gelation occurred in a methyl ethyl ketone solution of **P-oda**/BACY (1/1 mol/mol) blend after 24 h at 30 °C. The gel was also insoluble in tetrahydrofuran and dimethyl sulfoxide, suggesting that a crosslinking structure was present. Through IR and DSC analysis, we concluded that the tertiary amine of benzoxazine catalyzes the cyclotrimerization of cyanate ester, leading to gelation. Figure S5 shows the pictures of a dioxane solution of **P-tta** before and after thermal treatment. A homogeneous solution can be obtained after thermal treatment at 60 °C for 96 h. The result suggests that the built-in triazine structure can avoid the gelation resulting from the cyclotrimerization of cyanate ester in the benzoxazine/cyanate ester blend. Therefore, the one-component **P-tta** can avoid the gelation in the two-component benzoxazine/cyanate ester system when dissolved in a solvent to act as a varnish in preparing a copper clad laminate. This phenomena implies that **P-tta** is a potential material for making high-performance copper clad laminate.

Thermal properties of poly(P-tta). Figure 7 shows DMA thermograms of **P(P-tta)-X**, in which X is the final curing temperature. The T_g taken from the peak temperature of tanδ increased with the curing temperature, ranging from 247-279 °C. The value of 279 °C is even higher than that of all the thermosets of P-oda/BACY blend reported in our previous work.[15] In addition, the peak intensity of of the tanδ decreases with curing temperature. The result suggests that the rigidity increased with the curing process. The increased conversion and the resulting isocyanurate structure that was more rigid than the triazine structure[22, 27] might be responsible for the increased rigidity. Furthermore, the polar interaction between the carbonyl of isocyanurate and phenolic OH of ring-opened benzoxazine might also contribute to the rigidity. Figure 8 shows the TMA thermograms of **P(P-tta)-X**. The T_g taken from the onset temperature increased with the curing temperature, ranging from 231-265 °C. The coefficients of thermal expansion (CTE) are in the range of 27-32 ppm/°C, which are relatively small when compared with other polybenzoxazines (72 ppm/°C for P**(P-oda)**)[15] or poly(cyanate esters) (60 ppm/°C for thermoset of BACY)[15]. Figure 9 shows the TGA thermogram of **P(P-tta)-260** in a nitrogen atmosphere. The 5 wt% decomposition temperatures ($Td_{5\%}$) is 417 °C, and the char yield at 800 °C is 68%, demonstrating moderate-to-high thermal stability.

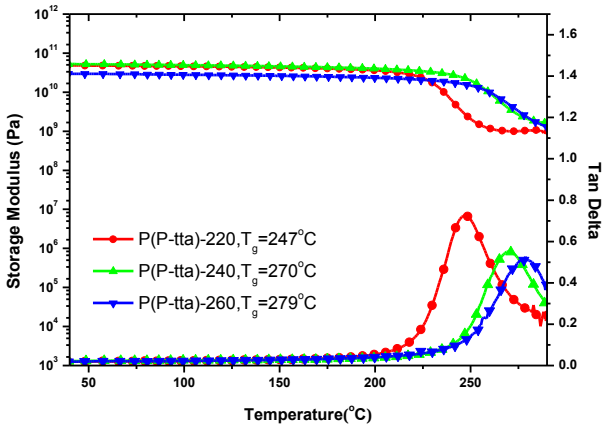


Figure 7. DMA thermograms of **P(P-tta)-X**.

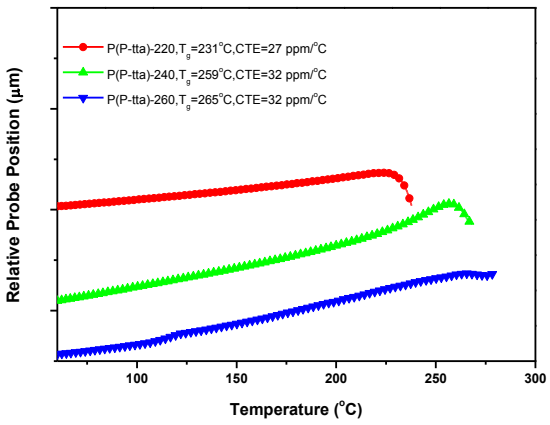


Figure 8. TMA thermograms of **P(P-tta)-X**.

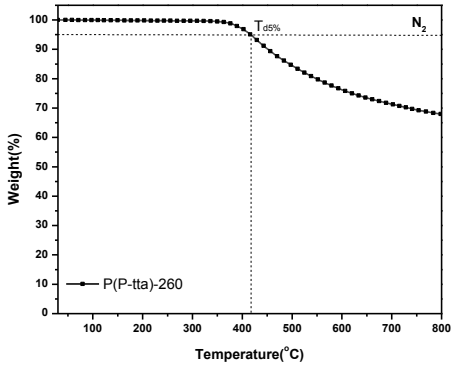


Figure 9. TGA thermogram of **P(P-tta)-260** in a nitrogen atmosphere.

Conclusions

We have successfully prepared a benzoxazine **(P-tta)** with a built-in triazine structure. We investigated the curing behaviors of **P-tta** and the thermal properties of its thermoset. According to the DSC and IR analyses, we propose that the curing reactions include a concerted co-reaction between the triazine and benzoxazine, and a self-polymerization of benzoxazine. The co-reaction of triazine and benzoxazine generates isocyanurate linkages, as supported by an increase in isocyanurate absorption at 1682 cm^{-1}, and a simultaneous decrease in triazine absorption at 1367 cm^{-1} and oxazine absorption at 947 cm^{-1}. In contrast to the instability of the benzoxazine/cyanate ester blend in a solution state, **P-tta** is stable in a solution state. The solubility test shows that the built-in triazine structure can avoid the gelation resulting from the cyclotrimerization of cyanate ester in the benzoxazine/cyanate ester blend, making **P-tta** a potential material for making a high-performance copper clad laminate. After thermal curing at 260 °C, the resulting thermoset shows a high-performance characteristic, with a T_g of 279 (DMA) and 265 °C (TMA), a coefficient of thermal expansion of 32 ppm/°C, a 5% decomposition temperature of 417 °C, and a char yield at 800 °C of 68%. The value of 279 °C is even higher than that of all the thermosets of P-oda/BACY blend reported in our previous work.[15]

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Graphical abstract

Study on the co-reaction of benzoxazine and triazine through a triazine-containing benzoxazine

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