

Branched phenyl-*s*-triazine moieties to enhance thermal properties of phthalonitrile thermosets

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ABSTRACT Heat-resistant materials have made tremendous progress in marine, aerospace, and microelectronic fields. Herein, a new class of phthalonitrile (PN) resins, branched poly (biphenyl ether triphenyl-*s*-triazine)-phthalonitriles (BP-CNs), were successfully synthesized via a two-step, one-pot reaction, on the basis of 2,4,6-tris(4-fluorophenyl)-1,3,5-triazine (TFPT) and 4,4'-biphenol (BP). 4,4'-diaminodiphenyl sulfone (DDS) was employed to facilitate the curing reaction, and successful realization of curing behavior was concluded from rheological behavior and differential scanning calorimetric studies, indicating the obtained resins possess propitious processability. The relationship between the molar ratio of 4,4'-biphenol and the properties of resins was systematically studied. After thermal curing, the E-glass fiber reinforced composite, prepared with the group number ratio of N(BP)/N(TFPT)=2.4, unveils admirable glass transition temperature of 486 °C, commendable thermal stability with 5% weight loss temperature in nitrogen of 572 °C, suggesting that the improvement of the thermal properties are stemmed from the branched structure and the phenyl-*s*-triazine units.

Keywords: Phthalonitrile resins; Branched; Phenyl-*s*-triazine; Thermal stability.

1. INTRODUCTION

Growth in the aerospace, marine, and microelectronic industries increasingly requires the development of heat-resistant materials.^[1, 2] PN-based resins, as a class of heat-resistant materials, have sparked great interests and attentions, due to its unique properties outstanding thermal stability, great flame retardance, low moisture resistance, and excellent mechanical properties. A factor that has impeded the application of neat PNs was their fairly sluggish curing condition.^[3] Keller et al found that the diamine could serve as curing agent of PN resins, which in turn can bring about shortened curing time and enhanced thermal stability.^[4, 5] Meanwhile, they have synthesized a great deal of PNs with various unique structures.^[6-9] After cured, the obtained polymers exhibit bunch of attractive properties, which enabled them as competent matrix for aerospace and microelectronic applications.

Recently, a heated direction of PN resins is to modify their thermal resistance. Thermostable moieties, such as heterocyclic pyridine moieties,^[10] aromatic naphthyl structures,^[11] silane-bearing structures,^[12] and *s*-triazine units^[13, 14] were separately introduced to the PN oligomer backbones. Some of the cured resins exhibit glass transition temperatures (T_g) exceeding 400 °C. However, the increasingly harsh application requirements demand for a higher thermal resistance. A series of self-catalyzed phthalonitrile compounds, possessing ultra-high crosslinking density, were reported by Zhou and co-workers.^[15, 16] The cured monomer exhibit high T_g above 500 °C, indicative of increasing the crosslink density can effectively promote the glass transition temperature.

In addition, certain researchers have made great efforts to introduce trifunctional structures into PN resins. A novel alkyl-center-trisphenolic-based PN thermoset and tris-phthalonitrile thermosets with amino-1,3,5-triazine structures were synthesized with excellent thermal stability.^[17] However, such molecular architecture inevitably introduces flexible units, such as alkyl and amino moieties, into the network structures, which drives a compromise of thermal resistance. Therefore, building new-type

PN-bearing polymers with rigid structures, which endow simultaneously them higher glass transition temperature and decomposition temperature, is of great importance for advanced application.

As a part of ongoing research, this work aims at pursuing ultrahigh performance PN polymers. The strategy includes two aspects: firstly, novel PN oligomers with branched structure were synthesized *via* trifluoro-monomers to promote the crosslinking density of the resulting thermosets, in turn to give high glass transition temperature; secondly, phenyl-*s*-triazine unit, among the plethora of rigid heteroatomic rings, was introduced into polymer backbones to further enhance their thermostability, imposed by the strong charge transfer interactions between *s*-triazine rings and aromatic rings, as compared with amino-1,3,5-triazine units. Thus, a novel series of branched-PN oligomers were prepared, followed by thermal curing. The resulting networks exhibit extremely high T_g and excellent thermal properties. This type of PN resins could be excellent candidates for high-temperature polymer-based structural materials.

2. EXPERIMENTAL

2.1. Materials

4,4'-Biphenol(BP, 99%) was obtained from Shanghai Haiqu Chemical Corporation. 4,4'-diaminodiphenyl sulfone (DDS, 99%) was purchased from Tianjin Fuyu Chemical Corporation. 4-Fluoro-benzonitrile(FBN, 99%) and 4-nitrophthalonitrile (NPh, 99%) were both purchased from the Wuhan Jiakailong Chemical Corporation. All solvents including N-methyl pyrrolidone (NMP), toluene, acetone, and chloroform are provided by Tianjin Kermel Chemical Reagent Corporation. Anhydrous potassium carbonate (K_2CO_3 , 99%) was purchased from Tianjing Chemical Corporation, and dried overnight at 80 °C in vacuum before used. All starting materials were used without further purification. E-glass fiber cloth (EW180-127) was purchased from Anhui Danfeng Electronic Material Corporation and soaked in acetone for 48h before used.

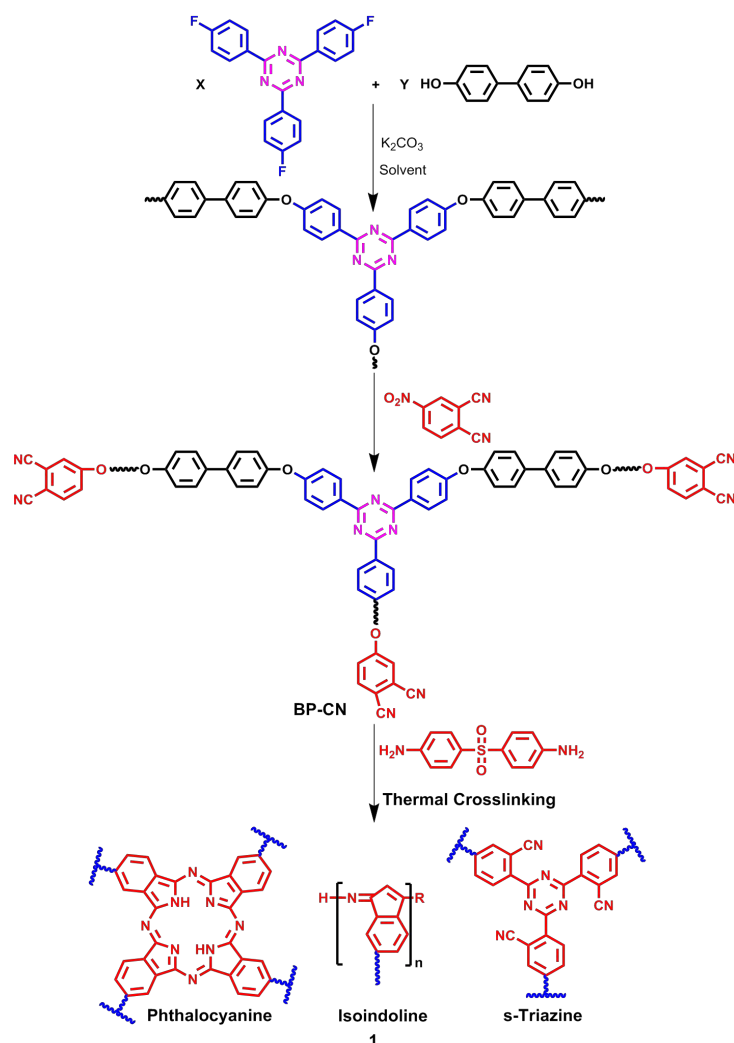
2.2. Characterization

Fourier transform infrared (FT-IR) spectrometry was performed on a Thermo Nicolet Nexus 470 FT-IR instrument (KBr pellet method). Especially, infrared reflection spectra of thermosets were performed on Thermo Fisher 6700 instrument. 1H -NMR spectra (400 MHz) were recorded with a Varian Unity Inova 400 spectrometer in $Cl_2CDCDCl_2$. Differential scanning calorimetric (DSC) experiment was performed on a modulated METTLER DSC822 instrument at a heating rate of 10 °C/min under a nitrogen flow (50 mL min^{-1}) to study the thermal properties of the oligomers and the resulting networks. The non-isothermal DSC method with the heating rate of 5, 10, 15, and 20 °C/min under a nitrogen flow (50 mL min^{-1}) was employed to carry out the kinetics study. Thermal Gravimetric Analysis (TGA) was measured on a METTLER TGA/SDTA851 analyzer at a heating rate of 10 °C/min under continuous N_2 or air. Rheological measurement was used to investigate the viscosity of the blends as the function of time and temperature, performed on a TA instruments AR2000 rheometer, using a 25 mm diameter parallel plates at a strain of 0.02 N and a frequency of 1 Hz. The dynamic mechanical analysis (DMA, TA Instruments Q800) was executed to characterize T_g at a frequency of 1 Hz in a single cantilever mode, with the heating rate of 5 °C/min. Data were all collected from room temperature to 500 °C under nitrogen atmosphere.

2.3. Synthesis of oligomer BP-CNs

TFPT (5.445 g, 0.015 mol), BP (8.370 g, 0.048 mol), K_2CO_3 (7.452 g, 0.054 mol), $n(BP)/n(TFPT)=3.6$, that is $N(BP)/N(TFPT)=2.4$, 138 ml NMP and toluene were added into a three-necked flask. The mixture was kept at 130 °C for 2 h under N_2 with continuous stirring. After the generated water was completely azeotroped off with toluene, the temperature was set at 150 °C for 8 h to obtain oligomers distinguished by the reactant concentrations. When the temperature was cooled to 80 °C, NPh (9.342 g, 0.054 mol) was chosen as end-capping reactant, and reacted with the oligomers for 10-12 h. Finally, the mixture was rinsed with dilute hydrochloric acid solution. After washed with deionized water to neutral, the product, named as BP-CN2.4, was obtained by suction filtration, following by dehydration at 80 °C in vacuum oven

overnight. Meanwhile, we use the same method to obtain BP-CN2.0, 2.2, 2.6, 2.8 with the different molar ratio of 4,4'-biphenol (BP), ¹H-NMR (400 M, Cl₂CDCl₂) [ppm]: δ 8.79-8.77 (d, 2H), δ 7.78-7.76 (d, 1H), δ 7.71-7.65 (m, 4H), δ 7.31-7.36 (dd, 2H).



Scheme 1. Synthetic route of *b*-PBP-Ph oligomers and network 1s formation.

2.4. Preparation of BP-CNs/GF laminates

The BP-CN oligomers, prepared with different concentration of the reactants, of 5 wt% DDS were selected to fabricate the E-glass fiber cloth reinforced composites. Thirteen layers of E-glass fiber cloth were dipped into the solution to obtain BP-CN prepregs. Then the prepregs were de-solvented in a muffle furnace until NMP was totally removed. Then resultant precursors were laminated in a tight steel mold with a pressure of 4 MPa at 220 °C for 1 h and 250 °C for 1h. Then the obtained laminate was cured in a muffle furnace with specific temperature raising procedure 250 °C for 3 h, 325 °C for 3 h, 350 °C for 2 h and 375 °C for 8 h. It should be sawed into 35×6×2 mm³ size for dynamic mechanical analysis (DMA) experiments.

3. Results and discussion

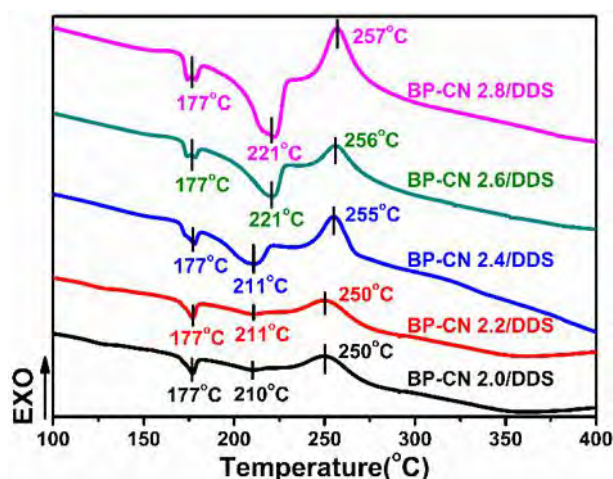


Figure. 1 DSC curves of BP-CNs/DDS blend.

Curing reaction studies of PN oligomers with 5wt% DDS were recorded by DSC, as shown in Figure 1. The endothermic peak at 177 °C, assigned to melting point of DDS, followed by the endothermic peak at 210-221 °C, attribute to the PN oligomers melting transition. The exothermic peak at 250-257 °C, implying the reaction occurred between the PNs and DDS. This data indicated that with the addition of bisphenol unit, the melting endothermic peak temperature and the exothermic peak temperature all increased, for the rigidity of bisphenol. In order to better understand the thermal curing reaction and cure kinetics of BPCNs with DDS, non-isothermal DSC tests at different heating rates were conducted. The experimental results are shown in Table 1.

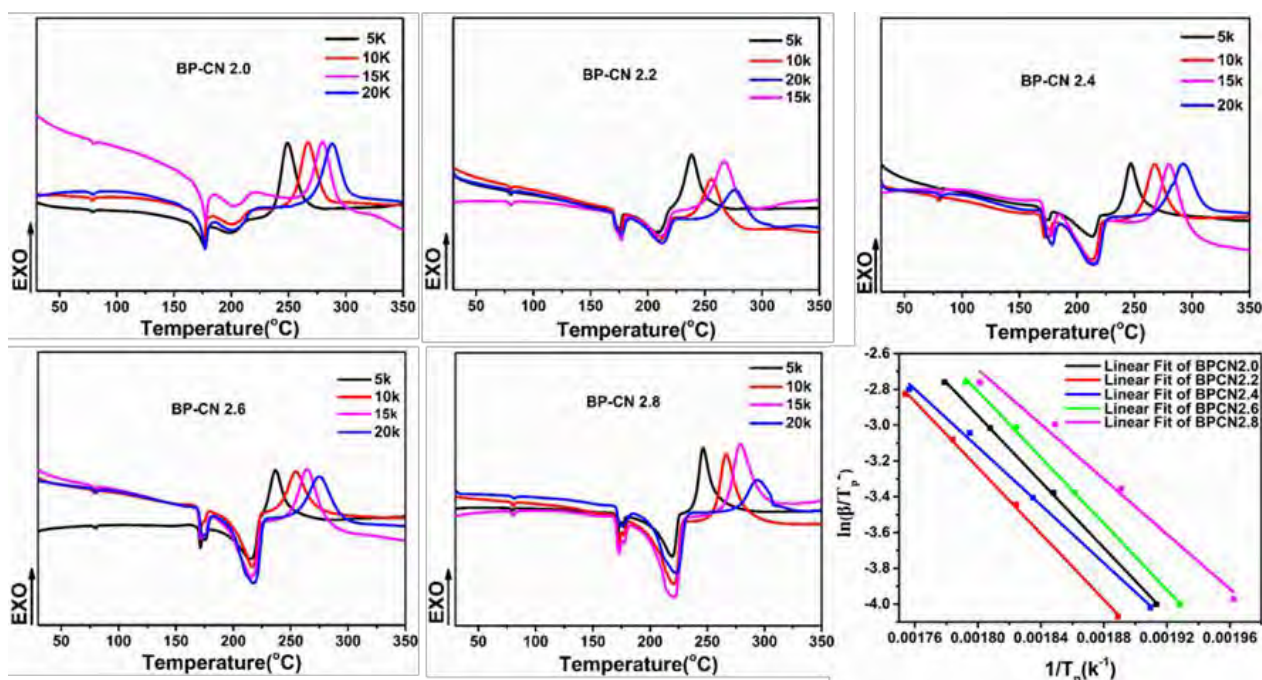


Figure 2 Non-isothermal DSC curves

Table 1 Non-isothermal DSC data and kinetic parameters of the curing reactions.

oligomer	T_{peak}				Ea(KJ/mol)	A	n
	5K/min	10K/min	15K/min	20K/min			
BP-CN 2.0							
BP-CN 2.2							
BP-CN 2.4							
BP-CN 2.6							
BP-CN 2.8							

BP-CN2.0	249.5	268	280	289	76.82	8.03E6	0.895
BP-CN2.2	238.5	256	267.5	276.5	76.75	1.20E7	0.897
BP-CN2.4	247	268	280	292	67.30	8.45E5	0.882
BP-CN2.6	237	255	265.5	275	76.84	1.30E7	0.897
BP-CN2.8	246.5	266.5	279	294	63.76	3.54E5	0.876

Non-isothermal DSC technique was utilized to study the curing kinetics of BP-CNs. Taking BP-CN 2.8 as an example, exothermic peaks appeared at 246.5 °C, 266.5 °C, 279 °C, and 294 °C were caused by the curing reaction, as shown in Figure 2. With the increase of heating rate, the exothermic peaks shift to higher temperatures. This phenomenon was in accord with the classic curing behavior of thermosetting resins. Kissinger method was used to calculate the apparent activation energy. Kissinger equation is ascribed as following:

$$-\ln \frac{\beta}{T_p^2} = \frac{E_a}{RT_p} - \ln \frac{A'R}{E_a}$$

Where β is the heating rate (°C/min); T_p is the peak temperature of curing reaction (K); R is the gas constant; and E_a is the reaction activation energy. Data of $\ln(\beta/T_p^2)$ and $1/T_p$ at different heating rates were listed in Table 1; The linear relationship of $\ln(\beta/T_p^2)$ vs. $1/T_p$ was shown in Figure 2. As calculated, the reaction activation energy was 63.76 kJ/mol based on slope of the straight. The activation energies of BP-CN2.0, 2.2, 2.4, 2.6 are 76.82 kJ/mol, 76.75 kJ/mol, 67.30 kJ/mol and 76.84 kJ/mol, respectively. The data is similar with the self-promoted PN polymers unveiled by Zhou, and the well-known Epoxy, implying the potential barrier could be overwhelmed relatively easy. Noteworthy, the reaction activation energy roughly increased with the concentration of polymerization, indicating high concentrations are prone to increase the barrier of the curing reaction.

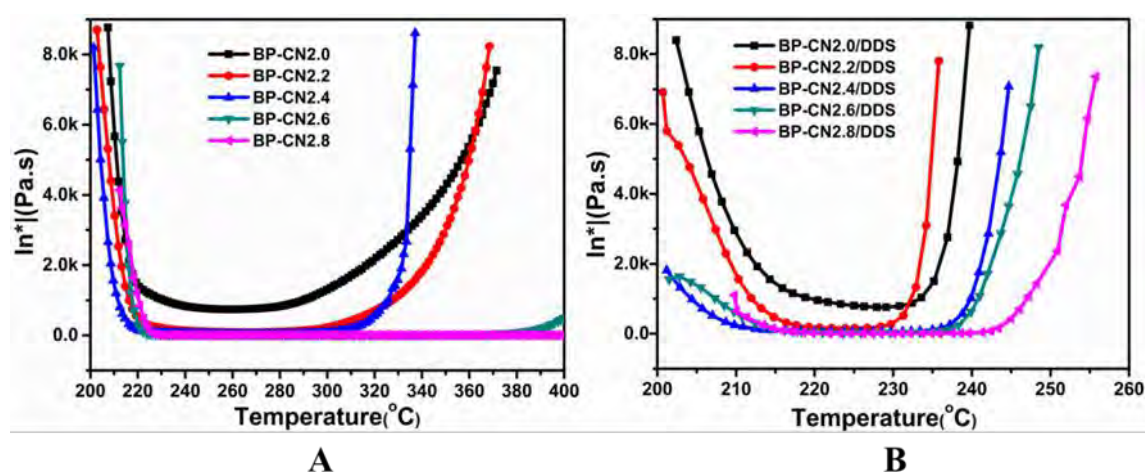


Figure 3 Complex viscosity (η^*) vs. temperature curve for oligomer BP-CNs(A) neat BP-CNs;(B) with 5 wt% DDS.

The meltability of BPCN polymers were investigated by rheological measurements. In Figure 3, the melt viscosity of neat BPCNs were determined as a function of temperature from 200 °C to 400 °C. The viscosity of each oligomer decreased sharply around its melting temperature, and then kept steady, finally increased significantly with the temperature. Interestingly, From the Figure 3A, the BPCNs with different ratio of bisphenol possessed different curing behavior, low ratio bisphenol in neat BPCN polymers displayed a self-curing behavior as the temperature increased, probably caused by the chain entanglement. The high ratio bisphenol in the oligomers, the molecular backbone show linear structure, the viscosity as low as 2.3 Pa•s. The additive DDS would promote the curing process (Figure 3B), the viscosity of two branched PN oligomers decreased sharply near their melting point and then increased sharply near the cure temperature. The more biphenol structure in the backbones, the more wide process window in processibility. The process

window of the BP-CNs/DDS mixture was about 20 °C with 5 wt% diamine inclusion, which was enough for the fabrication of advanced resin-based composites.

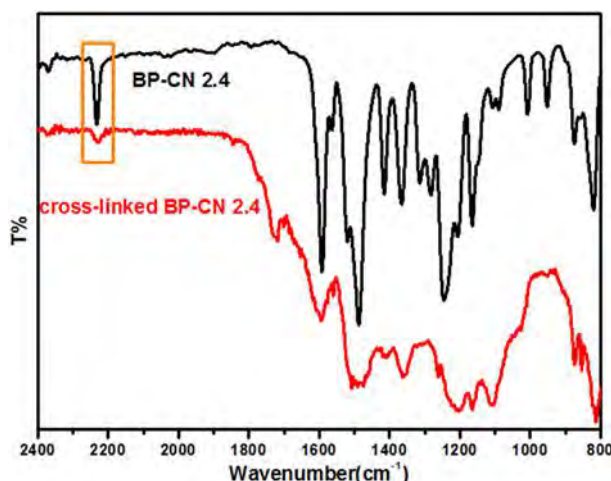


Figure 4 FT-IR spectra of BP-CN 2.4 before and after thermo-crosslinking

The FT-IR spectra of neat and thermal cured BP-CN 2.4 was shown in Figure 4. The absorption peak at 2230 cm^{-1} was attributed to the stretching vibration of nitrile group (-CN), which obviously diminished after cured. The nitrile groups could hardly completely vanished, as many studies have been reported, (steric hindrance effects will result in about 1/3 nitrile groups left). Therefore, cured BP-CN 2.4 resins still exhibited a weak absorption band at 2230 cm^{-1} . The wide absorption peaks at 1488 cm^{-1} and 1363 cm^{-1} (cured BP-CN2.4) demonstrated the formation of *s*-triazine structure. The peak at 1003 cm^{-1} belonged to phthalocyanine ring. The peaks at 872 cm^{-1} and 1720 cm^{-1} are corresponding to the isoindoline groups. The possible structures of cured BP-CN 2.4 were shown in Scheme 1.

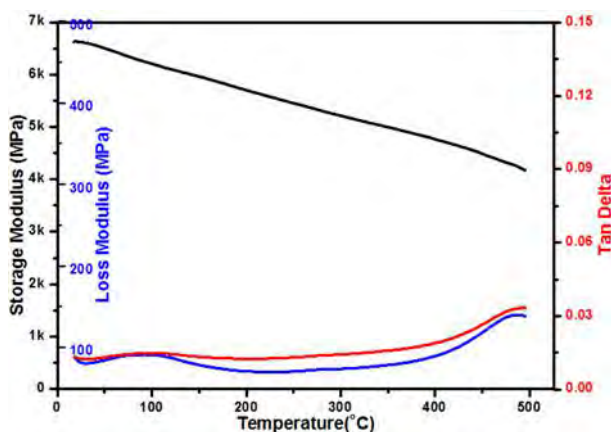


Figure 5 DMA curve of composites cured with BP-CN 2.4.

Glass transition temperature is one of the most fundamental features in developing high performance polymers. DMA was conducted to evaluate the T_g s of composites, derived from the oligomers and E-glass fiber cloth. Dynamic mechanical behavior of BP-CN 2.4 polymer including storage modulus, loss modulus, and loss tangent($\tan\delta$) recorded from 20 °C to 500 °C are shown in Figure 5. The storage modulus of BP-CN 2.4 polymer were 4172 MPa at 500 °C, which was 63% of its initial storage modulus. Notably, the $\tan \delta$ and loss modulus of the polymer maximized at around 486 °C, revealing a very high T_g . Compared with the phthalonitrile oligomers like BCBP,[10] BDCN,[11] 2CN-PEEK,[18] TDPE,[19] 1,6-BDCN,[20] the T_g of BP-CN 2.4 network is higher than that of most PN thermosets. The reason can be interpreted as T_g depends on several factors such as chemical structure and cross-linked state. With great rigid phenyl-*s*-triazine and

branched units, the formed cross-linking structures could more effectively hinder the chain mobility of molecular chain terminals, finally resulting in excellent thermal resistance. The $\tan \delta$ curves showed wider and lower peaks at high temperature, which might be caused by the backbone mobility.

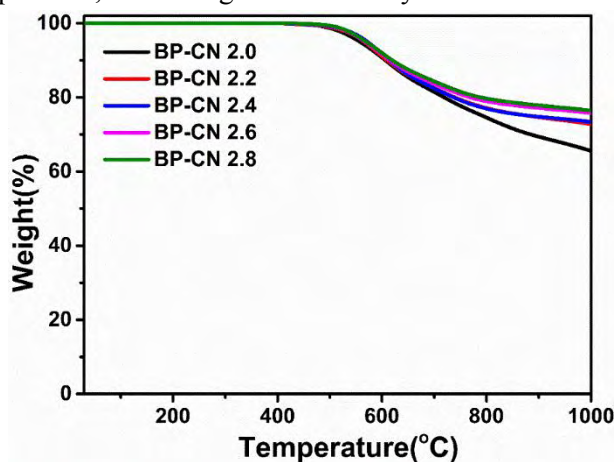


Figure 6 TGA curves of the network 1s under N₂ atmosphere.

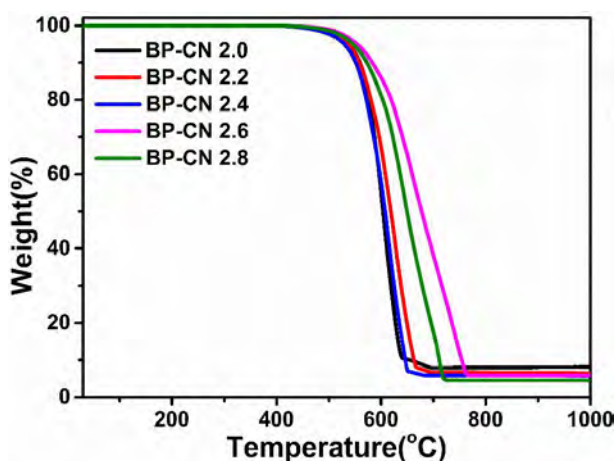


Figure 7 TGA curves of the network 1s under air atmosphere.

Table 2 The thermal data of network 1s.

Polymers	$T_{5\%}(\text{°C})^a$	$T_{10\%}(\text{°C})$	$C_{y800\text{°C}}(\%)$	$C_{y1000\text{°C}}(\%)$
BP-CN 2.0	558(536) ^b	606(560)	74.6(8.1)	65.6(8.1)
BP-CN 2.2	566(536)	610(559)	77.1(6.5)	72.8(6.5)
BP-CN 2.4	572(529)	614(552)	77.0(5.7)	73.4(5.7)
BP-CN 2.6	567(554)	615(583)	78.9(5.8)	75.8(5.8)
BP-CN 2.8	570(546)	619(573)	79.7(4.5)	76.5(4.5)

^a The values were recorded on TGA at the heating rate of 10 °C/min in N₂ or air.

^b The values in the brackets were recorded on TGA under air atmosphere.

To characterize the thermal stability of the branched PN networks, TGA analysis was performed. As shown in Figure 6, 7, and Table 2, the weight loss of BP-CN polymers could be hardly observed before 500 °C in N₂; their weight retention at 95% ranged from 558 °C to 572 °C, higher than most PN thermosets. When

detected in air, the 5% weight loss temperatures of the networks were more than 529 °C, stemmed from both the presence of phenyl-*s*-triazine and biphenyl moieties. It was notably that the char yield of the cured polymers at 1000 °C were all higher than 65.6% in N₂, which illustrated the network had a thermostable backbone.

4. CONCLUSION

A new family of branched PN oligomers (BP-CNs) were prepared by a facile solution polycondensation approach of biphenol and trihalide monomers, followed by end-capping with 4-nitrophthalonitrile. The BP-CNs possess commandable processability as evidenced by rheometer. After curing with diamine, the networks (BP-CN) show a maximum 5% weight loss temperature of 572 °C, accompanied with char yield of 73.4% at 1000 °C. Meanwhile, the resulting networks demonstrated high glass transition temperature of 486 °C, induced by the coordination of efficient cross-linking reaction and prominent rigidity of phenyl-*s*-triazine structure. This type of phenyl-*s*-triazine-bearing branched PN resin could be considered as a high performance matrix for heat-resistant materials.

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