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A study on the co-reaction of benzoxazine and triazine through a triazine-containing benzoxazine†

Ching Hsuan Lin,*[a] Yu-Chun Chou,[a] Meng Wei Wang[b] and Ru Jong Jeng[b]

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To study the co-reaction of benzoxazine and triazine, a triazine-containing benzoxazine (**P-tta**) was prepared through nucleophilic substitution of 4-(2*H*-benzo[*e*][1,3]oxazin-3(4*H*)-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 other benzoxazines 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 monitoring the curing process using IR, 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 per °C), and high thermal stability ($T_{d5\%}$ 417 °C) can be obtained through the curing of **P-tta**.

Introduction

Fully cured cyanate esters exhibit high glass transition temperatures, high thermal stabilities, and low dielectric constants.[1–11] They have been used in electronics, especially in printed circuit boards for high frequency communications. Based on the excellent thermal properties of cured cyanate esters, incorporating a cyanate ester into benzoxazine is expected to improve the 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 conclude 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 resulting from ring opening reaction of benzoxazine co-reacted with cyanate ester to form polycyanurate as 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 the 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 a **P-oda**/BACY (1/1 mol mol^{-1}) 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 (Fig. 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 literature, the triazine structure resulting from cyclotrimerization of cyanate ester plays an important role in the co-reaction. To the best of our knowledge, all of the 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.

Experimental

Materials

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

[a]*Department of Chemical Engineering, National Chung Hsing University, Taichung, Taiwan. E-mail: linch@nchu.edu.tw*

[b]*Institute of Polymer Science and Engineering, National Taiwan University, Taipei, Taiwan*

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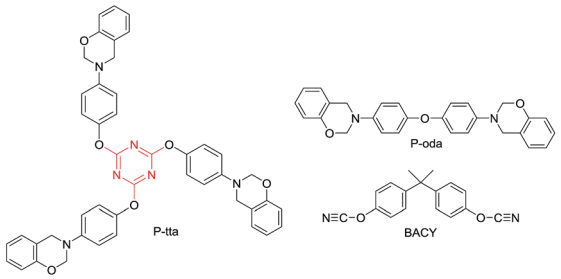


Fig. 1 The structures of **P-tta**, **P-oda**, and BACY.

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.

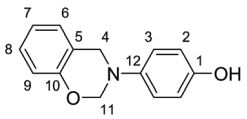
Characterization

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^{-1}. Thermogravimetric analysis (TGA) was performed with a Perkin-Elmer Pyris 1 at a heating rate of 20 °C min^{-1} 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 × 1.0 cm × 0.2 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^{-1} at a frequency of 1 Hz. The test was performed through 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^{-1} 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 through blending the 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-(2*H*-benzo[*e*][1,3]oxazin-3(4*H*)-yl)phenol (P-ap)

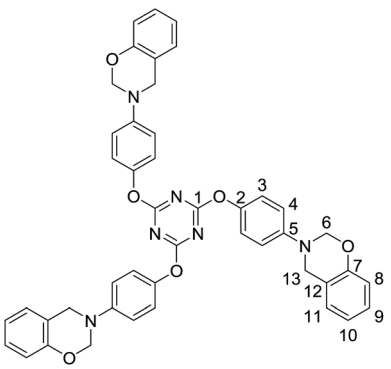
P-ap was prepared from 2-hydroxybenzaldehyde and 4-aminophenol using a three-step procedure.[19] 2-hydroxybenzaldehyde 5 g (40.9 mmol), 4-aminophenol 4.468 g (40.9 mmol) and ethanol 50 mL were introduced into a 500 mL round bottom glass flask equipped with a nitrogen inlet and a magnetic stirrer. The 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^{-1} 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 g (4.6 mmol), paraformaldehyde, 0.1524 g (5.1 mmol), and 25 mL of 1,4-dioxane 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-(2*H*-benzo[*e*][1,3]oxazin-3(4*H*)-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-(2*H*-benzo[*e*][1,3]oxazin-3(4*H*)-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 20 mL of acetone 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 1 h. Cyanuric chloride 0.2770 g (1.5 mmol) dissolved in 10 mL of 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 was 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

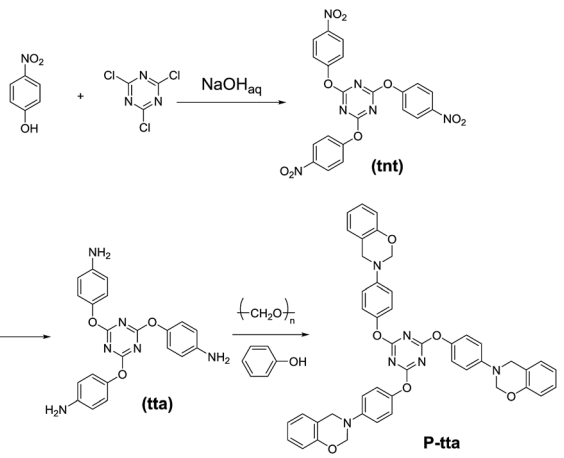
5.0 cm × 1.0 cm × 0.3 cm (for DMA measurement) and 1.0 cm × 1.0 cm × 0.3 cm (for TMA measurement), and cured at 180 °C (2 h), followed by 200 °C (2 h) and 220 °C (2 h). A further curing at 240 °C (2 h), or 240 °C (2 h) followed by 260 °C (2 h) was applied for property comparison. After that, the samples 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

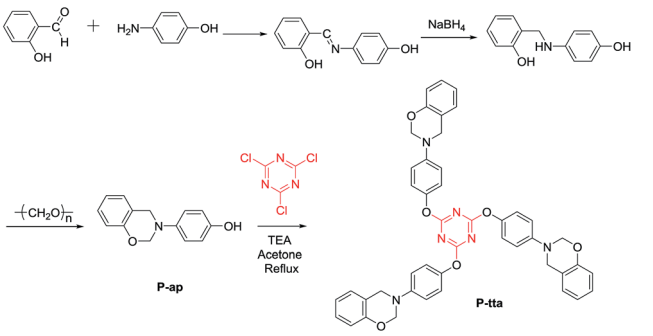
Synthesis of benzoxazine P-tta

We initially attempted to synthesize **P-tta** through a 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, Fig. S1†). To reduce **tnt** to **tta**, we initially chose hydrazine hydrate as a reducing agent. Fig. 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 the various conditions that we applied, so the synthetic route could not be carried out in this work.

We then redesigned our strategy and prepared **P-tta** through a nucleophilic substitution of 4-(2*H*-benzo[*e*][1,3]oxazin-3(4*H*)-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 using a three-step procedure from 4-aminophenol and 2-hydroxybenzaldehyde.[19] Fig. 2 shows the ^{1}H-NMR spectra of **P-ap** and **P-tta**. The disappearance of the signal for phenolic OH at 8.96 ppm 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 the synthesized benzoxazines. Fig. 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 the ^{1}H and ^{13}C-NMR spectra confirm the structure of **P-tta**.



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



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

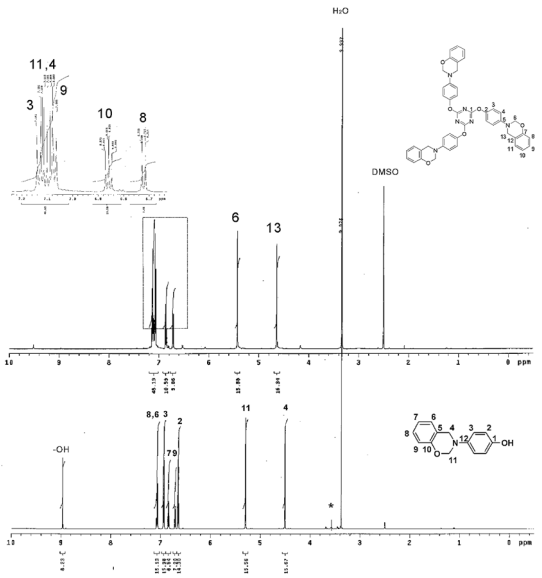


Fig. 2 ^{1}H-NMR spectra of **P-ap** and **P-tta**.

Microstructure

Fig. 4 shows the DSC thermograms of **P-oda** and **P-tta** at a heating rate of 10 °C min^{-1}. 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, Fig. 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.

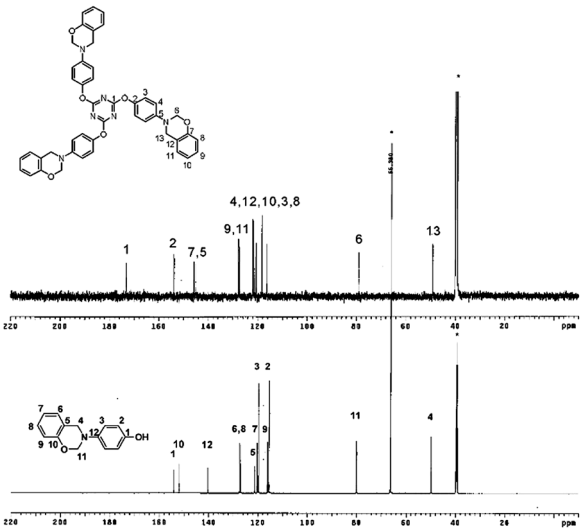


Fig. 3 ^{13}C-NMR spectra of **P-ap** and **P-tta**.

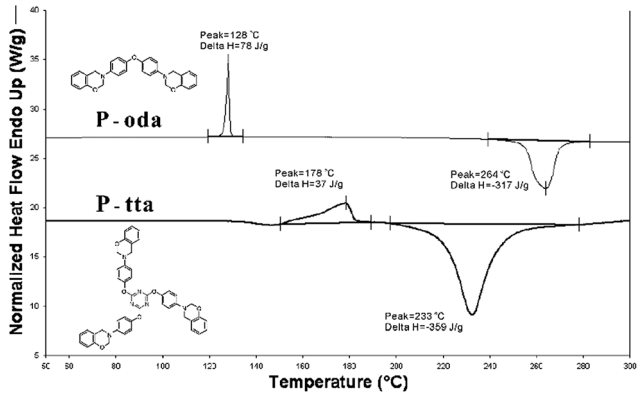


Fig. 4 DSC thermograms of **P-oda** and **P-tta** at a heating rate of 10 °C min^{-1}.

Fig. 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 the dicyanate ester of bisphenol A (BACY) after accumulative curing at each stage for 20 min (Fig. 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 Fig. 5 is speculated with the existence of the oxazine structure. As shown in Fig. 5, the benzoxazine-related absorptions of N–CH_2–O at 947 cm^{-1} and ph–O–C at 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

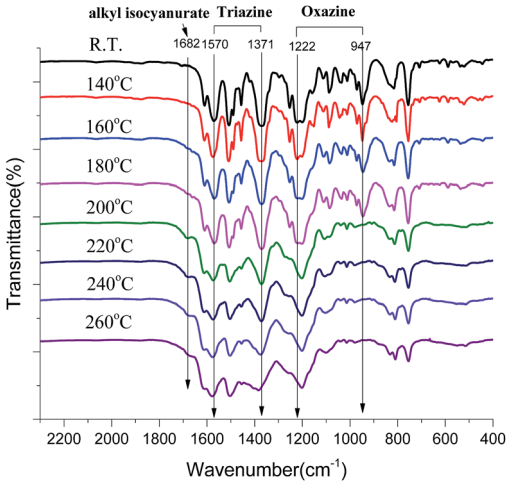
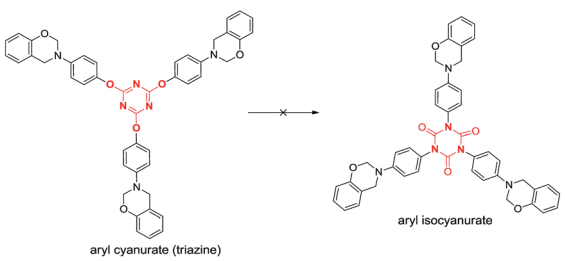
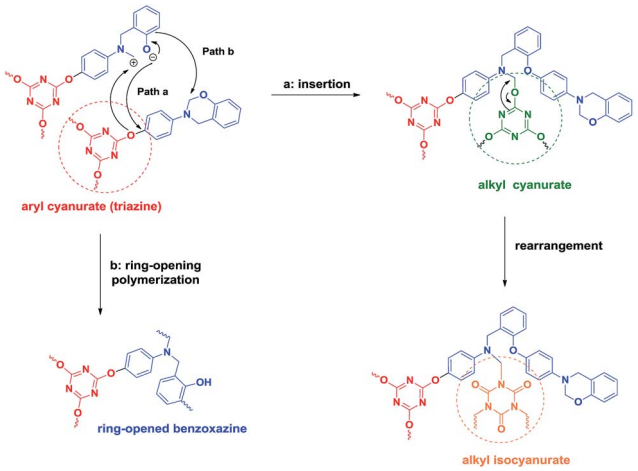


Fig. 5 FT-IR spectra of **P-tta** after accumulative curing at each stage for 20 min.

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 occur. The key point is how to explain the reduction in the triazine absorption (at 1371 cm^{-1}) and the occurrence of an isocyanurate absorption (at 1682 cm^{-1}) in Fig. 5. As shown in Fig. 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 to the existence of the triazine structure. In our previous work, we reported a concerted reaction between triazine and oxazine to explain the miscibility of the benzoxazine/cyanate ester blend, and to explain the reduction in triazine absorption and the formation of an isocyanurate linkage.[15] In that proposed one-step mechanism, the electron-rich oxygen (CH_2–**O**–ph) attacks the aromatic carbon next to the oxygen. Then, the C=N double bond opens, and attacks the electron-deficient methylene (O–**C**H_2–N) of benzoxazine, forming isocyanurate. Studying 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 breakup of oxazine was formed at temperatures around 180 °C (since the onset of isocyanurate absorption is at 180 °C, as shown in Fig. 5). The phenolate attacks the aromatic carbon next to oxygen (note that the carbon



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**.

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 an alkyl substituted cyanurate. This reaction is similar to the insertion of a glycidyl ether into an 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 oxazines 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 presence of phenolic OH signals at 3389 cm^{-1} in Fig. 6. This leads to no stoichiometric benzoxazine to react with triazine, and explains the co-existent triazine and isocyanurate absorptions in Fig. 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 by using only FTIR spectra, we have performed ^{1}H NMR analysis after accumulative thermal treatment of **P-tta** at 140, 160, and 180 °C for 20 min. As shown in Fig. S4,† there was no reaction after thermal treatment at 140 °C. Only slight ring-opening polymerization of the oxazine of **P-taa** occurred after thermal treatment at 160 °C. However, a further thermal treatment at 180 °C led to the reaction mixture being only partially soluble in DMSO-d_6. Therefore, we cannot elucidate the proposed mechanism using 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.

Storage stability

In our previous work, we observed that gelation occurred in a methyl ethyl ketone solution of a **P-oda**/BACY (1/1 mol mol^{-1}) 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. Fig. S5† shows 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 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 phenomenon implies that **P-tta** is a potential material for making high-performance copper clad laminates.

Thermal properties of poly(P-tta)

Fig. 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 tan δ 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 the **P-oda**/BACY blends reported in our previous work.[15] In addition, the peak intensity of tan δ

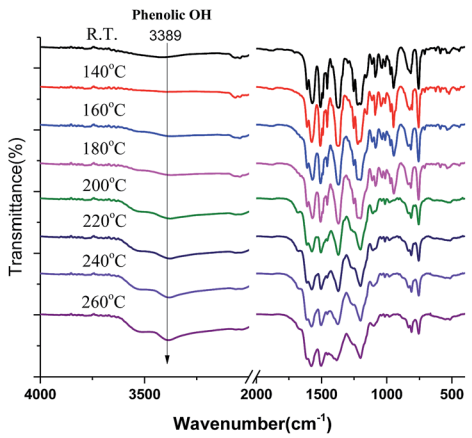


Fig. 6 Enlarged FT-IR spectra of **P-tta** after accumulative curing at each stage for 20 min.

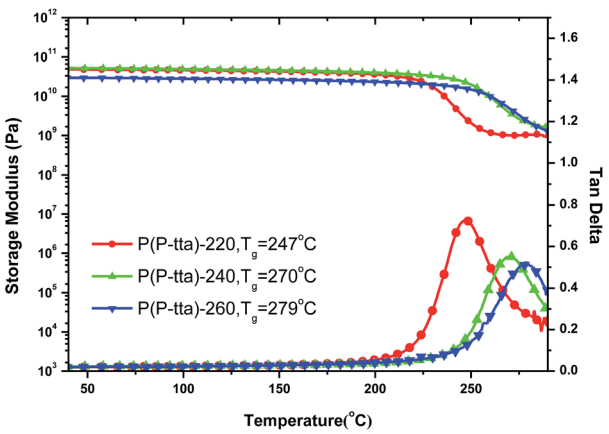


Fig. 7 DMA thermograms of P(P-tta)-*X*.

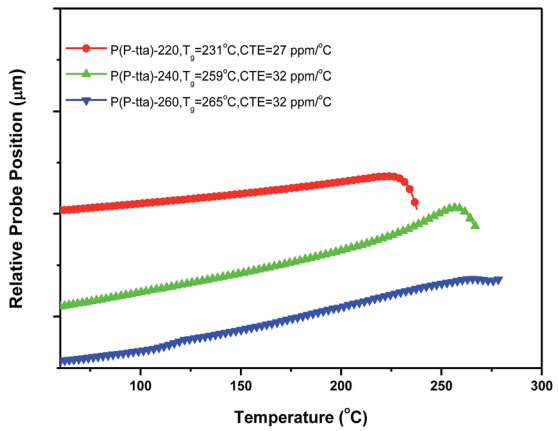


Fig. 8 TMA thermograms of P(P-tta)-*X*.

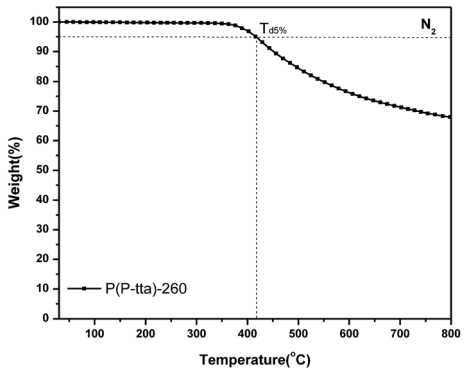


Fig. 9 TGA thermogram of P(P-tta)-260 in a nitrogen atmosphere.

decreases with curing temperature. The result suggests that 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 the isocyanurate and the phenolic OH of the ring-opened benzoxazine might also contribute to the rigidity. Fig. 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 per °C, which are relatively small when compared with other polybenzoxazines (72 ppm per °C for **P(P-oda)**)[15] or poly(cyanate esters) (60 ppm per °C for the thermoset of BACY).[15] Fig. 9 shows the TGA thermogram of **P(P-tta)-260** in a nitrogen atmosphere. The 5 wt% decomposition temperature ($T_{d5\%}$) is 417 °C, and the char yield at 800 °C is 68%, demonstrating moderate-to-high thermal stability.

Conclusions

We have successfully prepared a benzoxazine (**P-tta**) with a built-in triazine structure. We investigated the curing behavior 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 the isocyanurate absorption at 1682 cm^{-1}, and a simultaneous decrease in the 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. A 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 candidate material for making a high-performance copper clad laminate. After thermal curing at 260 °C, the resulting thermoset shows high-performance characteristics, with T_g values of 279 °C (DMA) and 265 °C (TMA), a coefficient of thermal expansion of 32 ppm per °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 the **P-oda**/BACY blends reported in our previous work.[15]

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Notes and references

1 T. Fang and D. A. Shimp, *Prog. Polym. Sci.*, 1995, **20**(1), 61–118.
2 S.-C. Lin and E. M. Pearce, *High performance thermosets: chemistry, properties, applications*, Hanser; Hanser/Gardner, Munich; New York; Cincinnati, 1994.
3 A. J. Guenthner, G. R. Yandek, M. E. Wright, B. J. Petteys, R. Quintana, D. Connor, R. D. Gilardi and D. Marchant, *Macromolecules*, 2006, **39**(18), 6046–6053.
4 A. J. Guenthner, K. R. Lamison, V. Vij, J. T. Reams, G. R. Yandek and J. M. Mabry, *Macromolecules*, 2012, **45**(1), 211–220.
5 E. M. Maya, A. W. Snow and L. J. Buckley, *Macromolecules*, 2002, **35**(2), 460–466.
6 A. W. Snow and L. J. Buckley, *Macromolecules*, 1997, **30**(3), 394–405.
7 B.-Y. Ryu and T. Emrick, *Macromolecules*, 2011, **44**(14), 5693–5700.
8 B. G. Harvey, A. J. Guenthner, W. W. Lai, H. A. Meylemans, M. C. Davis, L. R. Cambrea, J. T. Reams and K. R. Lamison, *Macromolecules*, 2015, **48**(10), 3173–3179.
9 A. J. Guenthner, M. E. Wright, A. P. Chafin, J. T. Reams, K. R. Lamison, M. D. Ford, S. P. J. Kirby, J. J. Zavala and J. M. Mabry, *Macromolecules*, 2014, **47**(22), 7691–7700.
10 E. Lopez and S. L. Simon, *Macromolecules*, 2015, **48**(13), 4692–4701.
11 H. C. Chang, H. T. Lin and C. H. Lin, *Polym. Chem.*, 2012, **3**(4), 970–978.

12 K. S. Santhosh Kumar, C. P. Reghunadhan Nair and K. N. Ninan, *Eur. Polym. J.*, 2009, **45**(2), 494–502.
13 H. Kimura, K. Ohtsuka and A. Matsumoto, *eXPRESS Polym. Lett.*, 2011, **5**(12), 1113–1122.
14 X. Li and Y. Gu, *Polym. Chem.*, 2011, **2**(12), 2778–2781.
15 C. H. Lin, S. J. Huang, P. J. Wang, H. T. Lin and S. A. Dai, *Macromolecules*, 2012, **45**(18), 7461–7466.
16 A. Sudo, R. Kudoh, H. Nakayama, K. Arima and T. Endo, *Macromolecules*, 2008, **41**(23), 9030–9034.
17 X. Li, X. Luo, M. Liu, Q. Ran and Y. Gu, *Mater. Chem. Phys.*, 2014, **148**(1–2), 328–334.
18 M. W. Wang, R. J. Jeng and C. H. Lin, *Macromolecules*, 2015, **48**(8), 2417–2421.
19 C. H. Lin, S. L. Chang, C. W. Hsieh and H. H. Lee, *Polymer*, 2008, **49**(5), 1220–1229.
20 X. Ning and H. Ishida, *J. Polym. Sci., Part A: Polym. Chem.*, 1994, **32**(6), 1121–1129.
21 Y. Nakamura, K. Mori, K. Tamura and Y. Saito, *J. Polym. Sci., Part A-1: Polym. Chem.*, 1969, **7**(11), 3089–3100.
22 J. K. Gillham and C. C. Mentzer, *J. Appl. Polym. Sci.*, 1973, **17**(4), 1143–1164.
23 Y. Saito, H. Matsumoto, T. Higashihara and M. Ueda, *J. Polym. Sci., Part A: Polym. Chem.*, 2013, **51**(18), 3950–3955.
24 K. Tsuchiya, E. Goto, Y. Ishida, T. Higashihara, A. Kameyama and M. Ueda, *J. Polym. Sci., Part A: Polym. Chem.*, 2015, **53**(5), 692–698.
25 J. P. Pascault, J. Galy and F. Méchin, Additives and modifiers for cyanate ester resins, in *Chemistry and Technology of Cyanate Ester Resins*, ed. I. Hamerton, Springer, Netherlands, 1994, pp. 112–150.
26 C. H. Lin, M. W. Wang, Y. W. Chou, H. C. Chang, T. Y. Juang and W. C. Su, *RSC Adv.*, 2015, **5**(14), 10165–10171.
27 J. K. Gillham and A. F. Lewis, *Nature*, 1962, **195**(4847), 1199.