Preparation of Phosphinated Bisphenol from Acid-Fragmentation of 1,1,1-Tris(4-hydroxyphenyl)ethane and Its Application in High-Performance Cyanate Esters

Ching Hsuan Lin,¹ Hung Tse Lin,¹ Yu Wei Tian,¹ Shenghong A. Dai,¹ Wen Chiung Su²

¹Department of Chemical Engineering, National Chung Hsing University, Taichung, Taiwan ²Department of Chemistry and Chemical Engineering, Chung Shan Institute and Technology, Lungtan, Tauyuan, Taiwan Correspondence to: C. H. Lin (E-mail: linch@nchu.edu.tw)

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ABSTRACT: We reveal a route for the preparation of phosphinated bisphenol, 1,1-bis(4-hydroxyphenyl)-1-(6-oxido-6H-dibenz <c,e> <1,2> oxaphosphorin-6-yl)ethane (2), via a one-pot reaction of 1,1,1-tris(4-hydroxyphenyl)ethane and 9,10-dihydro-9oxa-10-phosphaphenanthrene 10-oxide (DOPO) in the catalysis of p-toluenesulfonic acid. A two-step reaction mechanism, acid-fragmentation of 1,1,1-tris(4-hydroxyphenyl)ethane followed by nucleophilic addition of DOPO, is proposed for the synthesis. Based on (2), a dicyanate ester derivative, 1,1-bis(4cyanatophenyl)-1-(6-oxido-6H-dibenz <c,e> <1,2> oxaphosphorin-6-yl)ethane (3) was prepared and co-cured with a commercially available dicyanate ester, the dicyanate ester of

INTRODUCTION Cyanate esters have received considerable attention because of their exceptional properties, such as good thermal stability, low water absorption, and low dielectric properties. They have been found to be particularly useful in the preparation of electrical and structural laminates, potting formulations, molding formulations, and so forth. Dicyanate esters are generally prepared by the reaction of bisphenol and cyanogen bromide in the presence of triethylamine at low temperature. The cyanate group undergoes trimerization to form the s-triazine ring and generates a thermoset with high cross-linking density. A large variety of cyanate esters with different backbone structures and properties have been synthesized and are summarized by Shimp and coworker¹ and Lin and Pearce,² respectively. Over the past decade, many new cyanate esters were developed. For example, Guenthner et al. prepared a silicon-containing dicyanate ester in which isopropylidene of dicyanate ester of bisphenol A (BACY) is replaced by a quaternary silicon.³ The silane-based poly(cyanate ester) exhibits improved thermal oxidation and moisture resistance. Snow and coworkers prepared oligodimethylsiloxanes linked cyanate esters with low dielectric characteristic.⁴ Davis and coworkers used racemic/diastereomeric concept to prepare a liquid-type tricyanate ester for favorable processing

bisphenol A (BACY). Experimental data show that incorporating (3) into BACY enhances the flame retardancy and dielectric properties with little penalty to the thermal properties. A thermoset with T_g 274 °C, coefficient of thermal expansion (CTE) 49 ppm/°C, D_k 3.04 (1 GHz), T_d (5%,) N₂: 435 °C, air: 424 °C, and UL-94 V-0 rating can be achieved via this approach. © 2011 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 49: 4851–4860, 2011

KEYWORDS: cyanate ester; dielectric constant; DOPO; fragmentation of trisphenol; flame retardancy; flame retardant; synthesis; thermosets

characteristic and enhanced thermomechanical performance in wet environments.⁵ Wang and coworkers prepared phenolphthalein-based cyanate esters with high- $T_{\rm g}$ for higher temperature applications.⁶ Snow and Buckley prepared fluoromethylene cyanate ester with lower $T_{\rm g}$, dielectric constant, critical surface tension, and water absorption.⁷ Lin et al. prepared a dipentene-containing cyanate ester with low moisture absorptions and low dielectric properties due to the hydrophobic character of the aliphatic dipentene structure.⁸ Although poly(cyanate esters) display promising properties, the lack of flame retardancy is a drawback of cyanate ester for electronic applications, where meeting a flame retardancy standard, UL-94 V-0, is required. Literatures have reported that the flame retardancy of cyanate esters can be greatly enhanced by the incorporation of phosphorus element.^{5,9-18}

It has been reported that bisphenol A undergoes acid- or base-catalyzed fragmentation to phenol and 4-isopropenylphenol.^{19–21} According to the fragmentation chemistry of bisphenol A and our knowledge in conjugate addition chemistry of 9,10-dihydro-9-oxa-10-phosphaphenanthrene 10-oxide (DOPO),^{22,23} we speculated that DOPO might react with the resulting 4-isopropenylphenol via a conjugate addition. To prove our speculation, we reacted the bisphenol A

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and DOPO in the catalysis p-toluenesulfonic acid (p-TSA) as a model reaction. A model compound, phosphinate monophenol **(1)**, was successfully prepared. On the basis of successful model reaction, we prepared a phosphinated bisphenol **(2)** sia a one-pot reaction of 1,1,1-tris(4-hydroxyphenyl)ethane and DOPO in the catalysis of p-TSA. Then a dicyanate ester be derivative **(3)** was prepared from **(2)** and co-cured with definition of and discussed. The successful preparation of **(1-2)** via the combination of nucleophilic addition prof DOPO and acid-fragmentation of bisphenol A or 1,1,1- vris(4-hydroxyphenyl)ethane expands the chemistry of DOPO.

EXPERIMENTAL

nisms were reported in this work.

Materials

DOPO was purchased from TCI (Tokyo Chemical Industry Co., Ltd.). BACY, B-10, was kindly supplied by Rhone-Poulence. Bisphenol A, p-TSA, and 1,1,1-tris(4-hydroxyphenyl)-ethane were purchased from Acros. All solvents used are commercial products (High-performance liquid chromatography (HPLC) grade) and used without further purification.

Detailed synthesis, characterization, and proposed mecha-

Characterization

Differential scanning calorimetry (DSC) was performed with a Perkin-Elmer DSC 7 in a nitrogen atmosphere at a heating rate of 10 min/°C. Thermal gravimetric analysis (TGA) was performed with a Perkin-Elmer Pyris1 at a heating rate of 20 °C/min in a nitrogen or air atmosphere. Dynamic mechanical analysis (DMA) was performed with a Perkin-Elmer Pyris Diamond DMA with a sample size of 5.0 cm \times 1.0 cm \times 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 at a frequency of 1 Hz. The test was performed by a bending mode with an amplitude of 5 μ m. Thermal mechanical analysis (TMA) was performed with a Perkin-Elmer Pyris Diamond TMA at a heating rate of 5 °C/min. NMR measurements were performed using a Varian Inova 600 NMR in Dimethyl Sulfoxide (DMSO)- d_{6} , and the chemical shift was calibrated by setting the chemical shift of DMSO- d_6 as 2.49 ppm. IR spectra were measured by a Perkin-Elmer RX1 infrared spectrophotometer in KBr powder form. High resolution mass spectra were obtained by a Finnigan/Thermo Quest MAT 95XL mass spectrometer. The UL-94 vertical test was performed according to the testing procedure of FMVSS 302/ZSO 3975 with a test specimen bar of 127 mm in length, 12.7 mm in width, and about 1.27 mm in thickness. The height of the burner flame was 25 mm, and the height from the top of the burner to the bottom of the test bar was 10 mm. During the test, the polymer specimen was subjected to two 10 s ignitions. After the first ignition, the flame was removed, and the time for the polymer to self-extinguish (t_1) was recorded. Cotton ignition would be noted if polymer dripping occurred during the test. After cooling, the second ignition was performed on the same sample. The self-extinguishing time (t_2) and dripping characteristics were again

recorded. Five specimens were measured, and the average burning time was recorded. If t_1 plus t_2 is less than 10 s with no dripping, it is considered to be a V-0 grade, an industrial standard for flame retardancy. 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. If t_1 plus t_2 is in the range of 10–30 s with dripping that ignites a cotton indicator located below the sample, the polymer is considered to be a V-2 material. Dielectric measurements were performed with an Agilent E4991A measurement system at a temperature of 20 °C in an air atmosphere by the two parallel plate modes at 1 GHz. The applied voltage was 1 V. Before testing, samples (1 cm ×1 cm and 0.2 cm thickness) were dried under vacuum at 120 °C for 3 h.

Synthesis of Monophenol (1)

To a 100-mL round-bottom flask equipped with a nitrogen inlet and magnetic stirrer, 4.38 mmol (1.00 g) of bisphenol A, 4.7345 g (21.9 mmol) of DOPO, and 0.1894 g (4% based on DOPO) of p-TSA were added. The reaction mixture was gradually heated to 130 °C and maintained at that temperature for 12 h. After the reaction was complete, the product was crushed to powder and poured into ethanol to remove excess DOPO. 1.228 g of white powder (80% yield) with a melting point of 244 °C (DSC) was obtained.

High-resolution mass spectrometry (HR-MS) fast atomic bombardment (FAB+) m/z: calcd. for $C_{21}H_{19}O_3P$ 350.1072; anal, 351.1016 $[M+1]^+$ C21, H20, O3, P. ¹H NMR (DMSO- d_6), $\delta = 1.36-1.48$ (6H, H⁶, H^{6'}), 6.54 (2H, H²), 6.98 (2H, H³), 7.21 (2H, H¹⁵, and H¹⁷), 7.30 (1H, H¹¹), 7.40 (1H, H¹⁶), 7.45 (1H, H¹⁰), 7.71 (1H, H⁹), 8.00 (1H, H¹⁴), 8.11 (1H, H⁸), 9.31 (1H, OH). ¹³C NMR (DMSO- d_6), $\delta = 21.88-23.01$ (C⁶, C^{6'}), 41.38-41.98 (C⁵), 114.43 (C²), 119.14 (C¹⁷), 121.02 (C¹²), 121.26 and 121.98 (C⁷), 123.46 (C⁸), 123.93 (C¹⁵), 125.32 (C¹⁴), 127.03 (C¹⁰), 128.75 (C³), 129.28 (C¹³), 130.64 (C¹⁶),131.63 (C¹¹), 133.46 (C⁹), 136.07 (C⁴), 150.72 (C¹⁸), 156.13 (C¹).



Synthesis of Bisphenol (2)

To a 100-mL round-bottom flask equipped with a nitrogen inlet and magnetic stirrer, 32.6 mmol (10 g) of 1,1,1-tris(4-hydroxyphenyl)ethane, 163 mmol (35.2 g) of DOPO, and 1.41 g (4% based on DOPO) of p-TSA were added. The reaction mixture was gradually increased to 130 °C and maintained at that temperature for 12 h. After the reaction was complete, the product was crushed to powder and poured into ethanol to remove excess DOPO. About 12.03 g of white powder (86% yield) with a melting point of 298 °C (DSC) was obtained.

HR-MS (FAB+) m/z: calcd. for $C_{26}H_{21}O_4P$ 428.1177; anal., 429.1266 $[M+1]^+$ C26, H22, O4, P. ¹H NMR (DMSO- d_6), $\delta = 1.58$ (3H, H⁶), 6.59 (2H, H²), 6.61 (2H, H^{2'}), 7.09–7.22 (7H, H³, H¹⁷, H¹¹, H¹⁵, H^{3'}), 7.33–7.36 (2H, H¹⁶, H¹⁰), 7.67 (1H, H⁹),

TABLE 1	Thermal	Properties	of P0 -l	P2 and	P(3)
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	Р	Tan δ	T _v (°C)	T. (°C)	CTE	<i>T</i> _{d5%} (°C) ^e		Char Yield ^f	
Thermoset	(wt %)	(°C) ^a	(DSC) ^b	(TMA) ^c	(ppm/°C) ^d	N_2	air	N_2	air
P0	0	279	276	266	57	455	454	41	20
P0.75	0.75	278	278	240	53	441	444	40	23
P1	1.00	276	277	237	53	437	445	40	27
P1.25	1.25	275	275	237	55	438	433	39	27
P1.5	1.50	275	275	236	54	438	428	39	28
P2	2.00	274	273	235	49	435	424	40	32
P(3)	6.48	268	263	226	53	426	417	48	41

^a Measured by DMA at a heating rate of 5 °C/min.

 $^{\rm b}$ Measured by the second DSC heating scan at a heating rate of 20 $^\circ\text{C/min}.$

^c Measured by TMA at a heating rate of 5 °C/min.

 $^{\rm d}$ Coefficient of thermal expansion are recorded from 100 to 200 $^\circ\text{C}.$

7.98 (1H, H¹⁴), 8.08 (1H, H⁸), 9.35 (2H, OH). ¹³C NMR (DMSOd₆), $\delta = 24.22$ (C⁶), 51.48 (C⁵), 114.51 (C^{2'}), 114.73 (C²), 119.02 (C¹¹), 120.83 (C¹²), 121.98 (C⁷), 123.33 (C⁸), 123.94 (C¹⁵), 125.34 (C¹⁴), 127.83 (C¹⁶), 129.51 (C^{3'}), 130.60 (C^{3,10}), 131.87 (C¹⁷), 132.93 (C¹³), 133.36 (C⁹), 136.04 (C⁴), 136.22 (C^{4'}), 150.75 (C¹⁸), 155.86 (C^{1'}), 156.33 (C¹).



Synthesis of (3)

To a 100-mL round-bottom flask equipped with a nitrogen inlet and magnetic stirrer, 20 mL dry DMAc was added. The reaction mixture was gradually cooled to -15 °C, and then 30 mmol (3.17 g) of BrCN was added. A mixture containing 12 mmol (5.14 g) of **(2)**, 30 mmol (3.09 g) of triethylamine, and 20 mL of dry DMAc was added gradually in 2 h. The mixture was kept at that temperature for another 2 h. After the reaction was complete, the white Et3N·HBr salt was filtered. The filtrate solution was then poured into water (500 mL) with stirring, yielding a precipitate that was isolated by

 $^{\rm e}$ Temperature corresponding to 5% weight loss by TGA at a heating rate of 20 $^{\circ}\text{C/min}.$

Residual wt % at 800 °C.

filtration. After the precipitate was dried, 4.9 g (85% yield) of white powder was obtained. Then the yellow powder was recrystallized from hexane/Acetonitrile (ACN) and then dried in a vacuum oven at 100 °C. Light white powder (3.4 g, 70% yield) with a melting point of 158 °C (DSC) was obtained.

R-MS (FAB) m/z: calcd. for C₂₈H₁₉O₄N₂P 478.1082; anal, 479.1178 for C28, H20, O4, N2, P [M+1]⁺. FTIR (KBr): 920 cm⁻¹ (P–O–Ph), 1203 cm⁻¹ (P=O), 2267 cm⁻¹, and 2235 cm⁻¹ (cyanate stretch). ¹H NMR (ppm, DMSO- d_6), $\delta = 1.76$ – 1.79 (3H, H⁶), 7.14 (1H, H¹⁸), 7.15 (1H, H¹⁶), 7.28–7.30 (4H, H³, and H^{3'}), 7.34 (1H, H¹⁷), 7.36 (1H, H¹²), 7.43 (2H, H^{4'}), 7.46 (1H, H¹¹), 7.52 (2H, H⁴), 7.75 (1H, H¹⁰),7.92 (1H, H¹⁵), 8.09 (1H, H⁹). ¹³C NMR (ppm, DMSO- d_6), $\delta = 23.96$ (C⁶), 52.45 and 53.05 (C⁷), 108.41 (C^{1,1'}), 115.10 (C³), 115.28 (C^{3'}), 119.06 (C¹⁸), 120.22 and 120.99 (C⁸), 120.62 (C¹³), 123.60 (C⁹), 124.17 (C¹⁶), 125.33 (C¹⁵), 128.40 (C¹¹), 130.78 (C¹²), 131.03 (C⁴), 131.94 (C^{4'}), 132.05 (C¹⁷), 134.17 (C¹⁰), 136.43 (C¹⁴), 138.32 (C^{5'}), 140.95 (C⁵), 150.80 (C¹⁹), 151.13 (C^{2'}), 151.54 (C²).





SCHEME 1 One-pot synthesis of phosphinated monophenol (1). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



SCHEME 2 Proposed reaction mechanism for the synthesis of (1). According to ¹H and ¹³C NMR data, path A is the only reaction route of this reaction.





SCHEME 3 One-pot synthesis of phosphinated bisphenol (2). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



SCHEME 4 Proposed reaction mechanism for the synthesis of (2). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Curing Procedure

(3)/BACY with various ratios (the phosphorus content was controlled from 0.75 to 2 wt %) were mixed well in a hot plate at 160 °C. The mixtures were cured at 180 °C for 4 h, 200 °C for 4 h, 220 °C for 4 h, and 240 °C for 4 h. After that, samples were allowed to cool slowly to room temperature to prevent cracking. The relation between sample ID and the content of phosphorus was listed in Table 1. The number after P is the phosphorus content in the co-thermoset. Therefore, P0 means neat BACY thermoset, while P1.25 means the (3)/BACY thermoset with a phosphorus content of 1.25 wt %, and P2 means (3)/BACY thermoset with a phosphorus content of 2 wt %. The homopolymer of (3) is named as P(3).

RESULTS AND DISCUSSION

Synthesis of Monomer

By combining the acid-fragmentation of bisphenol A^{19-21} and conjugate addition of DOPO,²²⁻²⁴ we prepared a model compound, phosphinated monophenol **(1)**, from a one-pot reaction of DOPO and bisphenol A in the catalysis of p-TSA (Scheme 1).

A reaction mechanism for the synthesis is proposed in Scheme 2. In that mechanism, Compound **1(b)**, generated from the acid-fragmentation of bisphenol A, reacted with DOPO via a conjugate addition. According to the addition position, two possible addition paths might occur. Path A is



SCHEME 5 Synthesis of dicyanate ester (3). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



the same mechanism as that for DOPO and rosolic acid,²² whereas path B is the same mechanism as that for DOPO and benzoquinone.^{23,24}

If path B is the reaction route, signals corresponding to CH_3 and CH should be observed, respectively. However, according to the ¹H NMR spectrum of the product shown in Figure 1(a), only two doublets corresponding to methyl groups (H⁶ and H^{6'}) are observed at 1.4 ppm. The splitting of methyl peak is due to the ${}^{3}J_{P-H}$ coupling, and the coupling constant is 16.2 Hz. The assignment of each Ar—H is detailed in Figure 1(a).

Figure 1(b) shows ¹H NMR spectrum of **(1)**. For carbon C⁵ and C⁷, due to ¹ J_{P-C} coupling, the peak is split into doublets with a coupling constant of 90 (J_{P-C} ⁵) and 121 Hz (J_{P-C} ⁷), respectively. The patterns Ar—C also support the structure of **(1)**. These spectroscopic data remind us that path A is the only addition route. In addition, literature has reported that 4-isopropenylphenol is unstable and tends to dimerize to dimmer.^{19–21} In this case, the resulting 4-isopropenylphenol reacted with DOPO quickly, so no 4-isopropenylphenol dimmer was detected in the product.



FIGURE 3 DSC thermograms of (2), (3), and (BACY). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

On the basis of this success of the model reaction, we then prepared a phosphinated bisphenol **(2)** from a one-pot reaction of DOPO and 1,1,1-tris(4-hydroxyphenyl)ethane in the catalysis of p-TSA (Scheme 3).

A similar reaction mechanism is proposed in Scheme 4. In that mechanism, Compound 2(b), generated from the acid-fragmentation of 1,1,1-tris(4-hydroxyphenyl)ethane, reacted with DOPO via a conjugate addition. The structure of (2)



FIGURE 4 (a) DSC, (b) DMA, (c) TMA, and (d) TGA thermograms of P(3).



FIGURE 5 DMA thermograms of **P0–P2**. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

was confirmed by the ¹H, ¹³C, and ³¹P NMR spectra (Supporting Information Fig. S1). Although bisphenol **(2)** has been prepared by a different procedure in our previous article,²⁵ the strategy revealed in the work expands the chemistry of DOPO. On the basis of this strategy, preparation of multifunctional phosphinated phenols is in progress.

Phosphinated dicyanate ester **(3)** was prepared from the reaction of cyanogen bromide and **(2)** in the presence of triethylamine at low temperature (Scheme 5). There are two common side reactions in the preparation of cyanate ester.²⁶ The first is the formation of imidocarbonate when the phenol group is excess, and the second is the formation of diethylcyanamide when the reaction temperature is higher than 0 °C. To prevent side reactions, bisphenol and triethylamine were added dropwise into the cyanogen bromide/DMAc solution, and the temperature is maintained at about -15 °C.

Figure 2(a) shows the ¹H NMR spectrum of (3). The disappearance of phenolic OH suggests the transformation of phenolic groups of (2). The assignment of each Ar—H is detailed in Figure 2(a) to confirm the structure and purity. Figure 2(b) shows the ¹³C NMR spectrum of (3). The characteristic signals of cyanate ester appear at $\delta = 108.4$ ppm. The detailed assignment of each Ar—C is detailed in Figure 2b to confirm the structure and purity.

Figure 3 shows the DSC thermograms of **(2)**, **(3)**, and BACY. Because of the disappearance of intermolecular hydrogen bonding induced by the phenolic groups, the melting point of **(3)** is much lower than that of **(2)**. An exothermic peak corresponding to trimerization of cyanate esters starts at around 240 °C. The exothermic peak temperature is 305 °C with an exothermic enthalpy of 481 J/g. The wide temperature difference between melting point and exothermic peak temperature demonstrates a reasonable processing window. As shown in Figure 3, the melting points of **(3)** and BACY are 158 and 80 °C, respectively, suggesting they can easily be blended on a hot plate at 160 °C, and mixed well.

Thermal Properties of Homopolymer

Figure 4(a) shows the DSC thermogram of **P(3)** homopolymer. A T_g value of 263 °C was observed for **P(3)**. Figure 4(b) shows the DMA thermogram of **P(3)**. A T_g value of 268 °C was obtained from the peak temperature of tan δ . TMA measurement shows **P(3)** exhibits a T_g value of 226 °C, and a coefficient of thermal expansion of 53 ppm/°C [Fig. 4(c)]. TGA measurement shows the 5% decomposition temperature of **P(3)** is 426 (in N₂) and 417 °C (in air), respectively [Fig. 4(d)]. The char yield at 800 °C is 48 (in N₂) and 41 wt % (in air), respectively. DSC, DMA, TMA, and TGA data demonstrate **P(3)** exhibits high T_g and moderate to high thermal stability.

Thermal Properties of Copolymer

Figure 5 shows the DMA thermograms of BACY homopolymer **(P0)** and **(3)**/BACY copolymers **(P0.75–P2)**. The detailed results are presented in Table 1. DMA thermograms of **(3)**/BACY co-thermosets are almost the same as those of **P0**, suggesting very little penalty to the T_g value after incorporation of the bulky phosphinate pendant. Theoretically, a bulky pendant that separates the polymer chains should lead to loose networks of thermosets. Therefore, it is thought that the effect of restricted segmental mobility, caused by the polar P=0 bond and the rigid biphenylene phosphinate pendant, compensates for the loss of crosslinking density, and maintains high T_{gr} .

The thermal dimensional stability of all thermosets was measured by TMA. The results are detailed in Table 1. Figure 6 shows the TMA curve of **P2** and **P0**. Although no reduction in $T_{\rm g}$ is observed in DMA measurement, a small decrease in $T_{\rm g}$ is observed in the TMA measurement. $T_{\rm g}s$ defined by the onset of the TMA curve are 266 and 235 °C for **P0** and **P2** and CTEs are 57 and 49 ppm, respectively. The CTE data demonstrate better dimensional stability of co-thermosets. The restricted segmental mobility caused by the bulky phosphinate pendant might be responsible for the improved CTE values.



FIGURE 6 TMA curve of **P0** and **P2**. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary. com.]



FIGURE 7 TGA curves of P0–P2 in (a) N2 and (b) air atmosphere. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 7 shows the TGA thermograms of PO-P2, and the results are detailed in Table 1. In an N₂ atmosphere, the 5% degradation temperatures are 455 and 435 °C for PO and P2, respectively. The value of 435 °C is relatively high when compared with that of other phosphorus-containing polymers. The P-C chain has a lower bonding energy, so the initial degradation of the polymer occurs at that chain. In our previous studies,^{25,27,28} we reported that the thermal stability of phosphorus-containing thermosets is related to the electron density of the carbon adjacent to the phosphorus $(C^{7}, in this case)$. The lower the electron density of the carbon is, the lower its thermal stability. In this case, the methyl group, an electron-donating group, increases the electron density of C⁷, increasing the thermal stability of the P--C bond. As listed in Table 1, high thermal stability (T_{d5}) and improved char yield of (3)/BACY thermosets are also observed in an air atmosphere.

Table 2 also lists the UL-94 data for BACY and **(3)**/BACY cothermosets. Neat BACY thermoset belongs to burning grade, whereas phosphinated thermosets can reach V-0 grade if the phosphorus content is higher than 1.50 wt %. This result shows the good flame retardancy of the phosphinated cyanate esters.

Dielectric Properties

The dielectric constant and dissipation factor of **P0–P2** were measured by an Agilent E4991A RF Impedance Material Analyzer, and the results are in Table 2. The dielectric constant at 1 GHz decreases from 3.14 for **P0** to 3.04 for **P2**. Hougham et al. reported that the dielectric constant can be reduced by increasing molecule's hydrophobicity and free volume, and by decreasing polarization.^{26,29,30} Therefore, it is thought that the increased free volume due to the bulky phosphinate pendant might be responsible for the reduced dielectric constant.

CONCLUSIONS

By combining the acid-fragmentation of bisphenol^{19–21} and conjugate addition of DOPO,^{22–24} we first report the synthesis of a phosphinated bisphenol **(2)** from a one-pot reaction of DOPO and 1,1,1-tris(4-hydroxyphenyl) ethane in the catalysis of p-TSA. A two-step mechanism, an acid-fragmentation of 1,1,1-tris(4-hydroxyphenyl)ethane followed by nucleophilic addition of DOPO is proposed. On the basis of this strategy, preparation of multifunctional phosphinated phenols is in progress. Experimental data show that incorporating phosphinated dicyanate ester **(3)** into BACY enhances the flame retardancy and reduces dielectric properties with little penalty to the thermal properties. The combination of high T_{gr} good thermal stability, low dielectric, and high flame retardancy makes **(3)**/ BACY co-thermosets attractive in electronic applications like high-performance, halogen-free printed circuit boards.

Thermoset	D _k ^a	$D_{\rm f}^{\rm b}$	First Burning Time (s) ^a	Second Burning Time (s) ^a	Dripping	UL-94 Grade
P0	3.14 ± 0.005	4.52 ± 0.05	>60	-	No	Burning
P0.75	3.13 ± 0.003	4.59 ± 0.01	49.6	-	No	Burning
P1	3.08 ± 0.003	4.75 ± 0.15	40.6	0.1	No	Burning
P1.25	3.06 ± 0.004	4.65 ± 0.15	23.3	3.1	No	V-1
P1.5	3.05 ± 0.003	4.65 ± 0.05	8.5	1.4	No	V-0
P2	3.04 ± 0.004	4.40 ± 0.11	4.6	1.2	No	V-0

TABLE 2 Dielectric Properties and UL-94 Data for P0-P2

^a Dielectric constant at 1 GHz at room temperature.

^b Dissipation factor at 1 GHz at room temperature.



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