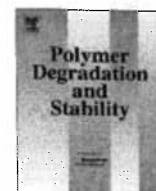




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## Biobased flame retardants from tartaric acid and derivatives

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## ABSTRACT

Biobased flame retardants represent attractive alternatives to traditional organohalogen compounds which are persistent in the environment, tend to bioaccumulate and may pose risks to human health. Tartaric acid is generated annually in great abundance as a by-product of wine making. It is nontoxic and widely used as a food ingredient. It is tetrafunctional which provides broad opportunity for conversion to a wide spectrum of useful materials. It has been used as a base for the generation of a variety of new compounds that display good flame retardancy in DGEBA (diglycidyl ether of bis-phenol A) epoxy. These range from simple phosphinate and phosphonate esters to oligomeric materials containing bromine, in both saturated and unsaturated units, or bromine and phosphorus.

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## 1. Introduction

The development of biobased flame retardants is of increasing interest [1–9]. The precursors to these materials are renewable, are generally nontoxic and are independent of the availability and cost of petroleum. Traditional organohalogen flame retardants, particularly brominated aromatics, have been widely used. These materials are low in cost, effective at relatively low levels and usually have a low impact on the properties of the polymeric matrices into which they are incorporated. However, these compounds migrate from most polymers and get into the environment. They are persistent in the environment, tend to bioaccumulate and are, increasingly, a threat to human health [10–13]. Human exposure to brominated flame retardants can occur in a variety of ways from breathing house dust to eating contaminated food. Because of the widespread distribution of these compounds in the environment, constant human exposure and negative health impacts there is an increasing need to find suitable replacements. To reduce the propensity for migration from the polymer matrix, oligomeric flame retardants containing brominated units have been developed [14,15]. These materials can function as effective flame retardants both in the presence and absence of antimony oxide promoter [15]. These are not as widely used as are small molecule counterparts which are coming under increasing societal and regulatory pressure [16–18]. Small molecules containing both bromine and

phosphorus can be particularly effective [19,20]. The incorporation of both in the same compound generally reduces the amount of additive (and the quantity of bromine) required for effective flame retardancy. Phosphorus compounds, particularly those derived from biomaterials, function as effective flame retardants and, in general, are much less toxic than organohalogen flame retardants [21–25]. In particular, derivatives of 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) are effective in imparting flame retardancy and display low toxicity [26–29]. Tartaric acid is a tetrafunctional compound found in many fruits, especially grapes [30–33]. It is precipitated during wine-making and is generated in abundance annually. It has been widely used in food to provide tart taste and to extend shelf-life. It has also been used in effervescent antacids and in the synthesis of pharmaceuticals. These uses account for a small portion of production. In this case, it and derivatives have been used to generate phosphorus compounds, compounds containing both phosphorus and bromine and oligomeric organobromine compounds which display good flame retardancy in DGEBA epoxy resin.

## 2. Experimental

## 2.1. Methods and instrumentation

In general, synthesis was carried out in a dry (all glassware was dried at 120 °C and allowed to cool under a stream of dry nitrogen prior to use) three-necked, round-bottomed flask fitted with Liebig condenser bearing a gas-inlet tube, a magnetic stirring bar, and a

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pressure-equalizing dropping funnel. Silica-coated Mylar plates (Thermo-Fisher Scientific) were used for thin layer chromatography (TLC). Chromatography was accomplished using SilaFlash P60 (230–400 mesh silica; Silicycle) in a column of appropriate size and petroleum ether/ethyl acetate as eluent. Purification was accomplished by recrystallization.

Thermal decomposition temperatures were obtained by thermogravimetric analysis (TGA) using a TA Instruments Q500 TGA instrument. Most generally, a heating rate of 10 °C/min was used. Samples (5–10 mg) were contained in a platinum pan. The sample compartment was purged with dry nitrogen of 50 ml/min during analysis. Melting points were determined by differential scanning calorimetry (DSC) at a heating rate of 10 °C/min using a TA Instruments Q2000 DSC instrument. All samples for DSC (5–10 mg) were contained in an aluminum pan. The DSC cell was purged with dry nitrogen at 50 ml/min during analysis. All samples for DSC were subjected to a heat/cool/heat procedure to eliminate thermal history (temperature ramp to 200 °C at a rate of 10 °C/min followed by cooling to –50 °C at a rate of 5 °C/min). TA Universal Analysis software was used for all data analysis. Nuclear magnetic resonance (NMR) spectra were obtained using a Varian Mercury 300 MHz spectrometer and 10%–25% solutions in deuterated chloroform or dimethyl sulfoxide- $d_6$ .  $^1\text{H}$  and  $^{13}\text{C}$  chemical shifts are reported in parts-per-million ( $\delta$ ) with respect to tetramethylsilane (TMS) as internal reference ( $\delta = 0.00$ ).  $^{31}\text{P}$  NMR spectra were recorded with the same instrument and triphenyl phosphate ( $\delta = -18.00$ ) as an internal reference. The number average molecular weight ( $M_n$ ) for the polymeric flame retardants was calculated from the ratio of the intensities of appropriate resonances in the quantitative  $^{13}\text{C}$  NMR spectrum (gated decoupling without Nuclear Overhauser Effect, NOE, 10-s relaxation delay). Infrared (IR) spectra were obtained using attenuated total reflectance and a Thermo Scientific Nicolet iS 50 FT-IR Spectrometer. Absorptions were recorded in wave numbers ( $\text{cm}^{-1}$ ) and absorption intensities were classified in the usual fashion as very weak (vw), weak (w), medium (m), strong (s), and very strong (vs) relative to the strongest band in the spectrum. Mass spectra were obtained using a Waters GCT Premier™ gas chromatograph/mass spectrometer (GC-MS) with an ionizing potential of 70 electron volts and temperature program elution into the spectrometer inlet (90–200 °C) or chemical ionization ( $\text{CH}_5^+$ ) and a Waters Micromass LCT Premier™ XE orthogonal acceleration time-of-flight (oa-TOF) mass spectrometer (ESI). For injection, the solution was introduced into the electrospray source at a constant flow rate of 50  $\mu\text{L}/\text{min}$  with a 10  $\mu\text{L}$  HPLC syringe. To examine the flame retarding impact of the incorporation of flame retardants into a polymer matrix, plaques containing the flame retardant were prepared using DGEBA epoxy with 2-ethyl-4-methylimidazole as hardener. Plaques were subjected to both the UL-94 vertical burn test (ASTM D568) and the limiting oxygen index (LOI) for combustion (ASTM D2863). For the vertical burn test a Fire Testing Technology UL-94 test chamber with properly calibrated flame intensity was used. For determination of LOI, a Fire Testing Technology Oxygen Index Module was used. Both UL-94 and LOI ratings reported represent the average of five determinations. Screening tests were also carried out at small scale using microscale combustion calorimetry (MCC). Samples with a size smaller than 5 mg were heated from 150 °C to 650 °C at a ramp rate of 1 °C/sec in a stream of nitrogen at a flow rate of 80 ml/min. The pyrolysis products in the nitrogen stream are mixed with pure oxygen at the inlet of a combustor held at 900 °C where complete combustion occurred. From the oxygen consumption a series of combustion parameters can be calculated. Two of the most important are the peak heat release rate (PHRR) and the total heat release (THR).

### 3. Materials

Common solvents and reagents were obtained from Thermo-Fisher Scientific or the Aldrich Chemical Company. Tetrahydrofuran (THF) was distilled from lithium aluminum hydride in a nitrogen atmosphere prior to use; methylene chloride from calcium hydride. Tartaric acid, diethyl tartrate, bromine, 2-butene-1,4-diol, 2-butyne-1,4-diol, phenylphosphonic dichloride, desoxyanisoin, carbon tetrachloride and terephthaloyl chloride were used as received from the Aldrich Chemical Company. 9,10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide was obtained from Tokyo Chemical Industries. Diphenylphosphinic chloride was obtained from the Alfa Aesar Company. DGEBA epoxy was used as received from the Dow Chemical Company and 2-ethyl-4-methylimidazole from the Aldrich Chemical Company.

#### 3.1. Synthesis

##### 3.1.1. Diethyl 2,3-diphenylphosphonatobutanedioate

A solution of diethyl tartrate (10.3 g, 50.0 mmol) and triethylamine (16.0 ml, 1.06 mol) in 30 ml of dry benzene was added dropwise, over a period of 20 min, to a stirred solution of diphenylphosphinic chloride (21.9 ml, 1.06 mol) in 40 ml of benzene maintained at room temperature. The resulting mixture was stirred at solvent reflux for three hours and then stirred at room temperature overnight. Water (300 ml) was added to dissolve triethylamine hydrochloride. A suspended solid was collected by filtration at reduced pressure to provide a grey solid which was crystallized from acetone to provide 20.23 g (66.8% yield) of diethyl 2,3-diphenylphosphinatobutanedioate as white crystals, mp 152 °C (DSC); decomposition onset temperature 267 °C (TGA); FTIR (ATR,  $\text{cm}^{-1}$ ) 3062 (m)  $\text{C}_{\text{sp}2}\text{-H}$ , 2989 (m), 2983 (m), 2911 (w)  $\text{C}_{\text{sp}3}\text{-H}$ , 1764 (vs)  $\text{C}=\text{O}$ , 1592 (m) aromatic nucleus, 1132 (s)  $\text{C}-\text{O}$ , 1224 (vs)  $\text{P}=\text{O}$ , 1106 (s)  $\text{P}-\text{Ar}$ , 935 (s), 752 (s)  $\text{P}-\text{O}-\text{C}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ) 0.98 (t,  $J_{\text{HH}} = 6.9$  Hz, 6H) methyl protons, 3.65 (qd,  $J = 10.8$ , 6.9 Hz, 4H) methylene protons, 5.50 (dd,  $J = 10.8$  Hz, 1.8 Hz, 2H) methine protons, 7.39–7.92 (m, 20H) aromatic protons;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ) 13.6 ( $\text{CH}_3$ ), 62.1 ( $\text{CH}_2$ ), 73.2 (d,  $J_{\text{PC}} = 22.9$  Hz, CH), 128.2 (dd,  $J_{\text{PC}} = 27.0$  Hz, ArCH), 130.3 (d,  $J_{\text{PC}} = 41.1$  Hz, ArCH), 131.6 (ArC–P), 131.8 (ArCH), 131.9 (ArCH), 132.3 (ArC–P), 166.53 (s,  $\text{C}=\text{O}$ ), 166.55 (s,  $\text{C}=\text{O}$ );  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ) 34.8; MS (ESI) ( $\text{C}_{32}\text{H}_{32}\text{O}_8\text{P}_2$ )  $m/z$ , 607.10 [ $\text{M}+\text{H}$ ] $^+$ , calculated 607.16 [ $\text{M}+\text{H}$ ] $^+$ .

##### 3.1.2. Diethyl 2,3-didopyloxybutanedicarboxylate

A solution of diethyl tartrate (20.6 g, 0.100 mol) and triethylamine (48.1 ml, 0.345 mol) in 40 ml of anhydrous THF was added dropwise, over a period of 50 min, to a stirred solution of DOPO (66.9 g, 0.300 mol) and carbon tetrachloride (33.4 ml, 0.345 mol) in 560 ml of anhydrous THF maintained at room temperature. The resulting mixture was stirred at solvent reflux for eight hours and then stirred at room temperature overnight. A precipitate was collected by filtration at reduced pressure and washed with three 200-ml portions of water and three 100-ml portions of methanol to afford a white powder. The filtrate was washed, successively, with 80 ml of 10% aqueous hydrochloric acid solution, 80 ml of saturated aqueous sodium bicarbonate solution and 80 ml of saturated aqueous sodium chloride solution. The solution was dried over anhydrous sodium sulfate and the solvent was removed by rotary evaporation at reduced pressure to provide a yellow oil. The oil was stirred with methanol (200 ml) at room temperature overnight to generate a white precipitate. The precipitate was collected by filtration at reduced pressure, washed with 50 ml of methanol, dried at 15 torr and 50 °C and combined with the initial precipitate to afford 31.12 g (49.0% yield) of diethyl 2,3-didopyloxybutanedicarboxylate: mp 212 °C (DSC); decomposition

onset temperature 278 °C (42.4%), 353 °C (57.5%) [TGA]; FTIR (ATR,  $\text{cm}^{-1}$ ) 3067 (w)  $\text{C}_{\text{sp}2}\text{-H}$ , 2989 (w), 2945 (w)  $\text{C}_{\text{sp}3}\text{-H}$ , 1764 (vs), 1740 (m)  $\text{C}=\text{O}$ , 1597 (w) aromatic nucleus, 1271 (vs)  $\text{P}=\text{O}$ , 1200 (s), 938 (s)  $\text{P}-\text{O}-\text{Ar}$ , 1114 (s)  $\text{P}-\text{Ar}$ , 1067 (s), 747 (m)  $\text{P}-\text{O}-\text{C}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ) 1.37 (m, 6H) methyl protons, 4.26 (m, 4H) methylene protons, 5.82 (m, 2H) methine protons, 6.42–7.88 (m, 16H) aromatic protons;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ) 14.1 (d,  $\text{CH}_3$ ), 62.6 ( $\text{CH}_2$ ), 73.9 (CH), 118.5, 119.5, 121.0, 123.1, 123.6, 124.3, 127.4, 129.3, 129.5, 133.3, 136.5 and 148.7 (m, ArC), 165.6 ( $\text{C}=\text{O}$ );  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ) 11.7 and 11.9; MS (ESI) ( $\text{C}_{32}\text{H}_{28}\text{O}_{10}\text{P}_2$ )  $m/z$ , 635.11  $[\text{M}+\text{H}]^+$ , calculated 635.12  $[\text{M}+\text{H}]^+$ .

### 3.1.3. 2,3-Dibromo-2-butene-1,4-diol

Bromine (14 ml, 272 mmol) was added dropwise over a period of 3 min–300 ml of anhydrous diethyl ether. The flask was kept away from direct light or any ultraviolet source (covered in aluminum foil) and placed in an ice bath. 2-Butyne-1,4-diol (23.4 g, 272 mmol) was added portionwise (about 2 g each time) over a period of one hour. Each addition caused the temperature of the mixture to rise. The solution was allowed to cool to room temperature prior to the next addition. A cloudy light yellow suspension was obtained after 2 days of stirring at room temperature. The solvent was removed from the suspension by rotary evaporation at reduced pressure. The residue solid was dissolved in 200 ml of tetrahydrofuran and washed, successively, with 60 ml of 10% aqueous sodium sulfite solution and 60 ml of saturated aqueous sodium chloride solution. The solution was dried over anhydrous sodium sulfate and the solvent was removed by rotary evaporation at reduced pressure. The residue was recrystallized from ethyl acetate and hexane (1:5) to provide 40.08 g of pure 2,3-dibromo-1,4-butanediol (60.4% yield) as pale yellow needles: FTIR (ATR,  $\text{cm}^{-1}$ ): 2843 (w), 2934 (w)  $\text{C}_{\text{sp}2}\text{-H}$ , 3208 (s)  $\text{O}-\text{H}$ , 561 (m)  $\text{C}-\text{Br}$ ;  $^1\text{H}$  NMR ( $\text{DMSO}-d_6$ ,  $\delta$ ) 4.32 (d,  $J = 6$  Hz, 2H) methylene protons, 3.33 (s, 1H), 5.52 (t,  $J = 6$  Hz, 1H) hydroxyl protons;  $^{13}\text{C}$  NMR ( $\text{DMSO}-d_6$ ,  $\delta$ ) 65.5 ( $\text{CH}_2$ ), 122.9 ( $\text{C}=\text{C}$ ).

### 3.1.4. 2,3-Dibromo-1,4-butanediol

Bromine (14 ml, 272 mmol) was added dropwise over 5 min to 300 ml of anhydrous diethyl ether. The flask was kept away from direct light or any ultraviolet source (covered in aluminum foil) and placed in an ice bath. 2-Butene-1,4-diol (22.4 ml, 272 mmol) was added portion wise (about 0.5 ml each time). Each addition brought about an increase in the temperature of the solution. The solution was allowed to cool to near room temperature prior to the next addition. A clear orange solution was obtained after 2 days of stirring at room temperature. The solution was washed, successively, with 60 ml of 10% aqueous sodium sulfite solution and 60 ml of saturated aqueous sodium chloride solution. The solution was dried over anhydrous sodium sulfate and the solvent was removed by rotary evaporation at reduced pressure. The residue was recrystallized from ethyl acetate and hexane (1:5) to provide 33.49 g (50.1% yield) pure 2,3-dibromo-1,4-butanediol as white crystals: FTIR (ATR,  $\text{cm}^{-1}$ ) 2944 (m), 2908 (w), 2867 (w)  $\text{C}_{\text{sp}2}\text{-H}$ , 3233 (s)  $\text{O}-\text{H}$ , 689 (m)  $\text{C}-\text{Br}$ ;  $^1\text{H}$  NMR ( $\text{DMSO}-d_6$ ,  $\delta$ ) 3.70 (m, 2H), methine proton, 4.44 (t,  $J = 6.5$  Hz, 4H) methylene protons, 5.43 (t,  $J = 6.0$  Hz, 2H) hydroxyl proton;  $^{13}\text{C}$  NMR ( $\text{DMSO}-d_6$ ,  $\delta$ ) 56.1 (CH), 64.2 ( $\text{CH}_2$ ).

### 3.1.5. 2,3-Dibromo-1,4-didopyloxybutane

Carbon tetrachloride (31.9 ml, 0.330 mol) was added dropwise, over a period of 70 min, to a stirred solution of 2,3-dibromo-1,4-butanediol (24.8 g, 0.100 mol), 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO, 67.5 g, 0.300 mol) and triethylamine (46.0 ml, 0.330 mol) in 500 ml of dry THF cooled to near 0 °C. The resulting suspension was allowed to stir near 0 °C for 30 min and then at room temperature overnight. A precipitate was

collected by filtration and washed with three 200-ml portions of water and three 200-ml portions of methanol to afford a white powder. The filtrate was washed with 80 ml of 10% aqueous hydrochloric acid solution, 80 ml of saturated aqueous sodium bicarbonate solution, and 80 ml of saturated aqueous sodium chloride solution. The solution was dried over anhydrous sodium sulfate and the solvent was removed by rotary evaporation at reduced pressure to provide a pale yellow oil. The oil was stirred in methanol (200 ml) at room temperature overnight to generate a white powder precipitate. This precipitate was collected by filtration, dried, and combined with the initial precipitate to provide 49.29 g (73.1% yield) of 2,3-dibromo-1,4-didopyloxybutane: mp 181 °C (DSC); decomposition onset temperature 281 °C (29.5% mass loss), 329 °C (62.6% mass loss) [TGA]; FTIR (ATR,  $\text{cm}^{-1}$ ) 3065 (w), 2955 (w)  $\text{C}_{\text{sp}2}\text{-H}$ , 1608 (w), 1596 (m), 1583 (w) aromatic nucleus, 1272 (vs)  $\text{P}=\text{O}$ , 1203 (s), 927 (s)  $\text{P}-\text{O}-\text{Ar}$ , 1155 (m), 1119 (m)  $\text{P}-\text{Ar}$ , 1006 (s), 754 (s)  $\text{P}-\text{O}-\text{C}$ , 603 (w)  $\text{C}-\text{Br}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ) 4.20 (m, 4H) methylene protons, 4.39 (m, 2H) methine protons, 7.11–7.99 (m, 16H) aromatic protons;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ) 48.9 (d,  $J_{\text{PC}} = 30.8$  Hz, CH), 66.4 (d,  $J_{\text{PC}} = 24.6$  Hz,  $\text{CH}_2$ ), 119.9, 120.2, 122.1, 122.3, 124.0, 125.1, 128.3, 130.3, 130.6, 133.9, 137.0 and 149.4 (m, ArC);  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ) 9.71, 9.82, 9.93, 9.99; MS (ESI) ( $\text{C}_{28}\text{H}_{22}\text{O}_6\text{Br}_2\text{P}_2$ )  $m/z$ , 674.91  $[\text{M}+\text{H}]^+$ , 676.92  $[\text{M}+\text{H}+2]^+$ , 678.91  $[\text{M}+\text{H}+4]^+$ .

### 3.1.6. 2,3-Dibromo-1,4-didopyloxy-2-butene

Carbon tetrachloride (24.2 ml, 0.250 mol) was added dropwise, over a period of 25 min, to a stirred solution of 2,3-dibromo-2-butene-1,4-diol (24.6 g, 0.100 mol), DOPO (51.6 g, 0.230 mol) and triethylamine (35.2 ml, 0.250 mol) in 350 ml of dry THF cooled to near 0 °C. The resulting suspension was allowed to stir in ice bath for 30 min and then at room temperature overnight. A white precipitate was collected by filtration at reduced pressure and washed with three 20-ml portions of water and three 200 ml portions of methanol. The filtrate was washed, successively, with 80 ml of 10% aqueous hydrochloric acid solution, 80 ml of saturated aqueous sodium bicarbonate solution, and 80 ml of saturated aqueous sodium chloride solution. The solution was dried over anhydrous sodium sulfate and the solvent was removed by rotary evaporation at reduced pressure to provide a pale yellow oil. The oil was stirred in 200 ml of methanol at room temperature overnight to generate a white precipitate. The precipitate was collected by filtration at reduced pressure, washed with methanol, dried and combined with the initial precipitate to provide 47.06 g (70.0% yield) of 2,3-dibromo-1,4-didopyloxy-2-butene: mp 196 °C (DSC); decomposition onset temperature 278 °C (28.6%), 343 °C (63.2%) [TGA]; FTIR (ATR,  $\text{cm}^{-1}$ ) 3054 (w), 2927 (w)  $\text{C}_{\text{sp}2}\text{-H}$ , 1611 (w), 1597 (m), 1584 (w) aromatic nucleus, 1264 (s)  $\text{P}=\text{O}$ , 1204 (m), 929 (m)  $\text{P}-\text{O}-\text{Ar}$ , 1155 (m), 1119 (m)  $\text{P}-\text{Ar}$ , 1001 (s), 732 (s)  $\text{P}-\text{O}-\text{C}$ , 603 (w)  $\text{C}-\text{Br}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ) 4.96 (m, 4H)  $\text{P}-\text{O}-\text{CH}_2$ , 7.16 to 7.99 (m, 16H) aromatic protons;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ) 68.8 (d,  $J_{\text{PC}} = 22.6$  Hz,  $\text{CH}_2$ ), 120.0 (d,  $J_{\text{PC}} = 8.5$  Hz,  $\text{C}=\text{C}$ ), 119.9, 120.1, 122.2, 122.4, 124.0, 124.9, 128.3, 130.3, 130.5, 133.8, 137.1 and 149.6 (ArC);  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ) 10.5; MS (ESI) ( $\text{C}_{28}\text{H}_{20}\text{O}_6\text{Br}_2\text{P}_2$ )  $m/z$ , 672.93  $[\text{M}+\text{H}]^+$ , 674.92  $[\text{M}+\text{H}+2]^+$ , 676.93  $[\text{M}+\text{H}+4]^+$ .

### 3.1.7. 1,4-Didopyloxy-2-butyne

Carbon tetrachloride (24.2 ml, 0.250 mol) was added dropwise, over a period of 57 min, to a stirred solution of 2-butyne-1,4-diol (8.70 g, 0.100 mol), DOPO (51.6 g, 0.230 mol) and triethylamine (34.8 ml, 0.250 mol) in 360 ml dry THF maintained near 0 °C. The resulting suspension was allowed to stir near 0 °C for 30 min and then at room temperature overnight. A solid, triethylammonium chloride, was removed by filtration at reduced pressure. The filtrate was washed, successively, with 80 ml of 10% aqueous hydrochloric acid solution, 80 ml of saturated aqueous sodium bicarbonate

solution, and 80 ml of saturated aqueous sodium chloride solution. The solution was dried over anhydrous sodium sulfate and the solvent was removed by rotary evaporation at reduced pressure to provide a pale yellow oil. The oil was dissolved in 600 ml of methanol to provide a solution from which crystals grew. The crystals were collected by filtration at reduced pressure, washed with 300 ml of methanol, and dried at reduced pressure (15 torr) and 50 °C for eight hours to provide 45.20 g (87.9% yield) of 1,4-didopyloxy-2-butyne as a white solid: mp 132 °C (DSC); decomposition onset temperature 262 °C (8.0%), 354 °C (75.8%) [TGA]; FTIR (ATR,  $\text{cm}^{-1}$ ) 3066 (w), 2942 (w)  $\text{C}_{\text{sp}^2}\text{-H}$ , 1608 (w), 1596 (m), 1582 (w) aromatic nucleus, 1270 (vs)  $\text{P}=\text{O}$ , 1203 (s), 924 (s)  $\text{P}-\text{O}-\text{Ar}$ , 1153 (m), 1118 (m)  $\text{P}-\text{Ar}$ , 1013 (s), 753 (s)  $\text{P}-\text{O}-\text{C}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ) 4.72 (m,  $\text{P}-\text{O}-\text{CH}_2$ , 4H) methylene protons, 7.20–7.97 (m, 16H) aromatic protons;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ) 53.6 (d,  $J_{\text{PC}} = 13.8$  Hz,  $\text{CH}_2$ ), 81.7 (dd,  $J_{\text{PC}} = 16.2$ , 7.0 Hz,  $\text{C}\equiv\text{C}$ ), 120.2, 120.6, 122.1, 122.3, 123.9, 124.9, 128.2, 130.3, 130.5, 133.8, 137.0 and 149.6 (ArC);  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ) 11.06 and 11.08; MS (ESI) ( $\text{C}_{28}\text{H}_{20}\text{O}_6\text{P}_2$ )  $m/z$ , 515.07  $[\text{M}+\text{H}]^+$ , calculated 515.08  $[\text{M}+\text{H}]^+$ .

### 3.1.8. 4,4'-Bishydroxydeoxybenzoin (BHDB)

Desoxyanisoin (30.0 g, 0.115 mol) and pyridine hydrochloride (53.2 g, 0.460 mol) were stirred at 200 °C for eight hours. The mixture was allowed to cool to room temperature and was poured into vigorously stirred water (300 ml). The precipitate was collected by filtration at reduced pressure and then recrystallized from ethyl acetate and hexane (1:9) to afford 26.01 g (99.2% yield) of BHDB as yellow powder: FTIR (ATR,  $\text{cm}^{-1}$ ) 3432 (vs), 3230 (vs) hydroxyl  $\text{O}-\text{H}$ , 3060 (w) aromatic  $\text{C}-\text{H}$ , 2900 (w) alkyl  $\text{C}-\text{H}$ , 1713 (w)  $\text{C}=\text{O}$ , 1660 (s), 1588 (s), 1514 (s) aromatic nucleus;  $^1\text{H}$  NMR ( $\text{DMSO}-d_6$ ,  $\delta$ ) 4.03 (d,  $J = 4.5$  Hz, 2H) methylene protons, 6.65 (d,  $J = 8.5$  Hz, 2H), 6.80 (d,  $J = 8.7$  Hz, 2H), 6.99 (d,  $J = 8.5$  Hz, 2H), 7.84 (d,  $J = 8.6$  Hz, 2H) aromatic protons;  $^{13}\text{C}$  NMR ( $\text{DMSO}-d_6$ ,  $\delta$ ) 43.5 ( $\text{CH}_2$ ), 115.2 (ArCH), 115.3 (ArCH), 125.6 (ArC), 127.9 (ArC), 130.4 (ArCH), 131.1 (ArCH), 155.9 ( $\text{CH}_2-\text{ArC}-\text{OH}$ ), 162.0 ( $\text{CO}-\text{ArC}-\text{OH}$ ), 196.2 ( $\text{C}=\text{O}$ ).

### 3.1.9. 4,4'-Bisdopyloxydeoxybenzoin

Carbon tetrachloride (12.8 ml, 133 mmol) was added dropwise, over a period of 15 min, to a stirred solution of 4,4'-bishydroxydeoxybenzoin (BHDB) (12.1 g, 53.0 mmol), DOPO (27.2 g, 122 mmol) and triethylamine (18.5 ml, 133 mmol) in 230 ml of dry THF maintained near 0 °C. The resulting suspension was allowed to stir near 0 °C for 30 min and then at room temperature overnight. A white precipitate was collected by filtration at reduced pressure and washed with three 200 ml portions of water and three 200 ml portions of methanol. The resulting white solid was dried to provide 25.97 g (74.7% yield) of 4,4'-bisdopyloxydeoxybenzoin: mp 186 °C (DSC); decomposition onset temperature 404 °C (74.7%); FTIR (ATR,  $\text{cm}^{-1}$ ) 3065 (w), 2925 (w)  $\text{C}_{\text{sp}^2}\text{-H}$ , 1687 ( $\text{C}=\text{O}$ ), 1596 (s), 1583 (m) aromatic nucleus, 1275 (vs)  $\text{P}=\text{O}$ , 1218 (s), 921 (s)  $\text{P}-\text{O}-\text{Ar}$ , 1162 (m), 1118 (m)  $\text{P}-\text{Ar}$ , 996 (w), 756 (s)  $\text{P}-\text{O}-\text{C}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ) 4.14 (s, 2H) methylene protons, 6.98–7.98 (m, 24H) aromatic protons;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ) 44.5 (s,  $\text{CH}_2$ ), 119.8, 120.2, 120.8, 122.4, 122.6, 124.0, 124.2, 125.0, 125.3, 128.4, 130.5, 130.6, 131.3, 133.4, 133.9, 137.1, 148.7, 149.7 and 153.6 (ArC), 195.8 ( $\text{C}=\text{O}$ );  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ) 6.2 (s), 6.3 (s); MS (ESI) ( $\text{C}_{38}\text{H}_{26}\text{O}_7\text{P}_2$ )  $m/z$ , 657.10  $[\text{M}+\text{H}]^+$ , calculated 657.12  $[\text{M}+\text{H}]^+$ .

### 3.1.10. Poly(2,3-dibromobutylene terephthalate)

A solution of phenylphosphonic dichloride (7.41 g, 38.0 mmol) in dry dichloromethane (60 ml) was added dropwise, over a period of 40 min, to a stirred solution of 2,3-dibromo-2-butene-1,4-diol (9.34 g, 38.0 mmol) and triethylamine (12.2 ml, 87.4 mmol) in dry dichloromethane (40 ml) maintained at 0 °C. The resulting suspension was allowed to stir at 0 °C for 2 h and then at room

temperature for 18 days. Triethylammonium chloride was removed by filtration and the solution was washed, successively, with 30 ml of 10% aqueous hydrochloric acid solution and 30 ml of saturated aqueous sodium bicarbonate solution. This solution was poured into 1 L of rapidly-stirred hexane. The precipitated polymer was collected by filtration and dried at 70 °C and 15 torr for two days. The polymer displays a glass transition (DSC) at 34 °C: FTIR (ATR,  $\text{cm}^{-1}$ ) 3059 (w)  $\text{C}_{\text{sp}^2}\text{-H}$ , 2953 (w)  $\text{C}-\text{H}$  alkyl, 1246 (vs)  $\text{P}=\text{O}$ , 1131 (s), 1087 (s)  $\text{P}-\text{Ar}$ , 978 (m), 749 (m)  $\text{P}-\text{O}-\text{C}$ , 545 (m)  $\text{C}-\text{Br}$ ;  $^1\text{H}$  NMR ( $\text{DMSO}-d_6$ ,  $\delta$ ) 4.93 (d,  $J_{\text{PH}} = 4.6$  Hz) methylene protons, 7.51 to 7.74 aromatic protons;  $^{13}\text{C}$  NMR ( $\text{DMSO}-d_6$ ,  $\delta$ ) 68.7 (s,  $\text{CH}_2$ ), 120.1 (d,  $J_{\text{PC}} = 19.0$  Hz,  $\text{C}=\text{C}$ ), 126.1, 129.2, 131.8, 133.7 (ArC);  $^{31}\text{P}$  ( $\text{DMSO}-d_6$ ,  $\delta$ ) 19.7.

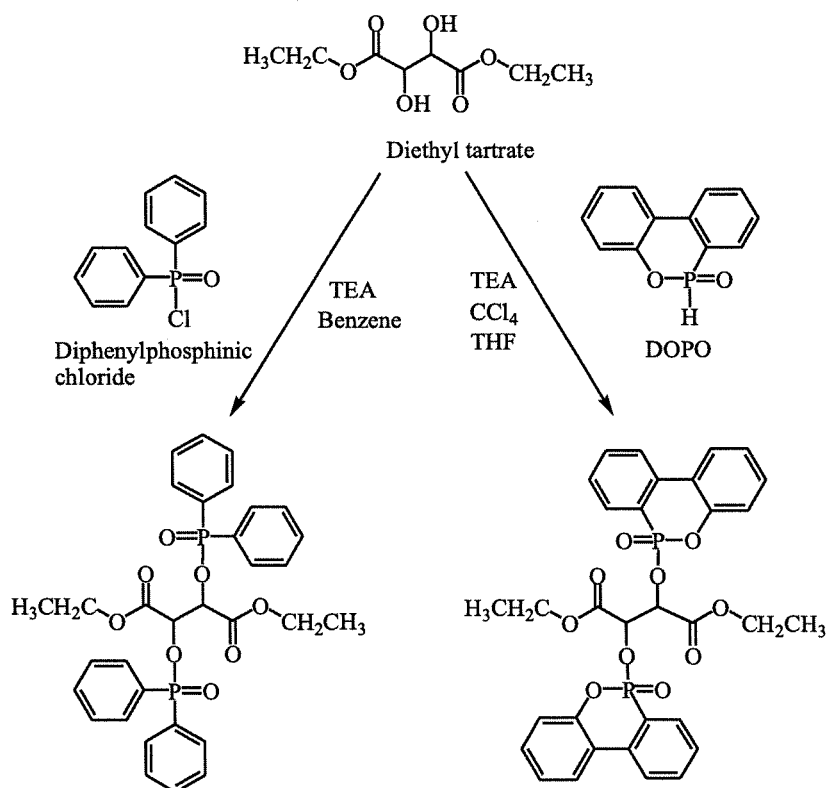
### 3.1.11. Poly(2,3-dibromo-2-butenylene phenylphosphonate)

A solution of terephthaloyl chloride (16.4 g, 80.7 mmol) in dry dichloromethane (120 ml) was added dropwise, over a period of 80 min, to a stirred solution of 2,3-dibromo-1,4-butanediol (20.0 g, 80.7 mmol) and triethylamine (26.0 ml, 186 mmol) in dry dichloromethane (80 ml) maintained at 0 °C. The polymerization was carried out as described above. The polymer displays a glass transition (DSC) at 102 °C: FTIR (ATR,  $\text{cm}^{-1}$ ) 2957 (w), 2883 (w)  $\text{C}-\text{H}$  alkyl, 1718 (vs)  $\text{C}=\text{O}$ , 1577 (w) aromatic nucleus, 689 (m)  $\text{C}-\text{Br}$ ;  $^1\text{H}$  NMR ( $\text{DMSO}-d_6$ ,  $\delta$ ) 4.70 (s) methylene protons, 5.05 (s) methine protons, 8.12 (s) aromatic protons;  $^{13}\text{C}$  NMR ( $\text{DMSO}-d_6$ ,  $\delta$ ) 48.8 (CH), 66.0 (internal  $\text{CH}_2$ ), 64.4 and 66.8 (end group  $\text{CH}_2$ ), 129.7 to 133.2 (ArC), 164.1 ( $\text{C}=\text{O}$ ).

## 4. Results and discussion

Tartaric acid (2,3-dihydroxybutanedioic acid) is generated in large quantities during the production of wine. It is tetrafunctional and may be converted to a variety of materials that are useful as polymer additives. The carboxyl group may be readily converted to alkyl esters [3,34]. Phosphorus esters may then be generated at the hydroxyl groups. This is illustrated in Scheme 1. Diethyl 2,3-diphenylphosphinobutanedioate is a white solid, mp 152 °C, thermally stable with an onset decomposition temperature of 267 °C. The infrared spectrum of this compound contains a strong carbonyl absorption at 1764  $\text{cm}^{-1}$ . It also contains  $\text{C}-\text{H}$  absorption at 3062  $\text{cm}^{-1}$  and absorption at 1592  $\text{cm}^{-1}$  for an aromatic nucleus. Several absorptions from the phosphinate ester are also present in the infrared spectrum:  $\text{P}=\text{O}$  at 1224  $\text{cm}^{-1}$ ,  $\text{P}-\text{Ar}$  at 1106  $\text{cm}^{-1}$ ,  $\text{P}-\text{O}-\text{C}$  at 935  $\text{cm}^{-1}$  and 752  $\text{cm}^{-1}$ . The  $^1\text{H}$  NMR spectrum of the compound contains a triplet at  $\delta$  0.98 (6H,  $J = 6.9$  Hz), a quartet of doublets at  $\delta$  3.65 (4H,  $J = 10.8$ , 6.9 Hz) for the ethyl protons, a doublet of doublets at  $\delta$  5.50 (2H,  $J = 10.8$  Hz, 1.8 Hz) for the methine protons, and absorption at  $\delta$  7.39 to  $\delta$  7.92 (20H) for the aromatic protons. The  $^{13}\text{C}$  NMR spectrum contains two peaks at  $\delta$  13.6 and  $\delta$  62.1 for the carbon atoms of the ethyl group, a doublet at  $\delta$  73.2 ( $J_{\text{PC}} = 22.9$  Hz) for the methine carbon atoms, a set of absorptions at  $\delta$  128.2,  $\delta$  130.3,  $\delta$  131.6,  $\delta$  131.8,  $\delta$  131.9 and  $\delta$  132.3 for the aromatic carbon atoms, and absorptions of  $\delta$  166.53 and  $\delta$  166.55 for the carbonyl carbon atoms. The  $^{31}\text{P}$  NMR spectrum contains a singlet at  $\delta$  34.8.

Diethyl 2,3-didopyloxybutanedicarboxylate is a solid melting at 212 °C which undergoes two-stage thermal degradation with an initial decomposition onset temperature of 278 °C. The infrared spectrum of this compound contains two carbonyl absorptions at 1764  $\text{cm}^{-1}$  and 1740  $\text{cm}^{-1}$ . It also contains  $\text{C}_{\text{sp}^2}\text{-H}$  absorption at 3067  $\text{cm}^{-1}$  and absorption for an aromatic nucleus at 1597  $\text{cm}^{-1}$ . Several absorptions specific to the phosphonate ester are also present in the infrared spectrum:  $\text{P}=\text{O}$  at 1271  $\text{cm}^{-1}$ ,  $\text{P}-\text{O}-\text{Ar}$  at 1200  $\text{cm}^{-1}$  and 938  $\text{cm}^{-1}$ ,  $\text{P}-\text{Ar}$  at 1114  $\text{cm}^{-1}$ ,  $\text{P}-\text{O}-\text{C}$  at 1067  $\text{cm}^{-1}$  and 747  $\text{cm}^{-1}$ . The  $^1\text{H}$  NMR spectrum of the compound contains



**Scheme 1.** Synthesis of Diethyl 2,3-Diphenylphosphinobutanedioate and Diethyl 2,3-Didiploxybutanedioate.

multiplets at  $\delta$  1.37 (6H) and  $\delta$  4.26 (4H) corresponding to the ethyl protons, a multiplet at  $\delta$  5.82 (2H) for the methine protons, and absorption at  $\delta$  6.42 to  $\delta$  7.88 (16H) for the aromatic protons. The  $^{13}\text{C}$  NMR spectrum contains two multiplets at  $\delta$  14.1 and  $\delta$  62.6 for the carbon atoms of the ethyl group, a multiplet at  $\delta$  73.9 for the methine carbon atoms, a set of absorptions at  $\delta$  118.5,  $\delta$  119.5,  $\delta$  121.0,  $\delta$  123.1,  $\delta$  123.6,  $\delta$  124.3,  $\delta$  127.4,  $\delta$  129.3,  $\delta$  129.5,  $\delta$  133.3,  $\delta$  136.5 and  $\delta$  148.7 for the aromatic carbon atoms, and a multiplet at  $\delta$  165.9 for carbonyl carbon atoms. The  $^{31}\text{P}$  NMR spectrum contains two singlets at  $\delta$  11.7 and  $\delta$  11.9 as would be expected for a set of conformational isomers.

Two unsaturated derivatives of tartaric acid have also been converted to compounds useful for the generation of effective flame retardants. Both 2-butene-1,4-diol and 2-butyne-1,4-diol were first subjected to bromination (Scheme 2).

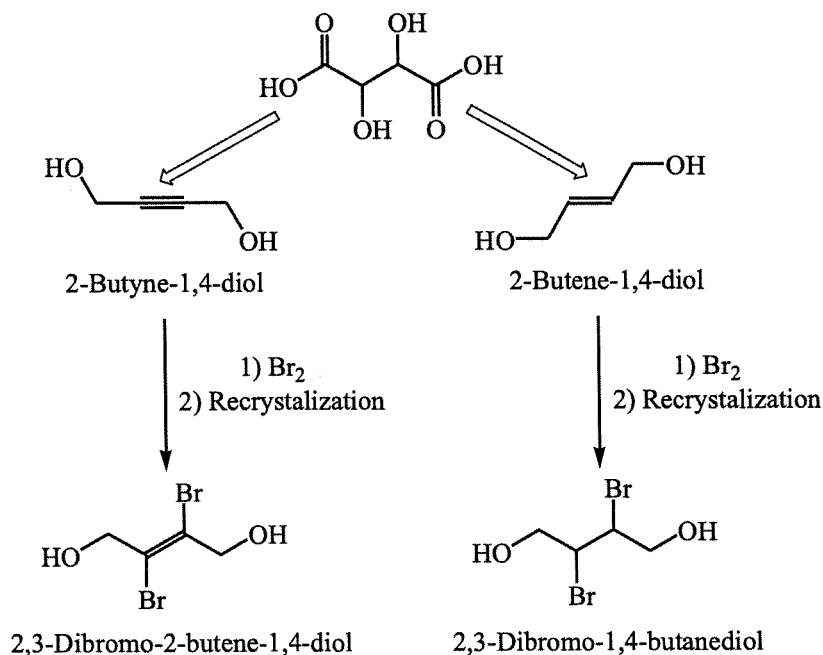
The infrared spectrum of 2,3-dibromo-2-butene-1,4-diol contains a characteristic absorption for C–Br stretching at  $561\text{ cm}^{-1}$  and broad hydroxyl absorption at  $3208\text{ cm}^{-1}$ . The infrared spectrum of 2,3-dibromo-1,4-butanediol contains a characteristic absorption for C–Br stretching at  $689\text{ cm}^{-1}$  and broad hydroxyl absorption at  $3233\text{ cm}^{-1}$ . The proton spectrum for 2,3-dibromo-2-butene-1,4-diol contains a doublet at  $\delta$  4.32 ( $J = 6.0\text{ Hz}$ ) for the methylene protons. It contains a triplet at  $\delta$  5.52 ( $J = 6.0\text{ Hz}$ ) for the hydroxyl protons.

The corresponding  $^{13}\text{C}$  spectrum contains a peak at  $\delta$  65.5 for the methylene carbon atoms and another at  $\delta$  122.9 for the olefinic carbon atoms. The proton NMR spectrum of 2,3-dibromo-1,4-butanediol contains a multiplet at  $\delta$  3.70 for the methine protons, a triplet at  $\delta$  4.44 for the methylene protons and a triplet at  $\delta$  5.43 for the hydroxyl protons. The corresponding  $^{13}\text{C}$  spectrum contains peaks at  $\delta$  56.1 (methine carbon atoms) and  $\delta$  64.2 (methylene carbon atoms).

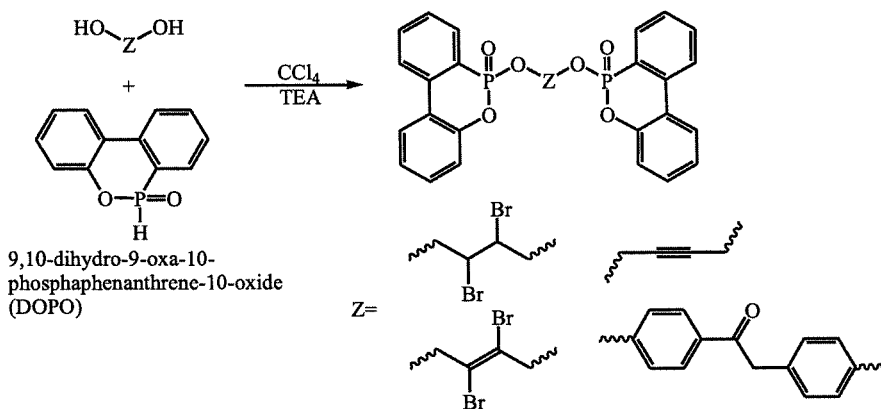
Several attempts to fully brominate 2-butyne-1,4-diol under a variety of conditions were unsuccessful. This is fully consistent with earlier observations [35–37].

The two brominated diols (*E*)-2,3-dibromo-2-butene-1,4-diol and 2,3-dibromo-1,4-butanediol, 2-butyne-1,4-diol and 4,4'-bishydroxydeoxybenzoin (BHDB) were converted to bisphosphonates by treatment with 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) in the presence of carbon tetrachloride as shown in Scheme 3. 4,4'-Bishydroxy deoxybenzoin was included for comparison since it may undergo thermal degradation via an alkyne intermediate.

2,3-Dibromo-1,4-didiploxybutane is a solid, mp  $181\text{ }^\circ\text{C}$ , with a thermal decomposition onset at  $281\text{ }^\circ\text{C}$ . The mass spectrum of this compound, determined using ESI, contains peaks in the molecular ion region at  $m/z$  674.91, 676.92, 678.91 in 1:2:1 ratio which supports the presence of two bromine atoms in the structure. The infrared spectrum of this compound contains aromatic absorption at  $1608\text{ cm}^{-1}$ ,  $1596\text{ cm}^{-1}$  and  $1583\text{ cm}^{-1}$ ,  $\text{C}_{\text{sp}^2}\text{-H}$  stretching bands at  $3065\text{ cm}^{-1}$  and  $2955\text{ cm}^{-1}$ , very strong  $\text{P}=\text{O}$  absorption at  $1272\text{ cm}^{-1}$ ,  $\text{P}-\text{O}-\text{Ar}$  absorption at  $1203\text{ cm}^{-1}$  and  $927\text{ cm}^{-1}$ ,  $\text{P}-\text{Ar}$  absorption at  $1155\text{ cm}^{-1}$  and  $1119\text{ cm}^{-1}$ ,  $\text{P}-\text{O}-\text{C}$  absorption at  $1006\text{ cm}^{-1}$  and  $754\text{ cm}^{-1}$ , C–Br absorption at  $603\text{ cm}^{-1}$ . The  $^1\text{H}$  NMR spectrum of the compound contains a multiplet at  $\delta$  4.20 (4H) for the methylene protons, a multiplet at  $\delta$  4.39 (2H) for the methine protons and absorption at  $\delta$  7.11 to  $\delta$  7.99 (16H) for the aromatic protons. The  $^{13}\text{C}$  NMR spectrum contains a doublet at  $\delta$  48.9 ( $J_{\text{PC}} = 30.8\text{ Hz}$ ) for the methine carbon atoms, a doublet at  $\delta$  66.4 ( $J_{\text{PC}} = 24.6\text{ Hz}$ ) for the methylene carbon atoms, and a set of absorptions at  $\delta$  119.9,  $\delta$  120.2,  $\delta$  122.1,  $\delta$  122.3,  $\delta$  124.0,  $\delta$  125.1,  $\delta$  128.3,  $\delta$  130.3,  $\delta$  130.6,  $\delta$  133.9,  $\delta$  137.0 and  $\delta$  149.4 for the aromatic carbon atoms. The  $^{31}\text{P}$  NMR spectrum contains a singlet at  $\delta$  9.82 for the major diastereomer and peaks at  $\delta$  9.71,  $\delta$  9.93 and  $\delta$  9.99 for the minor diastereomers.



Scheme 2. Bromination of Tartaric Acid Derivatives.



Scheme 3. Conversion of Diols to Dopyloxyphosphonates.

2,3-Dibromo-1,4-didopyloxy-2-butene is a solid, mp 196 °C, with an onset temperature for thermal degradation of 278 °C. The mass spectrum of this compound, using ESI, contains peaks in the molecular ion region at  $m/z$  672.93, 674.92, 676.93 in 1:2:1 ratio which supports the presence of two bromine atoms in the structure. The infrared spectrum of this compound contains aromatic absorption at 1611  $\text{cm}^{-1}$ , 1597  $\text{cm}^{-1}$  and 1584  $\text{cm}^{-1}$ ,  $\text{C}_{\text{sp}^2}\text{-H}$  stretching bands at 3054  $\text{cm}^{-1}$  and 2927  $\text{cm}^{-1}$ , very strong  $\text{P}=\text{O}$  absorption at 1264  $\text{cm}^{-1}$ ,  $\text{P}-\text{O}-\text{Ar}$  absorption at 1204  $\text{cm}^{-1}$  and 929  $\text{cm}^{-1}$ ,  $\text{P}-\text{Ar}$  absorption at 1155  $\text{cm}^{-1}$  and 1119  $\text{cm}^{-1}$ ,  $\text{P}-\text{O}-\text{C}$  absorption at 1001  $\text{cm}^{-1}$  and 732  $\text{cm}^{-1}$ , and  $\text{C}-\text{Br}$  stretching absorption at 603  $\text{cm}^{-1}$ .

The  $^1\text{H}$  NMR spectrum of the compound contains a multiplet at  $\delta$  4.96 (4H) for the methylene protons, and absorption from  $\delta$  7.16 to  $\delta$  7.99 (16H) for the aromatic protons. The  $^{13}\text{C}$  NMR spectrum contains a doublet at  $\delta$  68.8 ( $J_{\text{PC}} = 22.6$  Hz) for the methylene carbon atoms, a doublet at  $\delta$  120.0 ( $J_{\text{PC}} = 8.5$  Hz) for the alkene carbon atoms, and a set of absorptions at  $\delta$  119.9,  $\delta$  120.1,  $\delta$  122.2,  $\delta$  122.4,  $\delta$  124.0,  $\delta$  124.9,  $\delta$  128.3,  $\delta$  130.3,  $\delta$  130.5,  $\delta$  133.8,  $\delta$  137.1 and  $\delta$  149.6

for the aromatic carbon atoms. The  $^{31}\text{P}$  NMR spectrum contains a singlet at  $\delta$  10.5.

1,4-Didopyloxy-2-butyne is a solid, mp 132 °C, with an onset temperature for thermal degradation of 281 °C. The mass spectrum of this compound, determined using ESI, contains a molecular ion peak at  $m/z$  515.07  $\{[\text{M}+\text{H}]^+\}$ ; calculated for  $\text{C}_{28}\text{H}_{20}\text{O}_6\text{P}_2$  is 515.08. The infrared spectrum of this compound contains aromatic absorption at 1608  $\text{cm}^{-1}$ , 1596  $\text{cm}^{-1}$  and 1582  $\text{cm}^{-1}$ ,  $\text{C}_{\text{sp}^2}\text{-H}$  stretching bands at 3066  $\text{cm}^{-1}$  and 2942  $\text{cm}^{-1}$ , very strong  $\text{P}=\text{O}$  absorption at 1270  $\text{cm}^{-1}$ ,  $\text{P}-\text{O}-\text{Ar}$  absorption at 1203  $\text{cm}^{-1}$  and 924  $\text{cm}^{-1}$ ,  $\text{P}-\text{Ar}$  absorption at 1153  $\text{cm}^{-1}$  and 1118  $\text{cm}^{-1}$ , and  $\text{P}-\text{O}-\text{C}$  absorption at 1013  $\text{cm}^{-1}$  and 753  $\text{cm}^{-1}$ . The  $^1\text{H}$  NMR spectrum of the compound contains a multiplet at  $\delta$  4.72 (4H) for the methylene protons, and absorption at  $\delta$  7.20 to  $\delta$  7.97 (16H) for the aromatic protons. The  $^{13}\text{C}$  NMR spectrum contains a doublet at  $\delta$  53.6 ( $J_{\text{PC}} = 13.8$  Hz) for the methylene carbon atoms, a doublet of doublet at  $\delta$  81.7 ( $J_{\text{PC}} = 16.2, 7.0$  Hz) for the alkyne carbon atoms, and a set of absorptions at  $\delta$  120.2,  $\delta$  120.6,  $\delta$  122.1,  $\delta$  122.3,  $\delta$  123.9,  $\delta$  124.9,  $\delta$  128.2,  $\delta$  130.3,  $\delta$  130.5,  $\delta$  133.8,  $\delta$  137.0 and  $\delta$  149.6 for the aromatic carbon atoms.

The  $^{31}\text{P}$  NMR spectrum contains two equal-intensity peaks at  $\delta$  11.06 and  $\delta$  11.08.

4,4'-Bisdopoxyloxydeoxybenzoin is a solid, mp 186 °C, with an onset temperature for thermal degradation of 404 °C. The mass spectrum of this compound, determined using ESI, has a molecular ion at  $m/z$  657.10  $[[\text{M}+\text{H}]^+]$ ; calculated for  $\text{C}_{38}\text{H}_{26}\text{O}_7\text{P}_2$  is 657.12. The infrared spectrum of this compound contains aromatic absorption at 1596  $\text{cm}^{-1}$  and 1583  $\text{cm}^{-1}$ ,  $\text{C}_{\text{sp}2}\text{-H}$  stretching bands at 3065  $\text{cm}^{-1}$  and 2925  $\text{cm}^{-1}$ ,  $\text{C}=\text{O}$  absorption at 1687  $\text{cm}^{-1}$ , very strong  $\text{P}=\text{O}$  absorption at 1275  $\text{cm}^{-1}$ ,  $\text{P}-\text{O}-\text{Ar}$  absorption at 1218  $\text{cm}^{-1}$  and 921  $\text{cm}^{-1}$ ,  $\text{P}-\text{Ar}$  absorption at 1162  $\text{cm}^{-1}$  and 1118  $\text{cm}^{-1}$ , and  $\text{P}-\text{O}-\text{C}$  absorption at 996  $\text{cm}^{-1}$  and 756  $\text{cm}^{-1}$ . The  $^1\text{H}$  NMR spectrum of the compound contains a singlet at  $\delta$  4.14 (2H) for the methylene protons and absorption at  $\delta$  6.98 to  $\delta$  7.98 (24H) for the aromatic protons. The  $^{13}\text{C}$  NMR spectrum contains a singlet at  $\delta$  44.5 for the methylene carbon atoms, a set of absorptions at  $\delta$  119.8,  $\delta$  120.2,  $\delta$  120.8,  $\delta$  122.4,  $\delta$  122.6,  $\delta$  124.0,  $\delta$  124.2,  $\delta$  125.0,  $\delta$  125.3,  $\delta$  128.4,  $\delta$  130.5,  $\delta$  130.6,  $\delta$  131.3,  $\delta$  133.4,  $\delta$  133.9,  $\delta$  137.1,  $\delta$  148.7,  $\delta$  149.7 and  $\delta$  153.6 for the aromatic carbon atoms and a singlet at  $\delta$  195.8 for the carbonyl carbon atoms. The  $^{31}\text{P}$  NMR spectrum contains singlets at  $\delta$  6.2 and  $\delta$  6.3 as would be expected for the presence of two different phosphorus entities. A comparison of NMR aromatic carbon absorptions for 4,4'-bisdopoxyloxydeoxybenzoin, 4,4'-bishydroxydeoxybenzoin and DOPO is shown in Fig. 1. The absorptions for the aromatic carbon atoms of 4,4'-bisdopoxyloxydeoxybenzoin corresponding to the DOPO group appear as a set of two equivalent patterns. This indicates that the aromatic carbon atoms from the DOPO groups are in two different chemical environments.

This observation is supported by the presence of two singlets in the  $^{31}\text{P}$  NMR spectrum which indicates that the phosphorus atoms of the dopoxy groups exist in different environments (Fig. 2)

Oligomeric materials containing bromine and phosphorus were also prepared.

The solution polycondensation of two brominated diols with either isophthaloyl terephthaloyl chloride to afford bromine-containing polyesters poly(2,3-dibromobut-2-enyl isophthalate) [1], poly(2,3-dibromobut-2-enyl terephthalate) [2] and poly(2,3-dibromobutylene terephthalate) [3] is outlined in Scheme 4. The polymerization was conducted in dichloromethane with triethylamine as acid scavenger. Polyester 1 and 2 were insoluble in all solvents tested including DMSO,  $\text{CHCl}_3$ , DMF, DMA and several others. However, polyester 3 was soluble in chloroform and DMSO at room temperature.

Poly(2,3-dibromobutylene terephthalate) [3] is stable to 300 °C (TGA) and then undergoes a single stage decomposition with a mass loss of 93.6% of the initial sample mass at 800 °C. The polymer has a glass transition temperature of 102 °C determined using DSC. The infrared spectrum of this compound contains aromatic

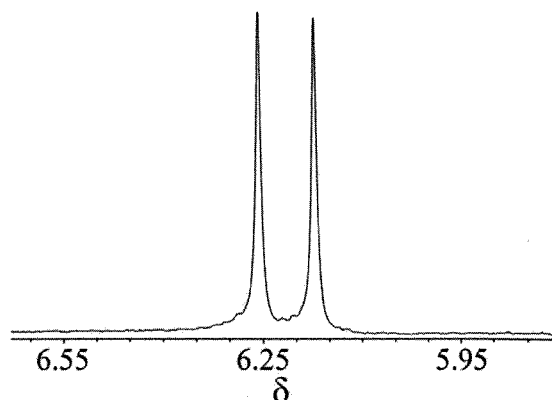


Fig. 2.  $^{31}\text{P}$  NMR spectrum of 4,4'-Bisdopoxyloxydeoxybenzoin.

absorption at 1577  $\text{cm}^{-1}$ ,  $\text{C}_{\text{sp}2}\text{-H}$  absorption at 2957  $\text{cm}^{-1}$  and 2883  $\text{cm}^{-1}$ ,  $\text{C}=\text{O}$  absorption at 1718  $\text{cm}^{-1}$  and a weak  $\text{C}-\text{Br}$  absorption at 689  $\text{cm}^{-1}$ . The  $^1\text{H}$  NMR spectrum of the compound contains a broad peak at  $\delta$  4.70 for the methylene protons, a broad peak at  $\delta$  5.05 for the methine protons and a broad peak at  $\delta$  8.12 for the aromatic protons. The  $^{13}\text{C}$  NMR spectrum contains a singlet at  $\delta$  48.8 for the methine carbon atoms, a singlet at  $\delta$  66.0 for the internal methylene carbon atoms, two methylene resonances of the end groups are at  $\delta$  64.4 and 66.8, a singlet at  $\delta$  129.7 for the hydrogen-bearing aromatic carbon atoms, a singlet at  $\delta$  133.2 for the substituted aromatic carbon atoms and a singlet at  $\delta$  164.1 for the carbonyl carbon atoms. The ratio of the intensity of the peak at  $\delta$  66.0 (internal methylene carbon atoms) to that at  $\delta$  66.8 (end-group methylene carbon atoms) is 14 which reflects the number average degree of polymerization. The corresponding number average molecular weight,  $M_n$ , is 5300 g/mole.

The solution polycondensation of 2,3-dibromo-2-butene-1,4-diol with phenylphosphonic dichloride to afford a polyester is illustrated in Scheme 5. The polymerization was conducted in dichloromethane with triethylamine as the acid scavenger. The polymer, poly(2,3-dibromo-2-butenylene phenylphosphonate), is stable to 244 °C (TGA). It then undergoes a two stage decomposition with an initial mass loss of 50.6% of the initial sample mass at 244 °C (40.2% calculated for the loss of two moles of hydrogen bromide) and a second mass loss of 33.0% of the initial sample mass at 331 °C. The polymer has a glass transition temperature of 34 °C determined using DSC. The infrared spectrum of this compound contains aromatic absorption at 1593  $\text{cm}^{-1}$ ,  $\text{C}_{\text{sp}2}\text{-H}$  stretching absorption at 3059  $\text{cm}^{-1}$ ,  $\text{C}-\text{H}$  alkyl absorption at 2953  $\text{cm}^{-1}$  and 2879  $\text{cm}^{-1}$ , very strong  $\text{P}=\text{O}$  absorption at 1246  $\text{cm}^{-1}$ ,  $\text{P}-\text{Ar}$  absorption at 1131  $\text{cm}^{-1}$  and 1087  $\text{cm}^{-1}$ ,  $\text{P}-\text{O}-\text{C}$  absorption at

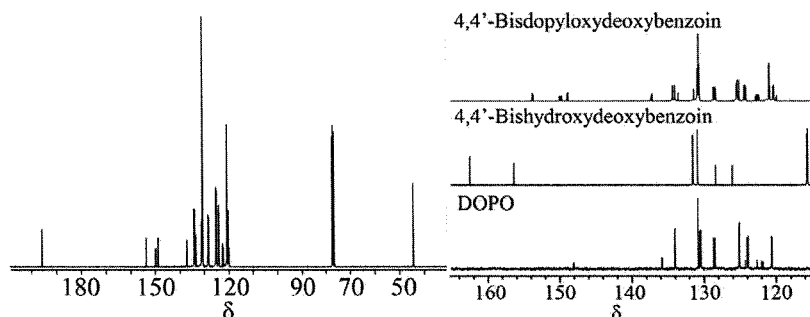
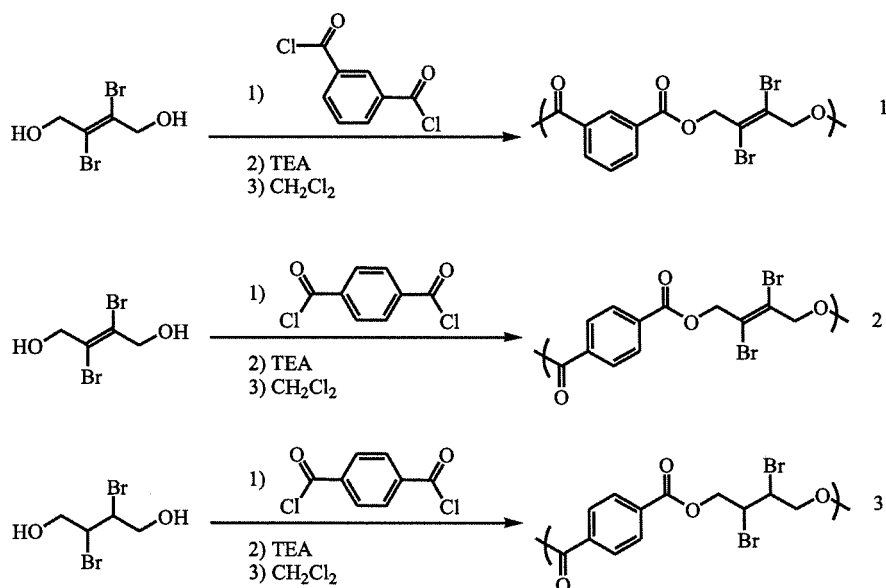
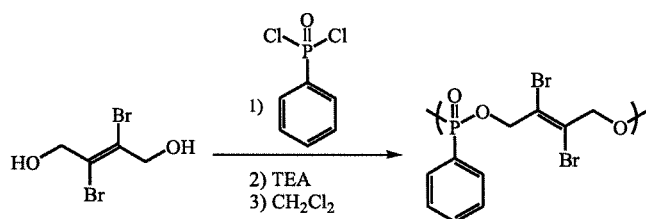


Fig. 1.  $^{13}\text{C}$  NMR spectrum of 4,4'-Bisdopoxyloxydeoxybenzoin (left) and Expanded aromatic portion of the spectrum (right) with comparison spectra.



Scheme 4. Polymerization of Dibromodiols with Isophthaloyl or Terephthaloyl Chloride.



Scheme 5. Synthesis of Poly(2,3-dibromo-2-butenylene phenylphosphonate).

978  $\text{cm}^{-1}$  and 749  $\text{cm}^{-1}$ , and a strong C–Br absorption at 545  $\text{cm}^{-1}$ . The  $^1\text{H}$  NMR spectrum of the compound contains a broad doublet at  $\delta$  4.93 ( $J_{\text{PH}} = 4.6$  Hz) for the methylene protons and absorption at  $\delta$  7.51 to  $\delta$  7.74 for the aromatic protons. The  $^{13}\text{C}$  NMR spectrum contains a singlet at  $\delta$  68.7 for the methylene carbon atoms, a doublet at  $\delta$  120.1 ( $J_{\text{PC}} = 19.0$  Hz) for the alkene carbon atoms and a set of absorptions at  $\delta$  126.1,  $\delta$  129.2,  $\delta$  131.8 and  $\delta$  133.7 for the aromatic carbon atoms (Fig. 3). The  $^{31}\text{P}$  NMR spectrum contains a singlet at  $\delta$  19.7.

For an assessment of flame-retarding properties, blends of each of the compounds in DGEBA epoxy were prepared. Thermal properties of the blends are collected in Table 1. Epoxy resin containing

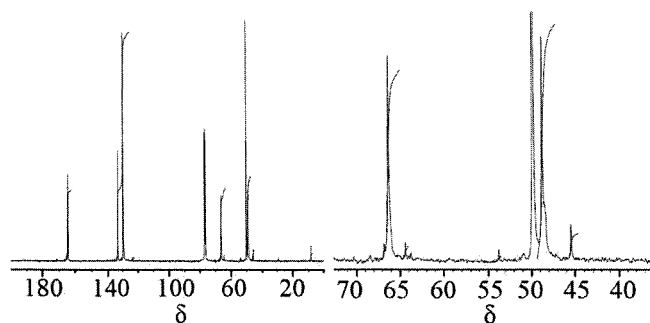


Fig. 3.  $^{13}\text{C}$  NMR spectrum of Poly(2,3-dibromobutylene terephthalate) (left) and expanded aliphatic carbon atoms region (right).

no flame retardant, prepared in the same way as the blends, has a glass transition temperature of 128  $^{\circ}\text{C}$  and a decomposition onset temperature (TGA) of 397  $^{\circ}\text{C}$  with 9.6% (of initial mass) residue at 800  $^{\circ}\text{C}$ . All the epoxy blends with tartaric acid-derived flame retardants display glass transition temperatures 0–34  $^{\circ}\text{C}$  higher than that for the untreated resin. Blending of the two phosphonates with the epoxy provided materials with the highest glass transition temperatures.

This increase in  $T_g$  may be due to antiplasticization, which is caused by more ordered structure of the host polymer as a result of blending with additives [39–41]. Antiplasticization is usually observed with low addition of molecules into the material which could restrict the movement of polymer chains rather than increase the free volume. Alternatively, the increase in  $T_g$  could reflect an increase in cross-linking brought about by reaction (transesterification) with the additive during epoxy curing.

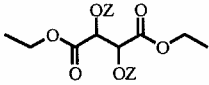
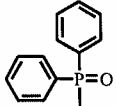

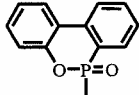
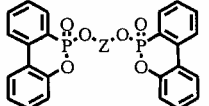
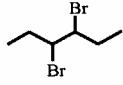
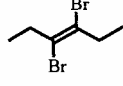
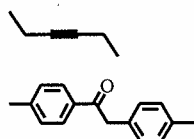
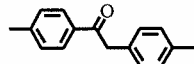
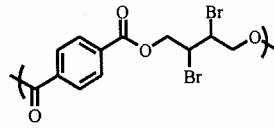
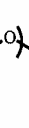
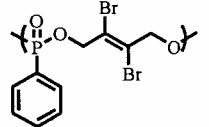
The thermal decomposition onset temperature for all epoxy resin blends was lower than that for the polymer containing no additive. The degradation onset temperatures for blends with phosphorus-containing additives are modestly lower (6–27  $^{\circ}\text{C}$  depending on the nature and loading of the additive) and may reflect the stability of the P–O bond at high temperature. The suppression of the degradation onset temperature ( $^{\circ}\text{C}$ ) is greater for bromine-containing flame retardants and probably reflects facile thermal dehydrobromination. However, the thermal stability of the polymer is not remarkably impacted by the presence of useful levels of any of these additives. It might be noted that the residue at 800  $^{\circ}\text{C}$  is greater than that for the resin alone. This may suggest that additive decomposition products promote resin char formation.

MCC is an effective and convenient screening method for flame retardancy [42–47]. The properties of all the blends were assessed using MCC. Peak heat release rates for blends containing diethyl 2,3-diphenylphosphonyl tartrate are shown in Fig. 4. The PHRR of the epoxy resin containing no additive (672.8 W/g) is diminished by incorporation of levels of the phosphonate ester sufficient to provide half to one percent phosphorus by weight. THR in Fig. 5 shows a similar trend.

The dopyl-substituted compound (Fig. 6) has a similar effect on



**Table 1**  
Properties of epoxy resin containing flame retardants.

Main structure	Z group	Loading of additive <sup>a</sup>	Loading of phosphorus (wt %)	Loading of bromine (wt %)	Tg <sup>b</sup> (°C)	Decomp. onset <sup>c</sup> (°C)	Residue at 800 °C (% of initial mass)
		4.90	0.5	0	133	391	10.0
		9.80	1.0	0	135	384	13.4
		19.6	2.0	0	123	346	16.8
		5.12	0.5	0	127	375	12.9
		10.2	1.0	0	142	371	15.7
		20.5	2.0	0	146	352	15.5
		5.46	0.5	1.3	128	374	11.5
		10.9	1.0	2.6	161	350	12.7
		5.44	0.5	1.3	132	375	12.6
		10.9	1.0	2.6	162	353	13.3
		4.15	0.5	0	124	390	15.8
		8.32	1.0	0	128	380	16.3
16.6		2.0	0	150	350	18.1	
5.30		0.5	0	141	386	15.8	
	10.6	1.0	0	139	383	19.2	
	21.2	2.0	0	149	351	19.6	
		7.06	0.0	3.0	142	366	10.4
		14.1	0.0	5.0	147	363	12.0
		3.56	0.3	1.5	145	349	13.9
		5.97	0.5	2.6	133	339	13.8

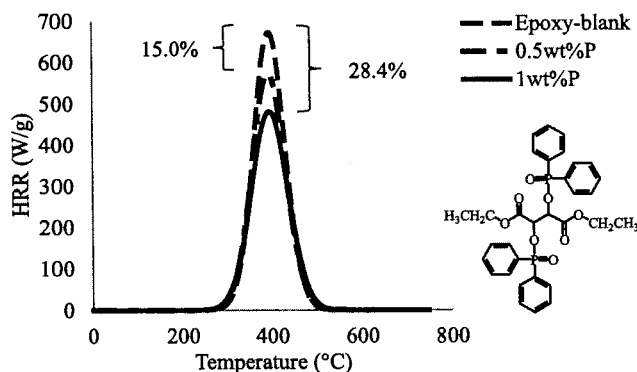
<sup>a</sup> Weight percent of additive in DGEBA epoxy resin.

<sup>b</sup> Glass transition temperature From DSC.

<sup>c</sup> Extrapolated onset temperature from the derivative mass loss versus temperature plot.

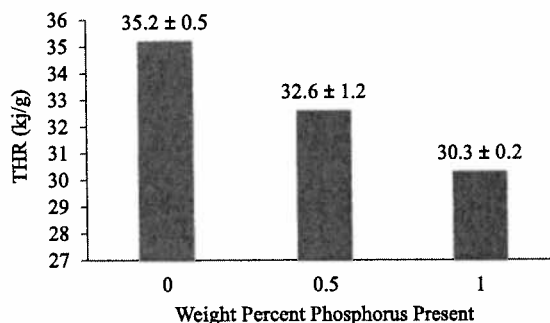
HRR as does the phosphonate compound. This was expected due to the similar chemical structures and similar level of phosphorus loading (see Fig. 7).

Blends of 2,3-dibromo-1,4-didiploxybutane with DGEBA epoxy show a 40.4% reduction in PHRR (Fig. 8) at 0.5% phosphorus



**Fig. 4.** Heat release rates for blends of diethyl 2,3-diphenylphosphonyl tartrate with DGEBA epoxy.

loading/1.3% bromine loading. This demonstrates that the presence of bromine has a significant impact on PHRR and strongly augments the impact of phosphorus on flame retardancy. A quite similar result also was obtained for 2,3-dibromo-1,4-didiploxy-2-butene blends. This additive diminished PHRR by 40.8% at 0.5% phosphorus loading/2.6% bromine loading. This also suggests that whether the bromine is bonded to a vinylic carbon atom or a saturated carbon



**Fig. 5.** Total heat release for blends of diethyl 2,3-diphenylphosphonyl tartrate with DGEBA epoxy.

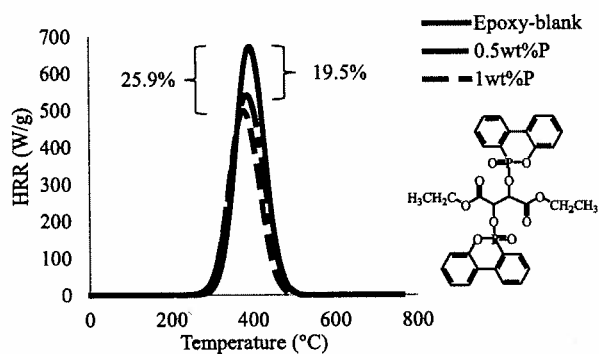


Fig. 6. Heat release rates for blends of diethyl 2,3-didipolyoxybutanedicarboxylate with DGEBA epoxy.

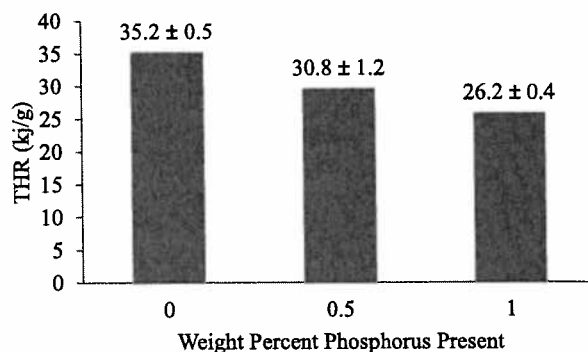


Fig. 9. Total heat release for blends of 2,3-dibromo-1,4-didipolyoxybutane with DGEBA epoxy.

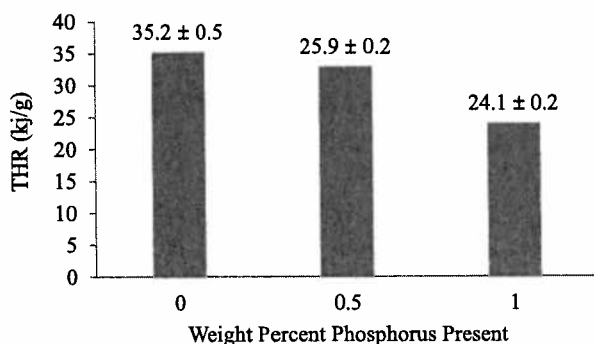


Fig. 7. Total heat release for blends of diethyl 2,3-didipolyoxybutanedicarboxylate with DGEBA epoxy.

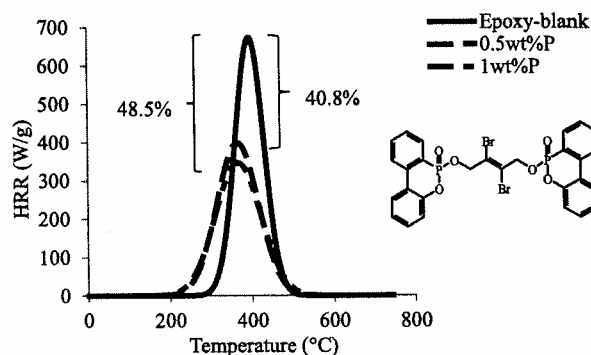


Fig. 10. Heat release rates for blends of 2,3-dibromo-1,4-didipolyoxy-2-butene with DGEBA epoxy.

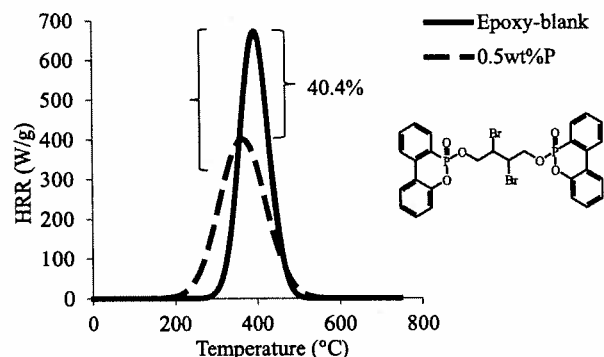


Fig. 8. Heat release rates for blends of 2,3-dibromo-1,4-didipolyoxybutane with DGEBA epoxy.

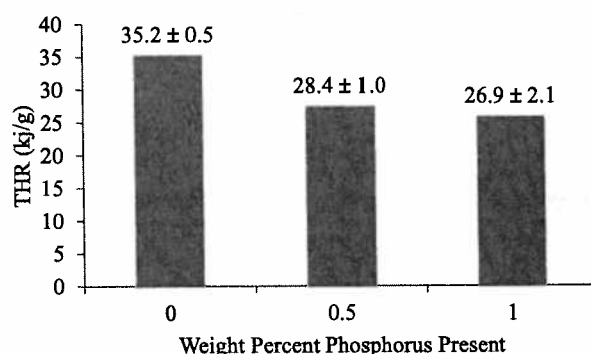


Fig. 11. Total heat release for blends of 2,3-dibromo-1,4-didipolyoxy-2-butene with DGEBA epoxy.

atom is of little consequence. This result is consistent with the dynamic TGA and LOI data, which all suggest that flame retardancy will not be affected significantly by this kind of structural difference (see Figs. 9–11).

The HRR plots for blends of 1,4-didipolyoxy-2-butyne with DGEBA epoxy, Fig. 12, show 16.9% reduction of PHRR at 0.5 wt percent loading of phosphorus. This is not as dramatic as the more than 40% reduction with 2,3-dibromo-1,4-didipolyoxybutane and 2,3-dibromo-1,4-didipolyoxy-2-butene. This suggests that the impact on HRR reduction of the presence of the triple bond is small. Although the triple bond promotes char formation, determined from TGA residue (percent of initial mass) at 800 °C, the MCC results suggest that there is no direct connection between char formation and reduction of PHRR (see Fig. 13).

Heat release rates for blends of 4,4'-bisdipolyoxydeoxybenzoin with DGEBA epoxy (Fig. 14) show 13.8% reduction in PHRR at 0.5% phosphorus loading and 41.6% reduction at 1% phosphorus loading. The significant increase in reduction of PHRR with increased phosphorus loading may be reflective of the impact of the deoxybenzoin functional group on PHRR reduction. The promotion of char formation by 4,4'-bisdipolyoxydeoxybenzoin is similar to that of 1,4-didipolyoxy-2-butyne. This is consistent with the earlier suggestion that the presence of a triple bond has a large impact on char formation [38,48,49]. However, this promotion of char formation cannot be correlated with HRR values (see Fig. 15).

The heat release rates for blends of poly(2,3-dibromobutylene terephthalate) with DGEBA epoxy are displayed in Fig. 16. A 56.0%

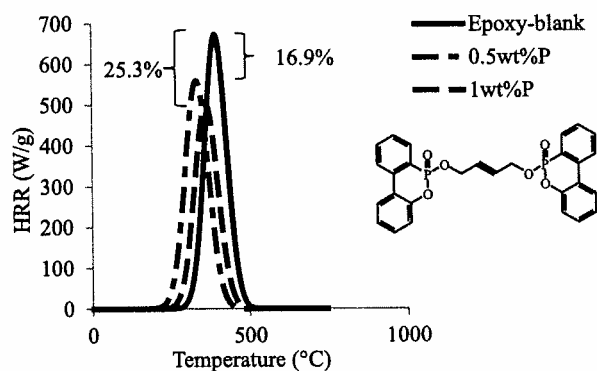


Fig. 12. Heat release rates for blends of 1,4-didiploxy-2-butylene with DGEBA epoxy.

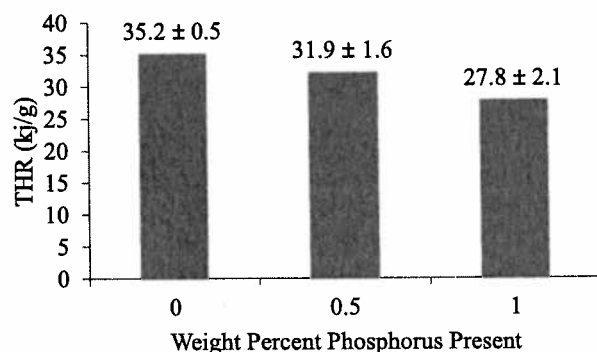


Fig. 13. Total heat release for blends of 1,4-didiploxy-2-butylene with DGEBA epoxy.

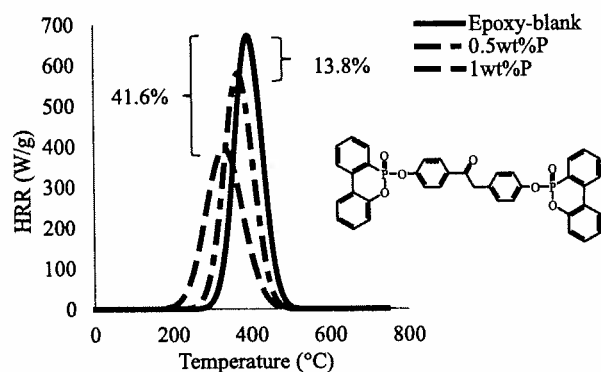


Fig. 14. Heat release rates for blends of 4,4'-Bisdiploxydeoxybenzoin with DGEBA epoxy.

reduction in PHRR is achieved with 3.0% bromine loading. This represents a tremendous reduction compared to that for all other additives examined. This reflects the very high impact of bromine on the reduction of PHRR. This may also be observed in the HRR results for 2,3-dibromo-1,4-didiploxybutane and 2,3-dibromo-1,4-didiploxy-2-butene blends with DGEBA epoxy. They all reflect the high impact of bromine on reduction of PHRR (see Fig. 17).

Heat release rates for blends of poly(2,3-dibromo-2-butenylene phenylphosphonate) with DGEBA epoxy show 34.6% reduction in PHRR at 0.3% phosphorus loading (1.5% bromine loading). This result again reflects the high impact of bromine on the reduction of PHRR.

The flammability of all the blends was determined from limiting oxygen index (LOI) measurements and the UL94 vertical burn test.

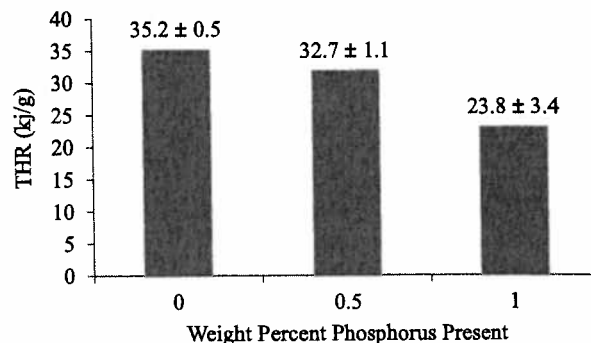


Fig. 15. Total heat release for blends of 4,4'-Bisdiploxydeoxybenzoin with DGEBA epoxy.

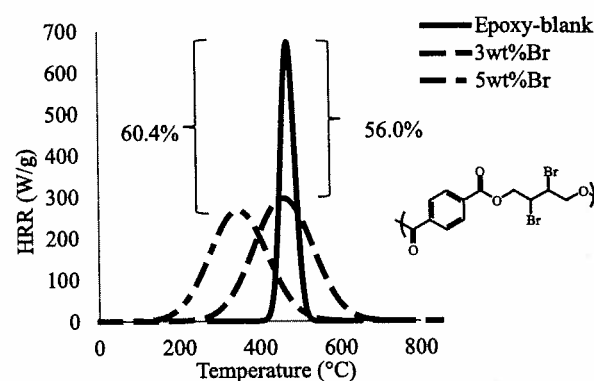


Fig. 16. Heat Release Rates for Blends of Poly(2,3-dibromobutylene terephthalate) with DGEBA Epoxy.

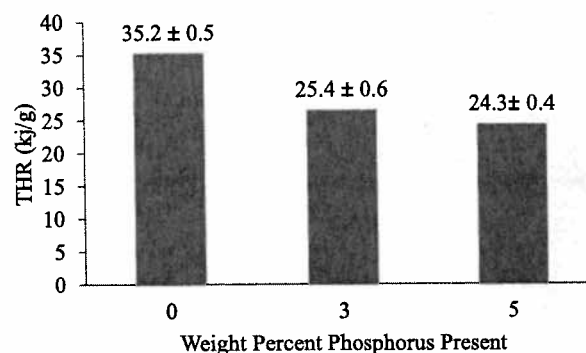


Fig. 17. Total Heat Release for Blends of Poly(2,3-dibromobutylene terephthalate) with DGEBA Epoxy.

Results are presented in Table 2.

The most general observation is that all the additives display flame-retarding properties in DGEBA epoxy. Several of them are quite effective (LOI of 30 and VO rating at a loading of 2% phosphorus). The phosphorus esters of diethyl tartrate are particularly effective. These contain phosphorus as phosphinate or phosphonate and are probably gas-phase active [50–57]. Phosphonate esters containing either saturated or unsaturated organobromine units behave similarly. Peak heat release rates and LOI values are quite similar. The compound containing aliphatic bromine does display a UL 94 V-1 rating at one percent loading of additive. This may reflect a greater propensity to release hydrogen bromide than that for the unsaturated analog. The presence of alkyne

**Table 2**  
Flammability data for blends of flame retardants with DGEBA epoxy resin.

Main structure	Z group	Loading of additive <sup>a</sup>	Loading of phosphorus	Loading of bromine	PHRR (W/g) <sup>b</sup>	LOI (%) <sup>c</sup>	UL-94 Designation
		4.90	0.5	0	572.2	27.3	–
		9.80	1.0	0	481.4	29.6	V-1
		19.6	2.0	0	360.5	33.8	V-0
		5.12	0.5	0	563.4	28.6	–
		10.2	1.0	0	561.3	31.3	V-1
		20.5	2.0	0	558.4	31.8	V-0
		5.46	0.5	1.3	401.1	23.6	–
		10.9	1.0	2.6	344.6	26.2	V-1
		5.44	0.5	1.3	398.4	23.5	–
		10.9	1.0	2.6	346.6	24.5	–
		4.15	0.5	0	559.0	23.7	–
		8.32	1.0	0	502.6	29.2	V-1
		16.6	2.0	0	409.3	34.5	V-0
		5.30	0.5	0	580.1	25.9	–
		10.6	1.0	0	393.2	30.6	V-1
		21.2	2.0	0	316.2	36.6	V-0
		7.06	0	3.0	296.3	22.1	–
		14.1	0	5.0	266.3	22.5	–
		3.56	0.3	1.5	440.1	23.6	–
		5.97	0.5	2.6	415.1	24.0	V-1

<sup>a</sup> Weight percent.

<sup>b</sup> Microscale Combustion Calorimetry (MCC); PHRR for epoxy resin containing no additive is 673 W/g.

<sup>c</sup> Limiting Oxygen Index (LOI); the LOI value for epoxy resin containing no additive is 19.0.

unsaturation, or moiety that may form an alkyne intermediate on thermal decomposition, in phosphonate esters has a positive impact on flame retardancy. It would appear that this arises from enhanced char formation as the polymer is degrading. Oligomeric compounds containing either bromine or both bromine and phosphorus may serve as effective flame retardants at relatively low loadings of additive and may be expected to display low migratory potential in a polymer matrix.

## 5. Conclusions

A variety of phosphorus-containing or phosphorus- and bromine-containing compounds derived from tartaric acid have been synthesized, fully characterized using spectroscopic and thermal methods, and evaluated as flame retardants in DGEBA epoxy resin. A range of tartaric acid derivatives may serve as effective flame retardants. In particular, simple phosphinate and phosphonate esters provide effective flame retardancy at low loadings (1–2% phosphorus) in epoxy. Compounds containing alkyne unsaturation may promote the action of phosphorus by enhancing char formation at the surface of the degrading polymer. Oligomer materials generated from unsaturated derivatives of tartaric acid and containing either bromine or both bromine and

phosphorus may function as flame retardants and can be expected to display low migratory potential when incorporated into a polymer matrix.

## Appendix A. Supplementary data

Supplementary data related to this article can be found at <https://doi.org/10.1016/j.polyimdeggradstab.2018.10.006>.

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