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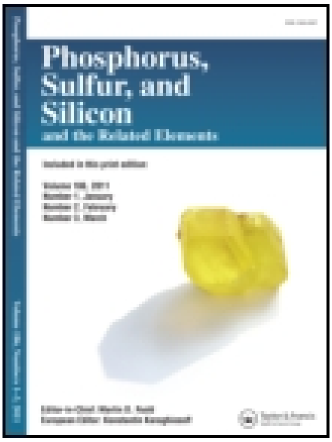

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Syntheses of Two Dopo-Based Reactive Additives as Flame Retardants and Co-Curing Agents for Epoxy Resins

Ling Xiao[a], De-chao Sun[a], Tian-li Niu[a] & You-wei Yao[a]
[a] Department of Materials Science and Engineering, Graduate School at Shenzhen, Tsinghua University, Shenzhen 518055, China

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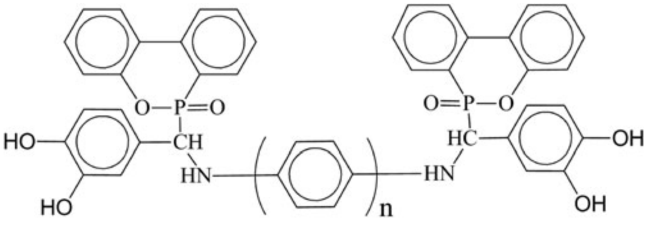
SYNTHESES OF TWO DOPO-BASED REACTIVE ADDITIVES AS FLAME RETARDANTS AND CO-CURING AGENTS FOR EPOXY RESINS

Ling Xiao, De-chao Sun, Tian-li Niu, and You-wei Yao
Department of Materials Science and Engineering, Graduate School at Shenzhen, Tsinghua University, Shenzhen 518055, China

GRAPHICAL ABSTRACT



n=1,2

Abstract *Two novel phosphorus-nitrogen-containing flame retardants, 1,1′,2,2′-tetra-hydroxyl-4″, 4‴-biphenylene-bis[amino-((10⁗-O-10⁗-H-9⁗-oxa-10⁗λ^5-phosphaphenanthrene-10⁗-yl))-methyl]}-bisphenol (**3**) and 1,1′,2,2′-tetra-hydroxyl-{4″,4‴-phenylene-bis[amino-((10⁗- O-10⁗- H-9⁗- oxa-10⁗λ^5-phosphaphenanthrene-10⁗-yl))-methyl]}-bis-phenol (**4**) were synthesized by two steps: 1,1′,2,2′-tetra-hydroxyl-{4″,4‴- bi-phenylene-bis[amino-methyl]}-bis-phenol, imine (**1**), was synthesized through condensation reaction between 3,4-dihydroxybenzaldehyde and 4,4′-diaminobiphenyl; and, 1,1′,2,2′-tetra-hydroxyl-{4″,4‴- phenylene-bis[amino-methyl]}-bis-phenol, imine (**2**) was synthesized by the reaction of 3,4-dihydroxybenzaldehyde and 1,4-phenylenediamine; then, addition reactions between 9,10-dihydro-9-oxa-10- phosphaphenanthrene-10-oxide and the two imines, the (**3**) and (**4**) were obtained, respectively. (**1**)–(**4**) were characterized by FTIR, NMR, and MS. (**3**) and (**4**) reacted with epoxy resins as co-curing agents with 4,4′-diaminodiphenylmethane. Compared with control samples, (**3**) or (**4**) co-cured epoxy thermosets with phosphorus content of 1.0 wt% possessed good flame retardant properties with LOI value reaching more than 36.0, higher char yields. The glass translation temperature (T_g) of thermosets containing (**3**) or (**4**) were characterized with suitable changes by DSC test.*

Keywords Flame retardant; epoxy resin; thermal stability; phosphorus

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Address correspondence to You-wei Yao, Department of Materials Science and Engineering, Graduate School at Shenzhen, Tsinghua University, Shenzhen 518055, China. E-mail: yaoyw@mail.tsinghua.edu.cn

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INTRODUCTION

Epoxy resins are widely used in lamination, adhesive, coating application, electronic insulation, because of their excellent performance, such as favorable chemical and electrical resistance, outstanding mechanical properties, moisture, and remarkable toughness.[1–3] However, epoxy resins have a flaw, inflammability, which limits their application severely. It is an exigent task to improve their thermal and flame resistance.[4,5] It has been reported that phosphorus-containing compounds able to molecularly incorporate in the resin network are expected to exhibit better flame retardancy.[6–10] As a typical flame retardant (FR) with active phenolic OH groups, 2-(6-oxid-6H-dibenz[c,e][1,2]-oxaphosphorin-6-yl)-1,4-benzenediol embody this incorporation strategy.[11] Another approach to realize this strategy is based on the addition reactions of 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) and imines, whose products are characteristic of binary functionality of FR and co-curing agent.[12–14]

In this paper, FRs, 1,1′,2,2′-tetra-hydroxyl-{4″, 4′′′′-biphenylene-bis[amino-((10′′′′-*O*-10′′′′-*H*-9′′′′-oxa-10′′′′λ^5- phosphaphenanthrene -10′′′′-yl))-methyl]}-bisphenol (**3**) and 1,1′,2,2′-tetra-hydroxyl-{4″,4′′′′-phenylene-bis[amino-((10′′′′-*O*-10′′′′-*H*-9′′′′-oxa-10′′′′λ^5- phosphaphenanthrene -10′′′′-yl))-methyl]}-bis-phenol (**4**) with active phenolic OHgroups in each of molecular structures are reported. Through the LOI and UL-94 vertical flame retardancy tests, (**3**) with building unit of biphenyl possesses better flame retardancy than that of (**4**) with building unit of phenyl. Thus, (**3**) and (**4**) display design of FR for epoxy resin based on modification of carbon-containing framework.

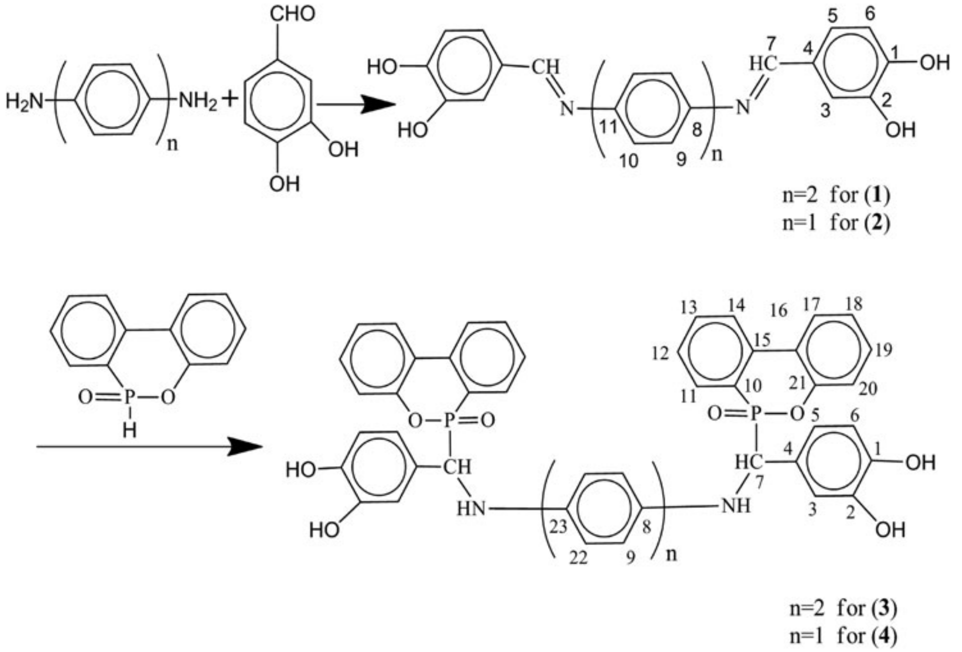
RESULTS AND DISCUSSION

Syntheses and Characterization of (1) and (2)

The syntheses of the imine compounds, 1,1′,2,2′-tetra-hydroxyl-{4″,4‴- biphenylene-bis[amino-methyl]}-bis-phenol (**1**), and 1,1′,2,2′-tetra-hydroxyl-{4″,4‴-phenylene-bis[amino-methyl]}-bis-phenol (**2**) were performed by the reaction of 3,4-dihydroxybenzaldehyde with 4,4′-diaminobiphenyl and 1,4-phenylenediamine, respectively, as described in Scheme 1. The ^{1}H NMR data displayed that the chemical shifts of amine hydrogen at 8.46 ppm in (**1**) and 8.43 ppm in (**2**) corresponded to the existence of imide structure. ^{13}C NMR data revealed that the chemical shifts of proton C_7 at about 149.8 ppm in (**1**) and 149.1 ppm in (**2**) identified the emergence of $C=N$ bond. Furthermore, according to the FTIR signals of the intermediates (**1**) and (**2**), the representative and strong absorptions of the $C=N$ bond at 1647, 1625 cm^{-1}, respectively, stated the imide group present in compounds (**1**) and (**2**).

Syntheses and Characterization of (3) and (4)

Scheme 1 showed that phosphorus-containing flame retardants, 1,1′,2,2′-tetra-hydroxyl-{4″, 4‴-biphenylene-bis[amino-((10′′′′-O-10′′′′-H-9′′′′-oxa-10′′′′λ^5-phosphaphenanthrene-10′′′′-yl))-methyl]}-bisphenol (**3**) and 1,1′,2,2′-tetra-hydroxyl-{4″,4‴-phenylene-bis[amino-((10′′′′-O-10′′′′-H-9′′′′-oxa-10′′′′λ^5-phosphaphenanthrene-10′′′′-yl)-methyl]}-bis-phenol (**4**) were obtained by the addition of DOPO with (**1**) and (**2**), respectively. In view of ^{1}H NMR data, the specific peaks of four OH groups in the range of 8.74–8.93 ppm, H_7, $H_{7'}$ with the range 4.37–4.82 ppm, it can prove the addition reactions between the DOPO and the imide compounds, respectively. Other peaks of NH and NH′



Scheme 1 Syntheses of (3) and (4).

at 6.61–6.64 ppm in (**3**), 5.66–5.73 ppm in (**4**) also confirmed the conclusion. According to the ^{13}C NMR, the chemical shifts of polymers (**3**) and (**4**), respectively, changed from the range of 149.7–149.8 ppm in (**1**) and 149.1 ppm in (**2**) to 55.3–56.7 ppm (C_7, $C_{7'}$), and 55.9–56.1 ppm (C_7, $C_{7'}$), suggesting the reaction of DOPO and the imide compounds. Moreover, from ^{31}P NMR data, the chemical shifts at 34.1, 31.3 ppm in (**3**) and 34.7, 31.3 ppm in (**4**) revealed that incorporating phosphorus to the imines (**1**) and (**2**) was successful. The typical absorptions of P–Ph bond at 1611, 1610 cm^{-1}, C–N bond at 1282, 1275 cm^{-1}, P=O bond at 1234, 1275 cm^{-1}, and N–H bond at 3503, 3556 cm^{-1}, respectively, potentially further proved the formation of (**3**) and (**4**). MS demonstrated results in consistency to the NMR and FTIR analyses.

DSC Analysis

As shown in Table 1, compared with T_g value of diglycidyl ether of bisphenol(DGEBA)/DDM, T_g values of the epoxy thermosets (**3**)/DDM and (**4**)/DDM decreased, which suggests that the addition of (**3**) and (**4**) decreases the cross-linking density of the epoxy thermosets. In addition, with the increasing contents of (**3**) and (**4**), T_g values of the epoxy thermosets reduced. T_g value of (**3**)/DDM was closer to that of DGEBA/DDM, probably indicating that (**3**) is suitable for moderate change of T_g values. With the identical phosphorus content, T_g values of (**3**)/DDM were much higher than that of (**4**)/DDM system, which probably attributed to that the cross-linking density of (**3**) with building unit of biphenyl was higher than that of (**4**) with building unit of phenyl.

Table 1 Thermal and flame-retardant properties of the epoxy thermosets (**3**) and (**4**)

Thermoset ID	P (wt%)[a]	N (wt%)[b]	T_g (°C)[c]	T_d (°C)[d]	Char yield[e]	UL-94 rating	LOI
DGEBA/DDM	0	2.83	160	378	15.97	Burning	25.1
(**3**–0.75)/DDM	0.75	2.49	157	351	23.20	V-1	36.8
(**3**–1.00)/DDM	1.00	2.37	150	350	24.69	V-0	37.0
(**3**–1.25)/DDM	1.25	2.25	149	346	24.91	V-0	37.1
(**3**–1.50)/DDM	1.50	2.13	148	343	25.54	V-0	37.2
(**4**–0.75)/DDM	0.75	2.51	142	348	22.27	V-1	36.0
(**4**–1.00)/DDM	1.00	2.40	140	344	23.08	V-0	36.2
(**4**–1.25)/DDM	1.25	2.29	137	341	23.69	V-0	36.7
(**4**–1.50)/DDM	1.50	2.18	135	340	23.71	V-0	36.9

[a]Phosphorus content; [b]Nitrogen content; [c]The glass transition temperature; [d]Thermal decomposition temperature of 5% weight loss; [e](wt%) Residual weight percentage at 800°C.

TGA Analysis

The thermal decomposition temperature of 5% weight loss (T_d) and the char yields of the epoxy thermosets (**3**)/DDM and (**4**)/DDM were obtained from TGA curves, as showed in Figure 1, respectively. T_d values of the epoxy systems (**3**)/DDM and (**4**)/DDM are in the range of 340–351°C, lower than that of DEGBA/DDM. With increasing of (**3**) and (**4**), T_d values of the epoxy thermosets decreased gradually. T_d values of (**3**)/DDM were higher than that of (**4**)/DDM with the same phosphorus content. Compared with 15.97 wt% char yield of DGEBA/DDM, char yields of (**3**)/DDM and (**4**)/DDM are in the range of 22.27–25.54 wt%, significantly increased. With the addition of phosphorus contents, the char yields increased gradually, as is in accordance with the some phosphorus-containing FRs.[15] Also, it can be clearly observed that the char yields of (**3**)/DDM were higher than that of (**4**)/DDM with identical phosphorus content. It was probably attributed to the reason that the polymer with a high content of aromatic possessed better fire retardancy and thermal stability.[13,15,16]

Analysis of Flame-Retardant Properties

The UL-94 flammability ratings and the LOI values of the epoxy thermosets were listed in Table 1. UL-94 V-1 rating was obtained with the phosphorus content of 0.75 wt%.

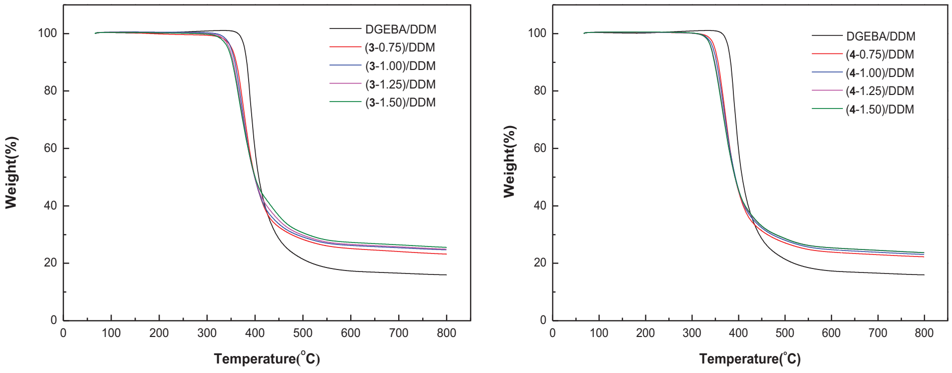


Figure 1 TGA thermograms of (**3**)/DDM thermosets and (**4**)/DDM thermosets.

And with increasing of phosphorus content, the UL-94 V-0 ratings were achieved. In addition, compared with the LOI value of 25.1 of DGEBA/DDM system, the LOI values of phosphorus-containing epoxy thermosets increased markedly from 36.0 to 37.2. And the LOI values of (**3**)/DDM were higher than that of (**4**)/DDM with identical phosphorus contents. Therefore, the UL-94 flammability ratings and the LOI values clearly demonstrated that the flame retardancy can be enhanced significantly by increasing the phosphorus content in epoxy systems, which was in excellent agreement with the consequence from the char yield.

CONCLUSION

Two novel phosphorus–nitrogen-containing FRs (**3**) and (**4**) with four OH groups were synthesized, and were used as co-curing agent for epoxy system. The T_g values, T_d values, char yields, and the LOI values of (**3**)/DDM were relatively higher than that of (**4**)/DDM system with same phosphorus contents.

EXPERIMENTAL

Materials

DGEBA(E51, epoxy equivalent = 0.51 mol/100 g) was provided by Guangzhou Dute Chemical Co., Ltd., China. DOPO was supplied by Huizhou Shengshida Technology Co., Ltd., China. 4,4′-diaminodiphenylmethane (DDM), 4,4′-diaminobiphenyl, and 1,4-phenylenediamine were all obtained from Shanghai Aladdin Reagent Co., Ltd., China. 3,4-dihydroxybenzaldehyde was received from Shanghai Energy Chemical, China. Ethanol was acquired from Tianjin Damao Chemical Reagent Factory, China. The Supplemental Materials (Figures S1–S16) contain extensive spectroscopic characterization of the novel compounds 1–4.

Preparation of 1,1′,2,2′-tetra-hydroxyl-{4″,4‴- bi-phenylene-bis[amino-methyl]}-bis-phenol **(1)**

To a 500 mL three-neck and round-bottom glass flask equipped with a condenser and a stirrer was added 4,4′-diaminobiphenyl (9.212 g, 0.05 mol), 3,4-dihydroxybenzaldehyde (13.812 g, 0.1 mol), and ethanol (200 mL). The reaction mixture was stirred at the temperature of 50°C for 2 h. After cooling down to room temperature, the precipitate was filtered and washed three times with ethanol. The deep orange-red powder (19.102 g, 90% yield) was collected after drying for more than 8 h in a vacuum oven. The structure of (**1**) was shown in Scheme 1. ^{1}H NMR (DMSO-d$_6$, ppm): $\delta = 9.35$–10.13 (meta-position OH, OH′, para-position OH, OH′), 8.46 (H_7), 7.70–7.72 (H_3, $H_{3'}$), 7.56 ($H_{7'}$), 7.38–7.45 (H_5, $H_{5'}$, H_9), 7.24–7.31 ($H_{9'}$, H_{10}), 6.87–6.93 (H_6, $H_{6'}$), 6.67 ($H_{10'}$). ^{13}C NMR (DMSO-d$_6$, ppm): $\delta = 160.4$ (C_1), 159.6 ($C_{1'}$), 152.6 (C_2), 151.4 ($C_{2'}$), 149.8 (C_7), 149.7 ($C_{7'}$), 148.6 (C_3), 147.0 ($C_{3'}$), 146.4 (C_8), 146.1 ($C_{8'}$), 138.4 (C_4), 137.2 ($C_{4'}$), 129.4 (C_5), 128.6 ($C_{5'}$), 127.4–127.6 (C_9), 126.4–126.5 ($C_{9'}$), 125.0 (C_{11}), 123.0 ($C_{11'}$), 121.9–122.0 (C_{10}), 116.0 ($C_{10'}$), 114.6–115.0 (C_6, $C_{6'}$). FTIR absorption (KBr, cm^{-1}): 1647 (C=N), 3347 (OH). MS: m/z = 423.1334 $[M-H]^-$.

Preparation of 4,4′-diaminobiphenyl and, 1,1′,2,2′-tetra-hydroxyl-{4″,4‴-phenylene-bis[amino-methyl]}-bis-phenol **(2)**.

Compound (**2**) was acquired in a similar synthetic procedure to compound (**1**). The deep yellow powder (27.870 g, 80% yield) was collected after the reaction of 1,4-phenylenediamine (10.814 g, 0.1 mol) and 3,4-dihydroxybenzaldehyde (27.624 g, 0.2 mol), as Scheme 1 shown the structure of (**2**). ^{1}H NMR (DMSO-d$_6$, ppm): $\delta = 9.32$–9.60 (meta-position OH, para-position OH), 8.43 (H_7), 7.41 (H_3), 7.25 (H_9), 7.18–7.21 (H_5), 6.83–6.85 (H_6). ^{13}C NMR (DMSO-d$_6$, ppm): $\delta = 159.2$ (C_1), 149.2 (C_2), 149.1 (C_7), 145.5 (C_8), 128.1 (C_3), 122.3 (C_5), 121.6 (C_9), 115.4 (C_4), 114.1 (C_6). FTIR absorption (KBr, cm^{-1}): 1625 ($C=N$), 3479 (OH). MS: m/z = 347.1040 $[M-H]^-$.

Preparation of $1,1',2,2'$-tetra-hydroxyl-$\{4'', 4'''$-biphenylene-bis[amino-((10$''''$-O-10$''''$-H-9$''''$-oxa-10$''''\lambda^5$-phosphaphenanthrene -10$''''$-yl))-methyl]$\}$-bisphenol (**3**).

To a 500 mL three-neck and round-bottom glass flask equipped with a condenser and a stirrer was added (**1**) (21.224 g, 0.05 mol), DOPO (21.600 g, 0.1 mol) and ethanol (300 mL), the reaction mixture was stirred at 50°C for 10 h. After cooling down to room temperature, the precipitate was filtered and washed three times with ethanol. The terreous powder (**3**) [36.400 g, 85% yield; mp (DSC): 183°C; $T_d = 268$°C (TGA)] was collected after drying for more than 8 h in a vacuum oven. Scheme 1 described the structure of (**3**).

^{1}H NMR (DMSO-d$_6$, ppm): $\delta = 8.81$–8.93 (meta-position OH, OH$'$, para-position OH, OH$'$), 8.04–8.17 (H_{11}, $H_{11'}$, H_{17}, $H_{17'}$, H_{14}), 7.73–7.74 ($H_{14'}$, H_{12}, $H_{12'}$), 7.55 (H_{13}, $H_{13'}$), 7.50 (H_{19}, $H_{19'}$), 7.45 (H_{18}, $H_{18'}$), 7.20 (H_3), 7.05 ($H_{3'}$, H_5, $H_{5'}$, H_6, $H_{6'}$), 6.82–6.87 (H_{20}, $H_{20'}$), 6.61–6.64 (H_9, $H_{9'}$, H_{22}, $H_{22'}$, NH, NH$'$), 4.82 (H_7), 4.37 ($H_{7'}$).

^{13}C NMR (DMSO-d$_6$, ppm): $\delta = 149.4$ (C_1), 149.3 ($C_{1'}$), 146.0 (C_2), 145.8 ($C_{2'}$), 145.5 (C_{21}), 145.4 ($C_{21'}$), 135.8 (C_8), 135.7 ($C_{8'}$), 134.1 (C_{16}), 134.0 ($C_{16'}$), 132.2 (C_{12}), 132.1 ($C_{12'}$), 131.3 (C_{14}), 131.1 ($C_{14'}$), 130.2 (C_{19}), 130.1 ($C_{19'}$), 128.9 (C_{13}), 128.8 ($C_{13'}$), 126.2–126.4 (C_3, $C_{3'}$, C_5, $C_{5'}$, C_{17}, $C_{17'}$), 126.0 (C_4), 125.9 ($C_{4'}$), 125.2 (C_{23}, $C_{23'}$), 125.1 (C_{18}), 124.9 ($C_{18'}$), 124.5 (C_{11}), 124.4 ($C_{11'}$), 123.8 (C_{10}), 123.7 ($C_{10'}$), 122.3 (C_{15}), 122.2 ($C_{15'}$), 120.6 (C_{20}), 120.5 ($C_{20'}$), 120.1 (C_6), 120.0 ($C_{6'}$), 116.3–116.4 (C_9), 115.6 ($C_{9'}$), 114.4 (C_{22}, $C_{22'}$), 55.3–56.7 (C_7, $C_{7'}$).
^{31}P NMR (DMSO-d$_6$, ppm): $\delta = 34.1$, 31.3.

FTIR absorption (KBr, cm^{-1}): 3503 (N–H), 3275 (OH), 1611 (P$-$Ph), 1282 (C$-$N), 1234 ($P=O$). MS: m/z = 855.2029 $[M-H]^-$.

Preparation of $1,1',2,2'$-tetra-hydroxyl-$\{4'',4'''$-phenylene-bis[amino-((10$''''$-O-10$''''$- H-9$''''$- oxa-10$''''\lambda^5$-phosphaphenanthrene-10$''''$-yl))-methyl]$\}$-bis-phenol (**4**).

(**4**) was obtained in a similar synthetic procedure to compound (**3**). The shallow terreous powder (**4**) [31.215 g, 80% yield; mp (DSC): 204°C; $T_d = 275$°C (TGA)] was collected after the reaction of (**2**) (17.419 g, 0.05 mol) and DOPO (21.600 g, 0.1 mol). The structure of (**4**) was depicted in Scheme 1.

^{1}H NMR (DMSO-d$_6$, ppm): $\delta = 8.74$–8.88 (meta-position OH, OH$'$, para-position OH, OH$'$), 813–8.16 (H_{11}, $H_{11'}$, H_{17}, $H_{17'}$), 7.95–7.80 (H_{14}, $H_{14'}$), 7.70–7.74 (H_{12}, $H_{12'}$), 7.50–7.52 (H_{13}, $H_{13'}$), 7.39–7.43 (H_{19}, $H_{19'}$), 7.28–7.32 (H_{18}, $H_{18'}$), 6.98–7.02 (H_3, $H_{3'}$), 6.72–6.75 (H_{20}, $H_{20'}$), 6.59–6.61 (H_5, $H_{5'}$), 6.53–6.54 (H_6, $H_{6'}$), 6.25–6.31 (H_9, $H_{9'}$), 5.66–5.73 (NH, NH$'$), 4.46–4.63 (H_7, $H_{7'}$).

^{13}C NMR (DMSO-d$_6$, ppm): $\delta = 162.2$ (C_1), 162.1 ($C_{1'}$), 148.8 (C_2), 148.7 ($C_{2'}$), 144.8 (C_{21}), 144.7 ($C_{21'}$), 138.8 (C_8), 138.6 ($C_{8'}$), 135.1 (C_{16}), 135.0 ($C_{16'}$), 133.3 (C_{12}), 133.2 ($C_{12'}$), 131.6 (C_{14}), 131.5 ($C_{14'}$), 130.7 (C_{19}), 130.6 ($C_{19'}$), 128.2 (C_{13}), 128.1 ($C_{13'}$), 125.6 (C_3, $C_{3'}$), 125.4 (C_5), 125.3 ($C_{5'}$), 124.6 (C_{17}), 124.5 ($C_{17'}$), 123.9 (C_4), 123.8 ($C_{4'}$), 123.6 (C_{18}), 123.4 ($C_{18'}$), 121.8 (C_{11}), 121.7 ($C_{11'}$), 120.0 (C_{10}), 119.9 ($C_{10'}$), 119.5 (C_{15}), 119.4 ($C_{15'}$), 115.9 (C_{20}), 115.8 ($C_{20'}$), 115.0 (C_6, $C_{6'}$), 114.8 (C_9, $C_{9'}$), 55.9–56.1 (C_7, $C_{7'}$).
^{31}P NMR (DMSO-d$_6$, ppm): $\delta = 34.7$, 31.3.

FTIR absorption (KBr, cm^{-1}): 3556 (N–H), 3278 (OH), 1610 (P$-$Ph), 1275 (C$-$N), 1229 ($P=O$). MS: m/z = 779.1730 $[M-H]^-$.

Preparation of the Epoxy Thermosets

Taking the active proton numbers of amino and phenol groups in (**3**), (**4**), and DDM into account, the DDM, (**3**), and (**4**) with an equivalent ratio to epoxy resins of 1:1 were mixed. The resins were cured in a mold at 140°C for 2 h, 180°C for 2 h, respectively. Finally, epoxy thermosets were cooled down gradually to room temperature to avoid cracking. The phosphorus contents of the epoxy thermosets were 0.75, 1.00, 1.25, and 1.50 wt%. And the epoxy thermosets were labeled as (**n**-m)/DDM (**n** stands for the (**3**) or (**4**), and m for the percentage content of phosphorous in thermosets) and listed in Table 1.

Characterization

Fourier transform infrared (FTIR) spectra were recorded on a Bruker Vertex 70 infrared spectrophotometer by KBr disc method with the optical range of 400–4000 cm^{-1}. ^{1}H NMR, ^{13}C NMR, and ^{31}P NMR spectra were registered with a Bruker spectrometer by using DMSO-d_6 as a solvent. Mass spectra were performed on a Waters Quattro X Premier mass spectrometer. DSC scans were obtained in the way that samples of approximately 5–10 mg were scanned in the range of 25–300°C under argon atmosphere at a heating rate of 10°C/min by using a Mettler-Toledo DSC 823e. And the glass transition temperature (T_g) was taken as midpoint of enthalpy transitions along the thermal analysis curve. Thermal gravimetric analyses (TGA) of samples were carried out with Mettler-Toledo TGA/DSC1 from 50 to 800°C under argon atmosphere at a heating rate of 10°C/min. The UL-94 test was measured according to the testing procedure of vertical burning test with the dimensions $127 \times 13 \times 3$ mm^3 of each sample. During the test, five samples hung vertically were ignited for two 10 s. After the first ignition, the time for the polymer to self-extinguish (t_1) was gained when the flame removed. Cotton ignition would be noted if polymer dripping occurred during the test. After cooling, a second ignition was performed on the same sample, and the self-extinguish time (t_2) and dripping characteristics were also recorded. The polymer would achieve the UL-94 V-0 flammability rating if $t_1 + t_2$ of each sample did not exceed 10 s without any dropping. If $t_1 + t_2$ was in the range of 10–30 s without any dropping, the polymer would reach the UL-94 V-1 flammability rating. The LOI test was performed according to the testing procedure of GB/T 2406–2009 with the dimensions $(70\text{–}150) \times 6.5 \times 3$ mm^3 of each sample.

SUPPLEMENTAL MATERIAL

Supplementary data for this article can be accessed on the publisher's website, www.tandfonline.com/gpss

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