Synthesis of Novel Phosphorous-Containing Biphenol, 2-(5, 5-Dimethyl-4-phenyl-2-oxy-1,3,2-dioxaphosphorin-6-yl)-1,4-benzenediol and Its Application as Flame-Retardant In Epoxy Resin

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ABSTRACT: A novel phosphorous-containing biphenol, 2-(5,5-dimethyl-4-phenyl-2-oxy-1,3,2-dioxaphosphorin-6-yl)-1,4-benzenediol (DPODB), was prepared by the addition reaction between 5,5-dimethyl-4-phenyl-2-oxy-1,3,2-dioxaphosphorinane phosphonate (DPODP) and *p*-benzoquinone (BQ). The compound (DPODB) was used as a reactive flame retardant in *o*-cresol formaldehyde novolac epoxy resin (CNE) for electronic application. The structure of DPODB was confirmed by FTIR and NMR spectra. Thermal properties of cured epoxy resin were studied using differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA). The flame retardancy of cured epoxy resins was tested by UL-94 vertical test and achieved UL-94 vertical tests of V-0 grade (nonflammable). © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 3842–3847, 2006

Key words: phosphorus; 2-(5,5-dimethyl-4-phenyl-2-oxy-1,3,2-dioxaphosphorin-6-yl)-1,4-benzenediol; epoxy resin; epoxy curing; flame retardancy

INTRODUCTION

Epoxy resins are widely used as structural adhesives, coatings, and advanced composite matrices in the aerospace and electronic industries because of their high tensile strength and modulus, low shrinkage on cure, high adhesion to many substrates, excellent chemical and corrosion resistance, and good dimensional stability.[1–3] However, the flammability of epoxy resins is a major disadvantage in their applications. Traditionally, most flame-retardant polymers are obtained by physically blending flame-retardant additive with the polymer. However, a major disadvantage of all flame-retarding additives is that they may be lost in processing, and during the use of the polymer, this may mean that high loadings are initially required. Another way to reduce the flammability of polymers is to chemically bond the flame retardant to the polymer backbone, i.e., to use a reactive flame retardant. This offers the advantage of permanent attachment of flame-retardant groups to polymer, leading to high efficiency in flame retardancy.[4–8] But the utilization of halogenated and antinomy compounds in polymeric materials is harmful to the environment and human health because toxic and corrosive gases as well as harmful endocrine-disrupting chemicals are released.[9,10] Therefore, the trend is trying to develop a halogen-free epoxy with high flame retardancy, high thermal stability, low cost, and to meet the requirements of the current and future electronic applications.[11–13] Recently, organic phosphorus compounds have demonstrated good ability as a flame retardant for epoxy resins and also to generate less toxic gas and smoke than halogen-containing compounds.[4,14–21] In this study, a rigid phosphorus-containing reactive 2-(5,5-dimethyl-4-phenyl-2-oxy-1,3,2-dioxaphosphorin-6-yl)-1,4-benzenediol (DPODB) was synthesized. The incorporation of this bulky pendant group into epoxy resin is expected to impart the required flame retardance, less fumes, and higher thermal stability than the conventional bromine-containing fire retardant systems.

EXPERIMENTAL

Materials

1-Phenyl-2,2-dimethyl-1,3-propanediol was prepared according to the literature.[10] Isobutyl aldehyde, phenyl aldehyde, *p*-benzoquinone (BQ), and PCl_3 were purchased from Shanghai Chemicals, China. All solvents were used without further purification. Bisphenol-A (BPA), tetrabromobiphenol-A (TBBA), diglycidyl ether of bisphenol-A (DGEBA, E51, EEW = 188 g/eq), *o*-cresol formaldehyde novoloc epoxy

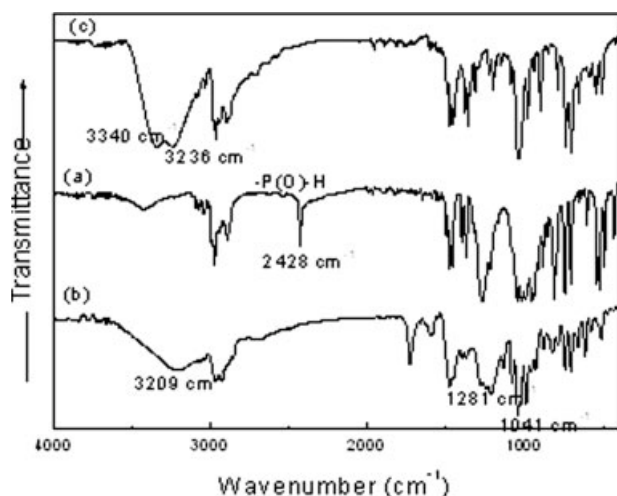*Correspondence to:* W.-J. Xu (weijxu@hnu.cn).
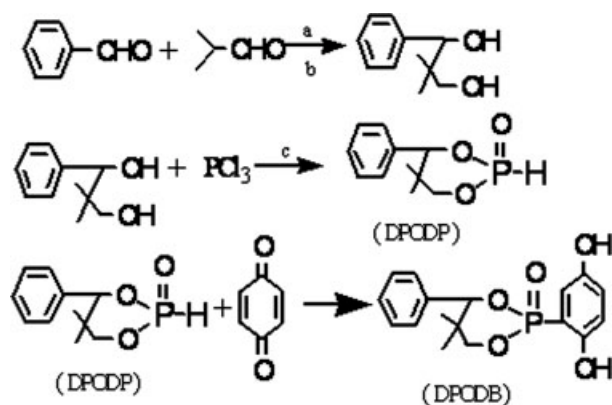
Scheme 1 Synthetic route of DPODB (a): KOH; (b): C₂H₅OH; (c): PCl₃ + CH₃OH.

Figure 2 The 1H-NMR spectra of DPODP and DPODB.

(CNE, epoxy equivalent weight, EEW = 207 g/eq), and a phenol formaldehyde novolac resin (PN) are used as curing agents with a hydroxyl equivalent weight of about 110 and these were kindly supplied by BaLing Petrochemical of China.
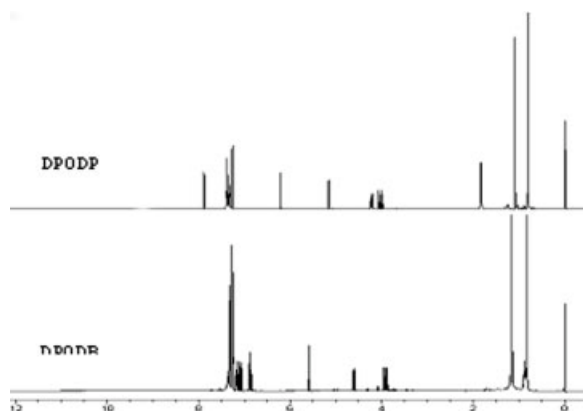
Synthesis

Synthesis of phosphorus-containing compounds

DPODP was prepared through 1-phenyl-2,2-di-methyl-1,3-propanediol and PCl₃.[22] Into a 250 mL round bottom flask equipped with a stirrer, heating mantle, thermocouple, temperature controller, nitrogen inlet, and reflux assembly, were charged 0.1 mol of 1-phenyl-2,2-dimethyl-1,3-propanediol, 0.1 mol methanol absolute, and 20 mL 1,2-dichloroethane in an ice bath. 0.1 mol PCl₃ and 10 mL of 1,2-dichloroethane were added incrementally in 2 h. The reaction mixture was maintained at room temperature for 12 h. After the solvent was removed by evaporation

under reduced temperature, the products were recrystallized with H_2O/C_2H_5OH (mp = 151.2–152.0, yield = 78%). IR (KBr, cm^{-1}): 2428 (—P(O)—H), 1267 (P=O), 1050–950 (P—O—C). ELEM. Fast atom bombardment mass spectrometry (FABMS) m/z: 226 (M^+). ^{1}H-NMR (CDCl₃, ppm): 7.263–7.393 (m, 5), 6.213 and 7.882 (split, 1-H), 5.166–5.174 (d, 1H, —CH—), 3.987–4.247 (m, 2H, —CH₂—), 1.100 (s, 3H, —CH₃), 1.100 (s, 3H, —CH₃).

Synthesis of DPODB

Into a 500 mL three-neck round bottom flask equipped with a stirrer, heating mantle, thermocouple, temperature controller, nitrogen inlet, and reflux assembly, were charged 0.33 mol of DPODP and 300 mL xylene. The temperature of the solution was raised to reflux ($\sim 140°C$) to distill the residual water. When the amount of water was completely removed, then 0.3 mol p-benzoquinone (BQ) was added incrementally. The reaction mixture was maintained at reflux for another 1 h after the completion of BQ addition. (Scheme 1) The precipitates were filtered

Figure 1 FTIR spectrum of (a) DPODP; (b) DPODB; and (c) DPOD.
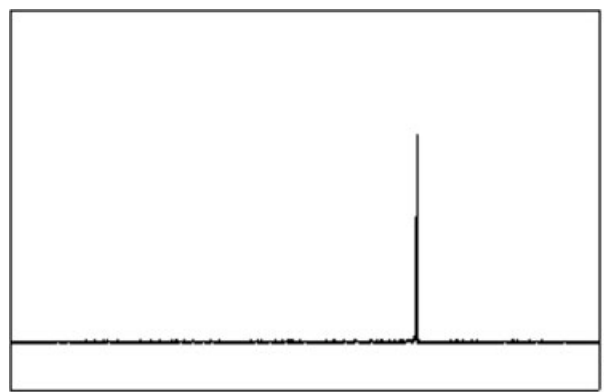
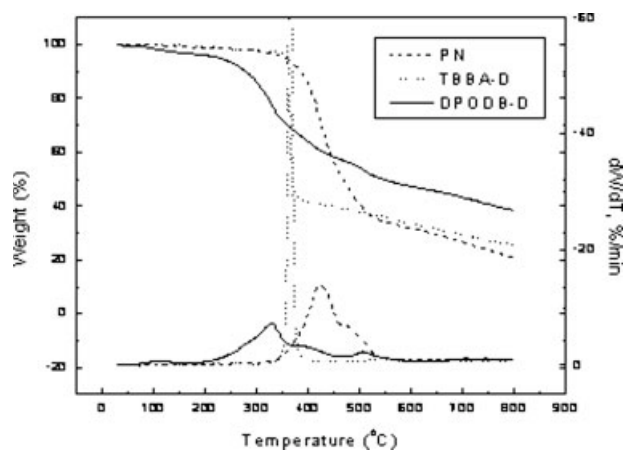**Figure 3** The ^{31}P-NMR spectra of DPODB.

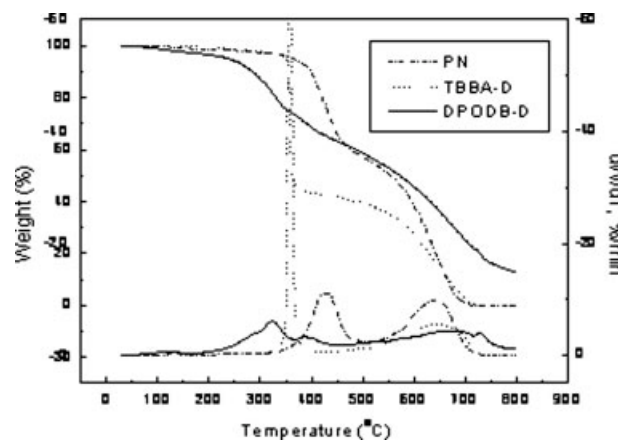**Figure 4** TGA thermograms of cured CNE resins in N$_2$.

Figure 5 TGA thermograms of cured CNE resins in Air.

and further recrystallized twice from CCl$_4$, and finally dried in a vacuum oven at 80°C to obtain coffee-colored solid (mp = 179–182°C, 95% yield). IR spectrum (KBr, cm^{-1}), 987, 1041 (P—O—C), 1281 (P=O), 1589 (p-ph), 3209 (Ph-OH). ^{1}H-NMR (CDCl$_3$, ppm): 6.871–7.335 (m, 8H), 5.585 (s, 1H), 4.591 (d, 1H), 3.872–3.958 (m, 1H), 1.148 (s, 3H), 0.821 (s, 3H). ^{31}P-NMR (DMSO-d$_6$, ppm): 23.795. Mass spectrometry (MS) m/z: 334.2 (M$^+$). Elem. Anal. Calcd for C$_{17}$H$_{19}$O$_5$P (334.2): C, 61.09%; O, 23.94%; P, 9.27%. Found: C, 61.12%; O, 23.97%; P, 9.09%.

Advancement of epoxy resin with DPODB

DPODB-epoxy resin (DPODB-EP) was prepared through the reaction of DPODB with diglycidyl ether of bisphenol-A (DGEB-A). Into a 250 mL round bottom flask equipped with a stirrer, heating mantle, thermocouple, temperature controller, and vacuum outlet, was initially charged with DGEBA(E51, EEW = 188, 75.2 g, 0.2 mol). The epoxy resin was

heated under full vacuum at 100°C to drive off the residual water in the epoxy resin for ∼ 1 h and then DPODB(33.4 g, 0.1 mol) was added. The reaction mixture was heated to 120°C to achieve a complete solution, and then 500 ppm Ph$_3$P was added as a catalyst. The reaction mixture was maintained at 150°C for 1 h to complete the reaction. The EEW was determined by the HClO$_4$/potentiometric titration method and was found to be 498.

Advancement of epoxy resin with TBBA and BPA

To compare the thermal, mechanical, and flame-retardant properties of DPODB versus TBBA, the advancements of epoxy resin with TBBA and bisphenol-A (BPA) were also performed. The same advancement procedure as DPODB was applied. The equivalent ratios of epoxy to phenolic hydroxyl of 2.4 : 1 (for TBBA) and 2.1 : 1 (for BPA) produced two advanced epoxy resins with the EEW of 512 (for TBBA) and 495 (for BPA), respectively.

TABLE I
Thermal Properties of Cured Neat CNE Epoxy Resin Using Various Ratios of DPODB/PN and TBBA/PN

Sample design		Temperature of weight loss				Rapid rate T_r (°C)						Char yields at (%)			
		5%		10%		Step 1		Step 2		Step 3		600°C		700°C	
		Air	N$_2$	Air	N$_2$	Air	N$_2$	Air	N$_2$	Air	N$_2$	Air	N$_2$	Air	N$_2$
DPODB/PN (wt %)															
Contol	0/100	365	358	398	386	427	423	642	–	–	–	39	32	1	27
DPODB-A	25/75	310	302	355	345	380	385	390	–	–	–	38	46	10	41
DPODB-B	50/50	259	265	315	314	358	363	532	–	662	–	43	48	20	44
DPODB-C	75/25	245	251	291	295	340	345	567	510	665	–	43	50	24	46
DPODB-D	100/0	238	228	285	278	323	328	388	508	673	–	46	48	25	43
TBBA/PN (wt %)															
TBBA-A	25/75	356	303	364	363	367	370	660	–	–	–	36	33	12	28
TBBA-B	50/50	361	363	371	373	375	378	650	–	–	–	33	40	4	35
TBBA-C	75/25	365	363	378	380	382	385	480	483	640	–	29	44	1	40
TBBA-D	100/0	353	358	358	363	360	365	655	–	–	–	28	34	3	29
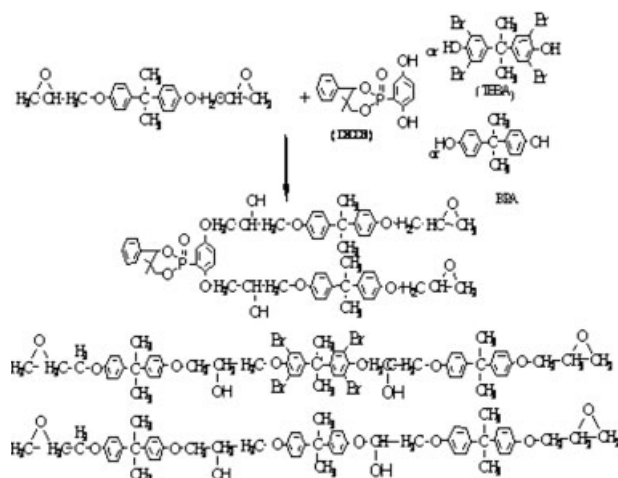
Scheme 2 Synthetic route of advanced epoxy resin.

Curing procedure of epoxy resin

Various amounts of DPODB were added to phenol novolac as a curing agent for cresol formaldehyde novolac epoxy (CNE) resin to determine the flame-retardant effect of phosphorus. The curing agents consisted of DPODB/PN in various weight ratios (0/100, 25/75, 50/50, 75/25, 100/0) were prepared. Ph_3P was used as a curing accelerator. The CNE resin was mixed with the above curing agents in a 1 : 1 equivalent ratio and 0.3% Ph_3P, and then the mixture were cured in a mold at 150°C and 50 Kg/cm^2 for a period of 1 h and then at 180°C for 2 h and then 200°C for 1 h to obtain cured specimens.

Curing procedure for the advanced epoxy resin

Various advanced epoxy resins and phenol novolac were mixed in a 1 : 1 equivalent ratio. The mixture was heated on a hot plate at 130–150°C with a continuous stirring until the curing agent was completely dissolved in epoxy and a homogeneous solution was obtained. Then the mixtures were cured at 150°C for 2 h and postcured at 180°C for 4 h.

Measurement

Elemental analyses were performed using a Heraeus CHN-O-S-Rapid elemental analyzer. IR spectra were recorded with an infrared spectrophotometer (WQF-410). Mass spectra were recorded by a G1946C GC/MS. Melting points of DPODB were determined in a polarizing microscope (Laboratory Devices MEL-TEMP II). DSC data and TGA data were obtained from 8 to 10 mg samples in a nitrogen atmosphere or in air atmosphere, respectively, at a heating rate of 5–20°C per minute using a STA449C Thermogravimetric Analyzer. ^{1}H-NMR and ^{31}P-NMR spectra were obtained with a INOVA-400 by using CDCl$_3$ and DMSO-d$_6$ as solvents using tetramethylsilane (TMS) and H$_3$PO$_4$ as internal standards, respectively. The LOI was determined with an Atlas limiting oxygen index chamber, according to the ASTM standard method. The percentage of O$_2$ in the O$_2$—N$_2$ mixture just sufficient to sustain the flame was taken as the LOI. EEW of DPODB epoxy resin was determined by the HClO$_4$/potentiometric titration method.

RESULTS AND DISCUSSION

Monomer synthesis and characterizations

The chemical structures of DPODP and DPODB were determined by FTIR, mass, elemental analysis, ^{1}H and ^{31}P-NMR spectroscopies. The results are in good agreement with the expected values.

The FTIR spectra of DPODP and DPODB are shown in Figure 1. As shown in the spectrum of DPODP in Figure 1, the peak at 3340 and 3236 cm^{-1} for —CH—OH and —CH$_2$—OH in 1-phenyl-2,2-dimethyl-1,3-propanediol disappeared, and a new distinctive absorption at 2428 cm^{-1} for —P(O)—H appeared, which demonstrated that the reaction between 1-phenyl-2,2-dimethyl-1,3-propanediol and PCl$_3$ proceeded. In the spectrum of DPODB, the distinctive absorption at 2428 cm^{-1} for —P(O)—H in DPODP disappeared, the appearance of a characterized absorption at 1589 cm^{-1} for P-Ph and the absorption peaks at 1281 cm^{-1} (P=O), 1041 cm^{-1}

TABLE II
Thermal Properties of Cured Advancement Resins with DDS

| Sample (advancement resin) | g/eq | T_g | Temperature of weight loss | | | | Rapid weight loss temp. (T_r, °C) | | | | Char yield (%) | |
| | | | 5% | | 10% | | Step 1 | | Step 2 | | (700°C) | |
			Air	N$_2$	Air	N$_2$	Air	N$_2$	Air	N$_2$	Air	N$_2$
DPODB	498	203.5	273	273	296	296	342	343	590	–[a]	22.0	31.2
BPA	495	127.5	357	372	366	380	365	430	570	–[a]	17.3	12.0
TBBA	512	137.2	348	356	351	358	358	360	602.5	–[a]	11.4	29

[a] Step 2 of rapid rate was not found.

TABLE III
LOI Values and UL-94 V test Results of Cured Epoxy Resins

Epoxy resins	Element for retardant	Average burning time (s)	Fume	Drip	UL-94 V test	LOI
DPODB-EP/PN	P (2.83%)	<1	−	−	V-0	29.5
BPA-EP/PN	No	95	+	++	V-2	23
TBBA-EP/PN	Br (17.12%)	<1	++	+	V-0	32.5

++, heavy; +, slightly; −, scarcely.

(P—O—C), and 3209 cm^{-1} (Ph—OH) further confirmed that DPODB was synthesized.

^{1}H-NMR spectra of DPODP and DPODB are shown in Figure 2. This coincidence between the peak integration data and proton ratios provides further evidence on the chemical structure of DPODP and DPODB. The ^{31}P-NMR spectrum of DPODB shows only a single peak, as can be seen in Figure 3.

Thermal properties

The thermal stability of epoxy resins is especially affected by the structure of the epoxy resin and the type of curing agent. The thermal behavior in nitrogen and air atmosphere of these cured resins characterized by TGA are shown in Figures 4 and 5, and the characteristic data obtained from these thermograms are summarized in Table I. The results showed that the DPODB/PN-cured epoxy resins are not as thermally stable as the phosphorus-free/PN cured resins. The relatively poor thermal stability of the phosphorous-containing cured epoxy resins comes from the phosphorous group degrading at relatively low temperatures.[17] This phenomenon has been observed in other phosphorylated polymer systems, and is classified to play an important role in improvement of the flame retardance of the phosphorus-containing epoxy resins.[1–19] It was also observed that CNE cured with various weight of DPODB/PN and TBBA/PN have higher char yield than that of the control CNE resin. This char yield has been correlated to denote the flame retardance and has been widely referred in the studies of the flame properties of the polymers.[5,16–19] It should be noted that the DPODB-A (2.83% of P-containing) has exhibited higher char yield (41% in N$_2$ at 700°C) than that of the control CNE resin and all TBBA/PN cured epoxy resins.

The phosphorus-containing resin exhibited a second stage of rapid weight loss, unlike the one-stage rapid weight loss of the control CNE resin, which is accordance with the result of the DPODB's, effect on the thermal stability of cured epoxy resins.[23] Advanced epoxy resins are particularly useful in printed circuit boards and other electrical laminate application.[24] The advanced epoxy resins are shown in Scheme 2. TGA were also performed to compare the thermal stability of the advanced epoxy resins made from three diols (BPA, TBBA, and DPODB) and the results are shown in Table II. The results indicated that the advanced epoxy resin made from DPODB had a higher char yield at 700°C than the other two advanced epoxy resins made from BPA and TBBA.

UL-94V test for advanced epoxy resin

The UL-94V test is usually used as an indicator to evaluate the flame retardancy of a polymer. For the UL-94V test, five specimens of each advanced epoxy resin were prepared and the test results are shown in Table III. The advanced resin made from BPA had a 95 s burning time after the Bunsen burner was removed, while advanced resin from TBBA and DPODB both passed the UL-94V flame retardance test. It should be noted that the advanced resin containing 2.8% P has exhibited better flame retardance than the advancement resin containing 17.12% bromine. The most important feature of the P flame retardant is that no fumes are generated.

CONCLUSIONS

A reactive phosphorous-containing biphenol, 2-(5,5-dimethyl-4-phenyl-2-oxy-1,3,2-dioxaphosphorin-6-yl)-1,4-benzenediol (DPODB) was successfully synthesized. The compound was used as curing agent for CNE resins to be used for semiconductor encapsulation applications and also to prepare advanced epoxy resin for electrical laminate applications. The DPODB compound provided not only good solubility in acetone and the better flame-retardant effect, but also generated much less fumes in the combustion test. However, any effort to characterize the new flame retardant in comparing between some well-known phosphorous-containing curing agent, such as ODPOB and some other commercial flame retardant has not been made and will be the main direction of our future work.

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