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Synthesis of three novel phosphorus-containing flame retardants and their application in epoxy resins

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ABSTRACT

One symmetric diamine (**4**) and two symmetric phenols (**5**) and (**6**) were synthesized as phosphorus-containing flame retardants. The synthesis comprised a two-step procedure: the condensation of *p*-phenylenediamine with benzaldehyde, 4-hydroxybenzaldehyde and 2-hydroxybenzaldehyde respectively, followed by the addition of 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide to the imine linkage. The structures of (**4**)–(**6**) were characterized by FTIR, NMR and mass spectra. (**4**)–(**6**) served as co-curing agents of diaminodiphenylmethane for epoxy resins, and epoxy thermosets exhibited excellent flame retardancy, moderate changes in glass transition temperature (T_g) and thermal stability. When the phosphorus content reached 1.0 wt.%, the epoxy resin system met the UL-94 V-0 classification and the limiting oxygen index (LOI) reached more than 35.6, probably because of the nitrogen–phosphorus synergistic effect.

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1. Introduction

In modern polymer industry, epoxy resins have been widely applied industrially for surface coatings, adhesives, painting materials, potting, composites, encapsulants for semiconductors, insulating materials for electric devices and laminates etc [1–3], because of their excellent characteristics of moisture, toughness, solvent and chemical resistance, low shrinkage on cure, superior electrical and mechanical resistance properties and good adhesion to many substrates. Traditionally, epoxy resins containing bromine atoms are particularly useful for printed circuit boards and encapsulation applications where flame retardancy is desired. Major problems encountered with this system are concerned with the generation of toxic and corrosive fumes during combustion [4,5]. In contrast, phosphorus-containing compounds [6–16] provide powerful flame retardancy by covering the outer layer of polymers with a non-flammable char during combustion. So epoxy resin modified by phosphorus-containing compounds is considered as a promising method due to its high flame-retardant efficiency.

In recent years, 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) and its derivatives have attracted considerable attention because they can react with various epoxy monomers. The active hydrogen of DOPO can react with electron-deficient compounds, such as maleic acid [17], bismaleimide [18], epoxy [19,20], diaminobenzophenone [21], terephthaldicarboxaldehyde [22], alkene [23], imine [24–26], isocyanate [27] and pararosaniline chloride [28]. In this study, three new phosphorus-containing flame retardants which contain activated functional groups were synthesized by nucleophilic addition of DOPO on the imine linkage. The structures of three new compounds were characterized by ^{1}H NMR, ^{13}C NMR, ^{31}P NMR, FTIR and mass spectra. Three phosphorus-containing flame retardant served as co-curing agents for diglycidyl ether of bisphenol A (DGEBA). The thermal and flame-retardant properties of epoxy thermosets were evaluated by DSC, TGA, LOI and the UL-94 vertical flame retardancy test.

2. Experimental

2.1. Materials

9,10-Dihydro-9-oxa-10-phosphaphenanthrene10-oxide (DOPO) was purchased from Youdi Trading Co. Ltd (Shanghai, China). Epoxy resin (DGEBA, commercial name: E-51) was purchased from Wuxi Diaisheng Epoxy Co. Ltd (Wuxi, China). Diaminodiphenylmethane (DDM) and *p*-phenylenediamine were purchased from Aladdin Reagent (Shanghai, China). Benzaldehyde and ethanol were purchased from Tianjin Damao Chemical Reagent Factory (Tianjin, China). 4-Hydroxybenzaldehyde and 2-hydroxybenzaldehyde were purchased from Sinopharm Chemical Reagent Co. Ltd (Shanghai, China).

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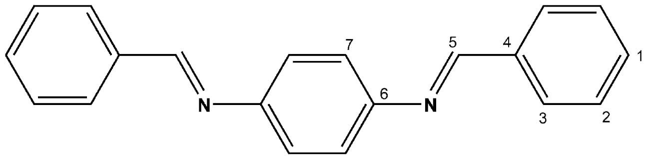
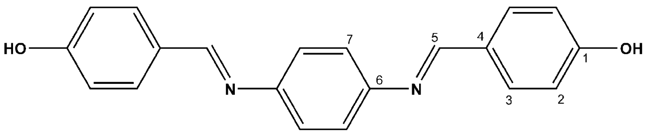
2.2. Preparation of (**1**)

0.10 mol (10.814 g) *p*-phenylenediamine, 0.20 mol (21.224 g) benzaldehyde, and 200 mL ethanol were added into a 500 mL round glass flask equipped with a condenser and a stirrer. The reaction mixture was stirred at 50 °C for 2 h. Then, the mixture was cooled down to room temperature. The yellow precipitate was filtered and washed twice with ethanol, and then dried at 60 °C in a vacuum oven for 8 h. After drying, light yellow crystals 26.16 g (92% yield) were obtained. FTIR absorption: C=N 1616 cm^{-1}. MS: m/z = 285 (M+1^{+}). ^{1}H HMR (ppm, DMSO-d$_6$), δ = 7.37 (H$_7$), 7.54 (H$_1$, H$_2$), 7.96 (H$_3$), 8.70 (H$_5$). ^{13}C NMR (ppm, DMSO-d$_6$), δ = 122.36 (C$_7$), 128.99 (C$_2$), 129.16 (C$_3$), 131.76 (C$_1$), 136.42 (C$_4$), 149.64 (C$_6$), 160.40 (C$_5$).



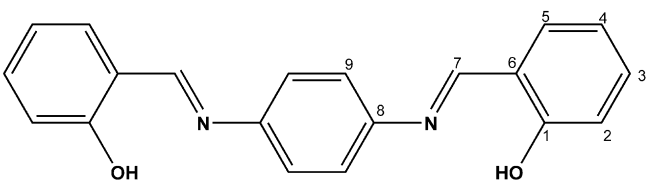
2.3. Preparation of (**2**)

Compound (**2**) was prepared in a synthetic procedure identical to that (**1**), using *p*-phenylenediamine and 4-hydroxybenzaldehyde as starting materials. Yellow powder (90% yield) was obtained. FTIR absorption: C=N 1619 cm^{-1}, OH 3271 cm^{-1}. MS: m/z = 317 (M+1^{+}). ^{1}H HMR (ppm, DMSO-d$_6$), δ = 6.89 (H$_2$), 7.26 (H$_7$), 7.78 (H$_3$), 8.52 (H$_5$), 10.11 (OH). ^{13}C NMR (ppm, DMSO-d$_6$), δ = 115.55 (C$_2$), 121.67 (C$_7$), 127.54 (C$_4$), 130.51 (C$_3$), 154.21 (C$_6$), 159.31 (C$_5$), 163.22 (C$_1$).



2.4. Preparation of (**3**)

Compound (**3**) was prepared in a synthetic procedure identical to that of (**1**), using *p*-phenylenediamine and 2-hydroxybenzaldehyde as starting materials. Light orange powder (88% yield) was obtained. FTIR absorption: C=N 1611 cm^{-1}, OH 3460 cm^{-1}. MS: m/z = 317 (M+1^{+}). ^{1}H HMR (ppm, DMSO-d$_6$), δ = 6.98 (H$_2$), 7.01 (H$_4$), 7.43 (H$_3$), 7.55 (H$_9$), 7.67 (H$_5$), 9.04 (H$_7$), 13.07 (OH). ^{13}C NMR (ppm, DMSO-d$_6$), δ = 116.51 (C$_2$), 119.10 (C$_6$), 119.27 (C$_4$), 122.45 (C$_9$), 132.46 (C$_5$), 133.25 (C$_3$), 146.582 (C$_8$), 160.19 (C$_7$), 163.05 (C$_1$).



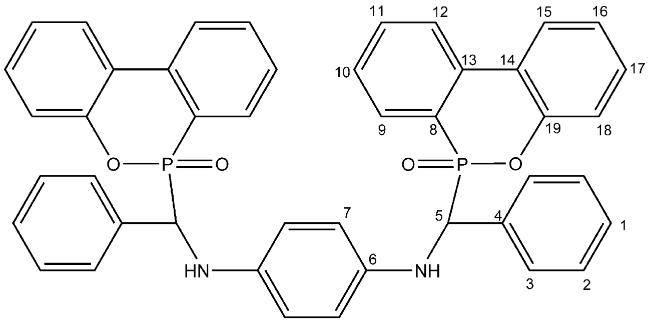
2.5. Preparation of (**4**)

0.2 mol (43.237 g) DOPO, 0.1 mol (28.435 g) (**1**) and 300 mL ethanol were added into a 500 mL round glass flask equipped with a condenser and a stirrer. The reaction mixture was stirred at 50 °C for 10 h. After that, the reaction mixture was cooled down to room temperature. The yellow precipitate was filtered and washed twice with ethanol, and then dried at 60 °C in a vacuum oven for 8 h. Light yellow powder 65.56 g (91% yield) was obtained. FTIR absorption: N–H stretching 3430 cm^{-1}, P–Ph 1595 cm^{-1}, C–N 1297 cm^{-1}, P=O 1209 cm^{-1}. MS: m/z = 717 (M+1^{+}).

^{1}H HMR (ppm, DMSO-d$_6$), δ = 4.86 (H$_5$), 5.33 (H$_{5'}$), 5.52 (NH′), 5.98 (NH), 6.29 (H$_7$), 6.35 (H$_{7'}$), 6.97 (H$_{18}$), 7.11 (H$_{18'}$), 7.15–7.45 (H$_{16}$, H$_{16'}$, H$_3$, H$_{3'}$, H$_1$, H$_{1'}$, H$_2$, H$_{2'}$, H$_{17}$, H$_{17'}$), 7.49–7.54 (H$_{11}$, H$_{11'}$), 7.68–7.76 (H$_{10}$, H$_{10'}$, H$_{12}$), 7.98 (H$_{12'}$), 8.11–8.17 (H$_9$, H$_{9'}$, H$_{15}$, H$_{15'}$).

^{13}C NMR (ppm, DMSO-d$_6$), δ = 148.8 (C$_{19}$), 148.5 (C$_{19'}$), 138.6 (C$_6$), 138.4 (C$_{6'}$), 135.4 (C$_4$, C$_{4'}$), 135.2 (C$_{14}$, C$_{14'}$), 133.5 (C$_{10}$), 133.1(C$_{10'}$), 131.5 (C$_{12}$, C$_{12'}$), 130.5 (C$_{17}$), 130.1 (C$_{17'}$), 128.4 (C$_{11}$), 128.1 (C$_{11'}$), 127.8 (C$_2$, C$_{2'}$), 127.3 (C$_3$, C$_{3'}$), 125.6 (C$_{15}$), 125.4 (C$_{15'}$), 124.6 (C$_{16}$), 124.5 (C$_{16'}$), 124.1 (C$_1$, C$_{1'}$), 123.9 (C$_9$), 123.7 (C$_{9'}$), 122.9 (C$_8$), 122.5 (C$_{8'}$), 121.6 (C$_{13}$), 121.5 (C$_{13'}$), 120.1 (C$_{18}$), 119.8 (C$_{18'}$), 114.8 (C$_7$, C$_{7'}$), 57.6 (C$_5$), 56.6 (C$_{5'}$).

^{31}P NMR (ppm, DMSO-d$_6$), δ = 31.19, 34.45.



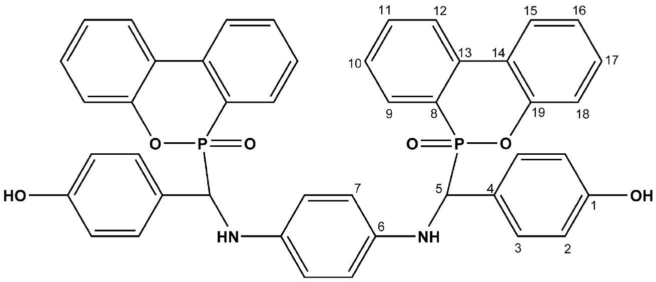
2.6. Preparation of (**5**)

(**5**) was prepared in a synthetic procedure identical to that of (**4**), using DOPO and (**2**) as starting materials. Grey–white powder (92% yield) was obtained. FTIR absorption: N–H stretching 3380 cm^{-1}, O–H 3350-3000 cm^{-1}, P–Ph 1595 cm^{-1}, C–N 1268 cm^{-1}, P=O 1215 cm^{-1}. MS: m/z = 749 (M+1^{+}).

^{1}H HMR (ppm, DMSO-d$_6$), δ = 4.70 (H$_5$), 5.10(H$_{5'}$), 5.37 (NH′), 5.80 (NH), 6.26 (H$_7$), 6.33 (H$_{7'}$), 6.56–6.65 (H$_2$, H$_{2'}$), 6.98 (H$_{18}$), 7.06–7.14 (H$_3$, H$_{3'}$), 7.27–7.34 (H$_{16}$, H$_{16'}$), 7.35–7.43 (H$_{17}$, H$_{17'}$, H$_{18'}$), 7.48–7.54 (H$_{11}$, H$_{11'}$), 7.60–7.76 (H$_{10}$, H$_{10'}$, H$_{12}$), 7.93–8.01 (H$_{12'}$), 8.12–8.18 (H$_9$, H$_{9'}$, H$_{15}$, H$_{15'}$), 9.30 (OH), 9.34 (OH′).

^{13}C NMR (ppm, DMSO-d$_6$), δ = 157.3 (C$_1$, C$_{1'}$), 149.3 (C$_{19}$, C$_{19'}$), 139.3 (C$_6$, C$_{6'}$), 135.6 (C$_{14}$, C$_{14'}$), 133.9 (C$_{10}$), 133.6(C$_{10'}$), 132.1 (C$_{12}$, C$_{12'}$), 131.1 (C$_{17}$), 130.7 (C$_{17'}$), 130.0 (C$_3$, C$_{3'}$), 128.8 (C$_{11}$), 128.5 (C$_{11'}$), 126.2 (C$_{15}$), 125.9 (C$_{15'}$), 125.7 (C$_4$), 125.5 (C$_{4'}$), 125.1 (C$_{16}$), 125.0 (C$_{16'}$), 124.5 (C$_9$), 124.2 (C$_{9'}$), 123.8 (C$_8$), 123.4 (C$_{8'}$), 123.3 (C$_{13}$), 123.1 (C$_{13'}$), 120.7 (C$_{18}$), 120.4 (C$_{18'}$), 115.3–115.4 (C$_2$, C$_{2'}$, C$_7$, C$_{7'}$), 57.5 (C$_5$), 56.4 (C$_{5'}$).

^{31}P NMR (ppm, DMSO-d$_6$), δ = 31.41, 34.68.



2.7. Preparation of (**6**)

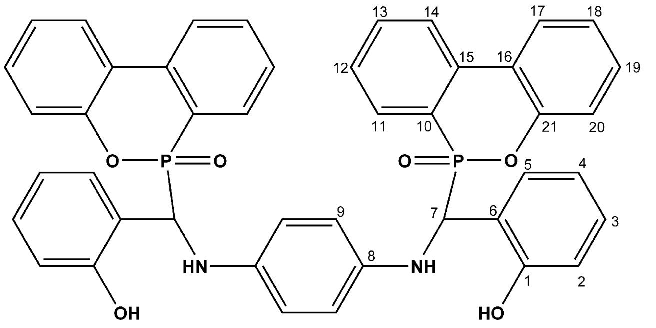
(**6**) was prepared in a synthetic procedure identical to that of (**4**), using DOPO and (**3**) as starting materials. Light yellow powder (88%

yield) was obtained. FTIR absorption: N–H stretching 3411 cm^{-1}, O–H 3350–3000 cm^{-1}, P–Ph 1595 cm^{-1}, C–N 1277 cm^{-1}, P=O 1215 cm^{-1}. MS: $m/z = 749$ ($M+1^+$).

^1H HMR (ppm, DMSO-d_6), $\delta = 5.05$ (H_5), 5.21($H_{5'}$), 5.55 (NH′), 5.89 (NH), 6.24–6.29 (H_9, $H_{9'}$), 6.48 (H_2), 6.67–6.75 ($H_{2'}$, H_4, $H_{4'}$), 6.91–6.99 (H_5, $H_{5'}$), 7.01–7.10 (H_{20}, $H_{20'}$), 7.24–7.44 (H_{13}, $H_{13'}$, H_3, $H_{3'}$, H_{19}, $H_{19'}$, H_{17}, $H_{17'}$), 7.50 (H_{14}), 7.66–7.76 (H_{12}, $H_{12'}$, 8.01 ($H_{14'}$), 8.07–8.18 (H_{18}, $H_{18'}$, H_{11}, $H_{11'}$), 9.31 (OH), 9.43 (OH′).

^{13}C NMR (ppm, DMSO-d_6), $\delta = 155.7$ (C_1), 155.6 ($C_{1'}$), 149.6 (C_{21}), 149.3 ($C_{21'}$), 139.2 (C_8, $C_{8'}$), 136.4 (C_6, $C_{6'}$), 135.5 (C_{16}, $C_{16'}$), 133.9 (C_{12}), 133.8 ($C_{12'}$), 132.1 (C_{14}, $C_{14'}$), 131.0 (C_{19}, $C_{19'}$), 129.6 (C_3, $C_{3'}$), 128.8 (C_5, $C_{5'}$), 128.4 (C_{13}, $C_{13'}$), 126.0 (C_{17}), 125.8 ($C_{17'}$), 125.1 (C_{18}), 124.8 ($C_{18'}$), 124.2 (C_{11}, $C_{11'}$), 123.8 (C_{10}), 123.3 ($C_{10'}$), 122.6 (C_4, $C_{4'}$), 121.8 (C_{15}, $C_{15'}$), 120.7 (C_{20}), 120.5 ($C_{20'}$), 119.3 (C_2, $C_{2'}$), 114.9 (C_9, $C_{9'}$), 51.2 (C_7), 50.1 ($C_{7'}$).

^{31}P NMR (ppm, DMSO-d_6), $\delta = 31.62, 35.36$.



2.8. Preparation of the epoxy thermosets

(**4**), (**5**) and (**6**) served as co-curing agents of DDM. The functionality of (**4**), (**5**) and (**6**) is taken as two or four for curing evaluation, considering the numbers of active protons in the amino and phenol groups of their molecular structures. The curing agent and epoxy resins were mixed homogeneously at a 1:1 equivalent ratio. The epoxy/(**n**)/DDM (**n** = **4**, **5**, **6**) systems cured at 140 °C for 2 h, at 180 °C for 2 h, respectively. Thereafter, the epoxy thermosets were allowed to cool slowly to room temperature, in order to prevent cracking. The epoxy thermosets with phosphorus content 0.75 wt.%, 1.00 wt.%, 1.25 wt.% and 1.50 wt.% were obtained and labelled as (**n** – m)/DDM listed in Table 1 (**n** corresponds to the title flame retardant, and m stands for the phosphorus content).

Table 1
Thermal and flame-retardancy properties of epoxy thermosets (**4**)–(**6**).

Thermoset ID	P (wt.%)[a]	N (wt.%)[b]	T_g (°C)	T_d (°C)[c]	Char yield[d]	UL-94 grade	LOI
DGEBA/DDM	0	2.86	163	380	18.1	Burning	24.9
(**4** – 0.75)/DDM	0.75	2.81	151	338	20.5	V-1	34.6
(**4** – 1.00)/DDM	1.00	2.77	145	332	20.7	V-0	35.6
(**4** – 1.25)/DDM	1.25	2.75	142	330	20.9	V-0	36.3
(**4** – 1.50)/DDM	1.50	2.71	140	326	21.3	V-0	37.0
(**5** – 0.75)/DDM	0.75	2.67	154	356	21.0	V-1	35.1
(**5** – 1.00)/DDM	1.00	2.63	150	348	22.3	V-0	36.2
(**5** – 1.25)/DDM	1.25	2.57	148	344	22.4	V-0	37.0
(**5** – 1.50)/DDM	1.50	2.53	147	342	24.6	V-0	37.5
(**6** – 0.75)/DDM	0.75	2.67	148	345	21.1	V-1	35.4
(**6** – 1.00)/DDM	1.00	2.63	143	340	21.6	V-0	36.9
(**6** – 1.25)/DDM	1.25	2.57	140	337	21.8	V-0	37.7
(**6** – 1.50)/DDM	1.50	2.53	138	335	23.0	V-0	38.6

[a] Phosphorus content.
[b] Nitrogen content.
[c] Decomposition temperature of 5% weight loss in argon atmosphere.
[d] (wt.%) residual weight percentage at 800 °C in argon atmosphere.

2.9. Characterization

Differential scanning calorimetry (DSC) scans were obtained from samples of about 5–10 mg in an argon atmosphere at a heating rate of 10 °C/min using a Mettler-Toledo DSC 823e. T_g was taken as midpoint of the enthalpy transitions along the thermograms. Thermal gravimetric analysis (TGA) was performed with a Mettler-Toledo TGA/DSC1 at a heating rate of 10 °C/min under argon atmosphere from 50 °C to 800 °C. Fourier transform infrared (FTIR) spectra of samples were obtained on a Bruker Vertex 70 infrared spectrophotometer by KBr disc method. Mass spectra were obtained using a Waters Quattro X Premier mass spectrometer. ^1H (400 MHz), ^{13}C (100.5 MHz) and ^{31}P (161.9 MHz) NMR spectra were performed in DMSO-d_6 using a Bruker spectrometer. The LOI tests were measured according to the testing procedure of GB/T 2406-2009 using JF-3 limited oxygen index instrument. Test specimen bar is 7–15 cm in length, 6.5 ± 0.5 mm in width and 3.0 ± 0.5 mm in thickness. The UL-94 vertical test was performed according to testing procedure of Horizontal and vertical burning chamber FZ-5401 with a test specimen bar of 127 mm in length, 12.7 mm in width and about 3.0 mm in thickness. In the test, the polymer specimen is subjected to two 10-s ignitions. After the first ignition, the flame is removed and the time for the polymer to self-extinguish (t_1) is recorded. Cotton ignition would be noted if polymer dripping occurs during the test. After cooling, the second ignition is performed on the same sample and the self-extinguishing time (t_2) and dripping characteristics are recorded. If t_1 plus t_2 is less than 10 *s* without any dripping, the polymer is considered to be a V-0 material. If t_1 plus t_2 is in the range of 10–30 *s* without any dripping, the polymer is considered to be a V-1 material.

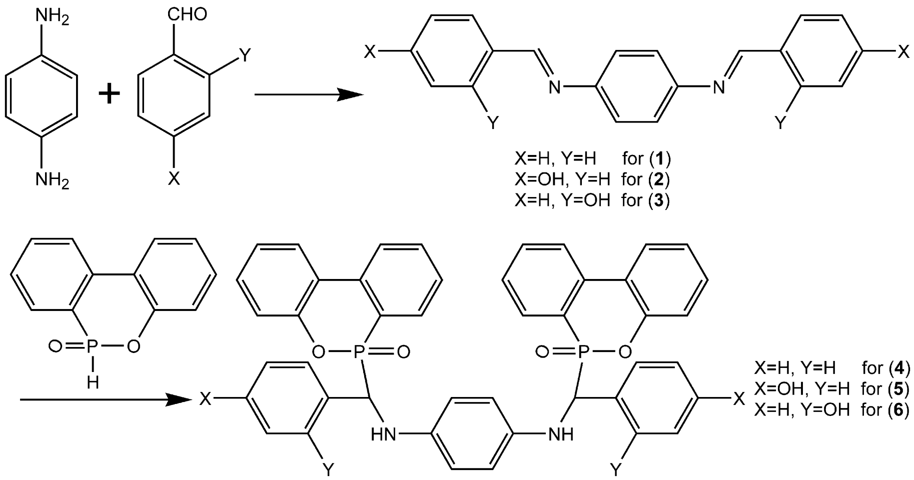
3. Results and discussion

3.1. Synthesis and characterization of (1)–(3)

As shown in Scheme 1, the imine-containing intermediates (**1**)–(**3**) were synthesized by the condensation of *p*-phenylenediamine with benzaldehyde, 4-hydroxybenzaldehyde and 2-hydroxybenzaldehyde, respectively. According to the ^1H NMR data of (**1**)–(**3**), the amino signal of *p*-phenylenediamine at 3.3 ppm and aldehyde signal at about 10.0 ppm disappeared, but a signal at 8.70 ppm (**1**), 8.52 ppm (**2**), 9.04 ppm (**3**) standing for an imine linkage appeared, supporting the formation of an imine linkage. In the ^{13}C NMR data, the characteristic peak of imine at around 160 ppm confirms the condensation. The detailed assignment of other peaks is shown in Section 2, and it confirms the structures of (**1**)–(**3**). In addition, FTIR and Mass spectra data also confirm the structures of (**1**)–(**3**).

3.2. Synthesis and characterization of (4)–(6)

(**4**)–(**6**) were synthesized by nucleophilic addition of DOPO on the imine linkage of (**1**)–(**3**) (Scheme 1). Since this nucleophilic addition reaction involves two DOPO and two imine functional groups, every of the three final products of (**4**)–(**6**), may probably be an isomeric mixture with sixteen configurations, taking account of the formation of two chiral aliphatic carbon atoms and two chiral phosphorus atoms within one molecule. Providing the coupling between the two chiral zones separated by a *p*-phenylenediamine group is weak enough, the sixteen configurations of the every product can be degenerated into two isomeric groups for NMR signals. Namely, the geminal couplings for (**4**)–(**6**) were observed in the NMR spectra. This is similar to the phenomena found in DOPO-containing products of isomeric mixture [24,25].



Scheme 1. Synthesis of (**1**)–(**6**).

3.3. T_g of epoxy thermosets

T_g values of the epoxy thermosets are listed in Table 1. Introducing curing agents (**4**)–(**6**) into the epoxy resin lowered the T_g values of the cured resins, which leads to low cross-linking density. Moreover, with the addition amount of (**4**)–(**6**) increasing, T_g values of epoxy thermosets decreased. T_g value of (**5**)/DDM sample was higher than that of (**4**)/DDM or (**6**)/DDM sample with the identical phosphorus content. It could be explained that the cross-linking density of the (**5**)/DDM system was higher than other two, because of the existence of para-position OH group. That the T_g value of (**6**)/DDM system is lower might result from lower cross-linking density caused by stereo-hindrance of ortho-position OH group.

3.4. Thermal stability of epoxy thermosets

The TGA curves of epoxy thermosets with various contents of phosphorus under argon atmosphere are shown in Figs. 1–3. The decomposition temperature of 5% weight loss (T_d) and the fraction of the char yields at 800 °C were obtained from the TGA curves. These data are listed in Table 1. T_d values of epoxy thermosets (**4**)–(**6**) ranged from 326 to 356 °C, lower than 380 °C of DGEBA/DDM. Therefore introducing (**4**)–(**6**) into the DGEBA lowered the thermal stability of the cured resins, which may be attributed to the fact that the O=P–O bond in epoxy resin is more active than common C–C bond [29]. The char yields of epoxy thermosets (**4**)–(**6**) at 800 °C were in the range 20.5–24.6 wt.%, which were higher than 18.1 wt.% of DGEBA/DDM. This could be explained that the degradation of phosphorus-containing groups generates heat-resistant residues which lead to high char yields. It can be seen from Table 1 that the degradation temperature and char yield of (**5** – m)/DDM were slightly higher than those of (**4** – m)/DDM and (**6** – m)/DDM, where m is set to the same value in every control group (the same below).

3.5. Flame-retardant properties of epoxy thermosets

The UL-94 grade and LOI values of epoxy thermosets are listed in Table 1. It is clear that a UL-94 V-0 grade can be achieved for the (**4**)–(**6**)/DDM systems and meanwhile the LOI value reached over 35.6. The flame retardancy of epoxy thermosets increases with the phosphorus content increasing. When the phosphorus content is 0.75 wt.%, UL-94 V-1 grade can be achieved. However, when the

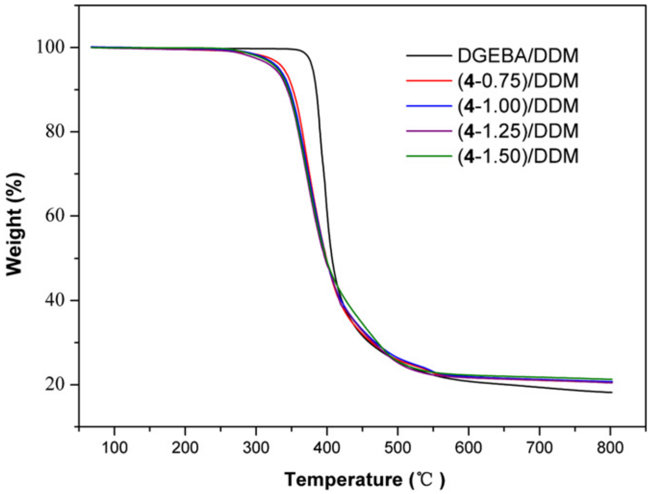


Fig. 1. TGA thermograms of (**4**)/DDM thermosets. (NOTE: The black-white version of Fig. 1 only for Print; The colour version of Fig. 1 only for Web).

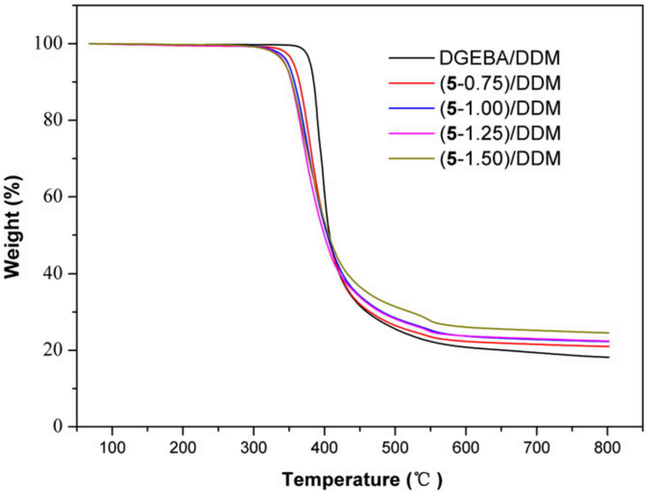


Fig. 2. TGA thermograms of (**5**)/DDM thermosets. (NOTE: The black-white version of Fig. 2 only for Print; The colour version of Fig. 2 only for Web).

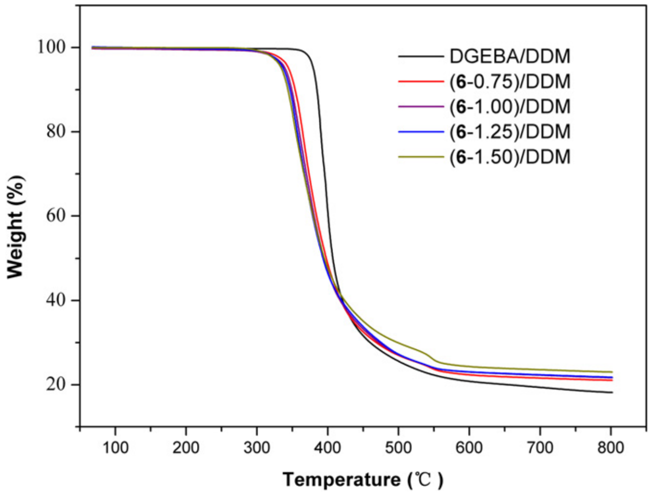


Fig. 3. TGA thermograms of (**6**)/DDM thermosets. (NOTE: The black-white version of Fig. 3 only for Print; The colour version of Fig. 3 only for Web).

phosphorus content is 1.00 wt.%, UL-94 V-0 grade of thermosets can be obtained. (**6** − m)/DDM has higher LOI than those of (**4** − m)/DDM and (**5** − m)/DDM. It is obvious that introducing (**4**)–(**6**) into the epoxy resins obtained excellent flame retardant efficiency, probably resulting from nitrogen–phosphorus synergistic effect.

4. Conclusions

Three new phosphorus-containing flame retardants (**4**), (**5**) and (**6**) were synthesized respectively, and their structures were confirmed by NMR, FTIR, and mass spectra. They can serve as co-curing agents of DDM. The as-made epoxy thermosets exhibited excellent flame retardancy, moderate changes in T_g and thermal stability. T_g value of (**5** − m)/DDM was higher than that of (**4** − m)/DDM or (**6** − m)/DDM. The degradation temperature and char yield of (**5** − m)/DDM was slightly higher than those of (**4** − m)/DDM and (**6** − m)/DDM. (**6** − m)/DDM possesses higher LOI value, compared with (**4** − m)/DDM and (**5** − m)/DDM.

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