Synthesis and Testing of Nonhalogenated Alkyne/Phosphorus-Containing Polymer Additives: Potent Condensed-Phase Flame Retardants

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ABSTRACT: In this article, the syntheses and thermal properties of several alkyne- and phosphorus-containing materials are discussed. The materials were synthesized using substituted phenolic molecules which were added to phosphorus oxychloride. The materials synthesized include phosphine oxides, phosphates, diphosphates, and oligophosphates. The thermal properties of the synthesized materials were studied using differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA). In general, the DSC and TGA data showed that synthesized materials containing alkynes and phosphorus had good-to-excellent thermal stability with high-onset decomposition temperatures. Materials with a high alkyne-to-phosphorus ratio showed the highest char yields. DSC data showed crosslinking events for the alkynes and the phosphorus moieties. DSC also showed that the alkynes crosslinked at lower temperatures than the phosphates. Based on the TGA and DSC data of the alkyne-containing phosphorus materials, alkynes generally appeared to be better char-inducing groups than was phosphorus. The materials were blended into polycarbonate and tested for ignition resistance using the UL-94 flame test. In two cases, these halogen-free compounds, with their dual alkyne/phosphorous crosslinking mechanisms, are condensed-phase flame retardants that can be easily blended into polycarbonate at 10 wt % loadings to afford blends that give a UL-94 V-0 rating. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 707–718, 1999

Key words: alkynes; phosphorus; flame retardants; polycarbonate; UL-94 V-0

INTRODUCTION

Phosphates and polyphosphinates have been used for many years in a variety of flame-retardant applications.[1] Recently, phosphorus groups have been incorporated as part of the backbone for engineering plastics, showing increased flame retardancy, char formation, and lower rates of heat release.[2] What makes phosphorus-containing materials so attractive is their ability to act as intumescent flame retardants. An intumescent flame retardant works to form a large foamy char which blocks heat from doing further damage in the condensed phase.[3] This foamy char is usually superior in inhibiting flame propagation to the typical, more condensed char. While the exact mechanism of phosphorus action in the condensed phase is unknown, it is thought that phosphorus acts as a crosslinking group during thermal decomposition.[4] Alkynes have been used as functional groups for polymers and oligomers to produce high-performance polymers and composite matrices after thermal curing.[5] This occurs due to the ability of the alkyne to form crosslinked alk-

enes and cyclotrimeric crosslinks.[6] Combinations of alkynes and phosphorus units could provide efficient flame retardants since they would make available two complementary mechanisms for crosslinking in the condensed phase. We describe here a series of nonhalogenated alkyne/phosphorous-containing materials, two of which can be easily blended into polycarbonate at 10 wt % loadings to afford blends that give UL-94 flame test V-0 ratings.

EXPERIMENTAL

Char Yield Calculation from Thermal Gravimetric Analysis (TGA) Data at 900°C

One hundred weight percent − weight percent loss at 900°C = char yield at 900°C.

General Procedures

^{1}H-NMR spectra were recorded at 300 MHz on a Brüker AM-300 spectrometer and at 400 and 500 MHz on Varian Mercury 400 and INOVA 500 spectrometers, respectively. The ^{13}C-NMR spectra at 75 MHz was recorded on a Brüker AM-300 spectrometer and at 100 or 125 MHz on Varian Mercury 400 and INOVA 500 spectrometers, respectively. The ^{31}P-NMR spectra at 162 MHz was recorded on a Varian Mercury 400 spectrometer. Proton chemical shifts (δ) are reported in ppm downfield from tetramethylsilane (TMS). [13]C resonances were recorded using the 77.0-ppm $CDCl_3$ resonance as an internal reference and are reported in ppm downfield from TMS. [31]P resonances are reported in ppm ± from 0 ppm (85% H_3PO_4) using the 141-ppm trimethylphosphite ($P(OMe)_3$) resonance in C_6D_6 as an internal standard. Infrared (IR) spectra were recorded on a Perkin–Elmer 1600 Series FTIR. TGA was performed with a Perkin–Elmer TGA7. Differential scanning calorimetry (DSC) was performed with a Perkin–Elmer DSC7. Molecular weight analyses were performed using two 30 × 75-cm Burdick and Jackson GPC columns (10^5 Å 10 μ and 500 Å 5 μ) eluted with tetrahydrofuran (THF) at 60°C (flow rate 1.0 mL/min, 700 psi). Molecular weight results were based on five polystyrene standards (M_w = 435500, 96000, 22000, 5050, and 580; correlation coefficient > 0.997) purchased from Polymer Laboratories Ltd., Church Stretton, UK. Melting points were obtained on a Melt-Temp apparatus and are uncorrected. A Custom Scientific Instruments CSI-183MMX Mini-Max Blend-

er/Extruder was used and an Atlas Electric HVUL-94 flame test station was used for the flame tests. Reagent-grade THF and diethyl ether (Et_2O) were distilled under nitrogen from sodium benzophenone ketyl. Bulk-grade hexane was distilled prior to use. Benzene, toluene, and triethylamine were distilled over CaH_2 under nitrogen. Bisphenol A, 4-bromophenol, hydroquinone, resorcinol, and 2,4,6-tribromophenol were recrystallized prior to use. 4-Iodophenol was purchased from Alfa/Aesar Organics, Ward Hill, MA. 2,4,6-Tribromophenol (Great Lakes PH-73) was provided by Great Lakes Chemical Corp., W. Lafayette, IN. All other reagents were used as received unless otherwise noted. Gravity column chromatography, silica gel plugs, and flash chromatography was carried out on silica gel (230–400 mesh from EM Science, Gibbstown, NJ). Thin-layer chromatography was performed using glass plates precoated with silica gel 60 F_{254} with a layer thickness of 0.25 mm purchased from EM Science. Mass spectrometry work was done by the University of South Carolina Mass Spectrometry Laboratory. Elemental analysis was performed by the Atlantic Microlab (Norcross, GA). All synthetic operations were carried out under a dry, oxygen-free, nitrogen atmosphere unless otherwise noted.

Tri(phenylethynyl)phosphine oxide (1)[10]

A dry 100-mL round-bottom flask equipped with a magnetic stirbar was purged with N_2 and then sealed with a rubber septum under a N_2 atmosphere. Phenylacetylene (14.9 mL, 136.0 mmol) and THF (150 mL) were then added and the flask was cooled to −78°C. *tert*-Butyllithium (80.5 mL, 122.4 mmol, 1.52M in pentane) was added dropwise, whereupon the reaction turned an orange–red color. The reaction was allowed to stir for 2 h at −78°C, eventually becoming a cloudy tan color. Phosphorus oxychloride (3.73 mL, 40.0 mmol) was then added and the reaction became black. The reaction was allowed to stir at −78°C for 2 h and then was quenched with H_2O (20 mL). The reaction was then allowed to warm to room temperature, and the THF was removed via a rotary evaporator. The crude mixture was then dissolved in CH_2Cl_2 and washed with H_2O (3×). The combined aqueous layers were extracted with CH_2Cl_2 (1×). The combined organic layers were dried over $MgSO_4$ and filtered through Celite, and the solvent was removed via a rotary evaporator. The crude material was then redissolved in a minimum of CH_2Cl_2 and then precipitated into hexane

to give a fluffy white solid which was washed with hexane (3×) to give 10.16 g (72%) of a white solid.

FTIR (KBr): 3446.2, 3138.5, 2174.4, 2102.6, 1487.2, 1441.0, 1384.6, 1235.9, 1210.3, 1174.4, 1066.7, 1020.5, 923.1, 861.5, 759.0, 687.2, 666.7 cm^{-1}. ^{1}H-NMR (300 MHz, CDCl$_3$): δ 7.63 (d, J = 7 Hz, 6 H), 7.46 (t, J = 14.8, 7.5 Hz, 3 H), 7.38 (t, J = 7.6, 6.1 Hz, 6 H). ^{13}C-NMR (100 MHz, CDCl$_3$): δ 132.7 (d, J_{C-P} = 1.5 Hz), 130.9, 128.5, 119.4 (d, J_{C-P} = 5.3 Hz), 102.3 (d, J_{C-P} = 46.3 Hz), 83.0 (d, J_{C-P} = 238.5 Hz). ^{31}P-NMR (162 MHz, CDCl$_3$): δ −51.5. HRMS: Calcd for C$_{24}$H$_{15}$OP: 350.0855. Found: 350.0861.

General Procedure for the Synthesis of Trisubstituted Aryl Phosphates[11]

To a round-bottom flask equipped with a water-cooled West condenser and a magnetic stirbar was added the phenol (3.0 equivalents per phosphorus oxychloride). The vessel was then sealed with a rubber septum under a N$_2$ atmosphere. Benzene and triethylamine (1.1 equivalents per phenol) were added and the reaction was allowed to stir for 5 min under a N$_2$ atmosphere. Phosphorus oxychloride was then added. Varying amounts of a white gas, presumably NEt$_3$ · HCl, were released and the reaction was usually cloudy due to the precipitation of insoluble NEt$_3$ · HCl salts. The reaction was then heated to reflux. Heating times are listed for each of the phosphates synthesized. Upon completion of the reaction, the NEt$_3$ · HCl salts were removed by filtration and washed with toluene (3×). The solvent was removed via a rotary evaporator, and the resulting crude product was purified by either recrystallization or fractional precipitation. Modifications to this procedure are described below for each compound.

Tri(4-bromophenyl)phosphate (2)[12]

4-Bromophenol (1.56 g, 9.0 mmol) was treated with phosphorus oxychloride (0.28 mL, 3.0 mmol) as described above using benzene (50 mL) and triethylamine (1.38 mL, 9.9 mmol). Upon addition of the phosphorus oxychloride, the reaction became a cloudy yellow–green color. The reaction was allowed to stir at room temperature for 30 min and then was heated to reflux for 6 h. After workup, the crude material was purified by recrystallization from MeOH to give 1.46 g (86%) of pearl white flake crystals.

Mp: 104–106°C. FTIR (KBr): 3058.5, 3053.8, 1892.3, 1771.2, 1638.5, 1580.8, 1476.9, 1390.4, 1298.1, 1228.9,

1188.5, 1165.4, 1061.5, 1009.6, 975.0, 830.8, 733.1, 692.3, 628.6, 611.5, 582.7, 5356.5, 496.2, 450.0, 392.3, 363.5, 340.4 cm^{-1}. ^{1}H-NMR (300 MHz, CDCl$_3$): δ 7.46 (dd, J = 9.0, 0.7 Hz, 6 H), 7.08 (dd, J = 9.0, 1.2 Hz, 6 H). ^{13}C-NMR (100 MHz, CDCl$_3$): δ 149.2 (d, J_{C-P} = 7 Hz), 133.0, 121.8 (d, J_{C-P} = 4.6 Hz), 119.0. ^{31}P-NMR (162 MHz, CDCl$_3$): δ 18.2. HRMS: Calcd for C$_{18}$H$_{12}$Br$_3$O$_4$P: 559.8013. Found: 559.8023.

Tris(2,4,6-tribromophenyl)phosphate (3)[13]

2,4,6-Tribromophenol (2.98 g, 9.0 mmol) was treated with phosphorus oxychloride (0.28 mL, 3.0 mmol) as described above using benzene (50 mL) and triethylamine (1.38 mL, 9.9 mmol). Upon addition of the phosphorus oxychloride, the reaction became a cloudy yellow–white color. The reaction was allowed to stir at room temperature for 30 min and then was heated to reflux for 1 day. After workup, the light orange oil solidified upon standing. The phosphate was redissolved in approximately 50 mL of hot CH$_2$Cl$_2$. Reagent-grade acetone was added, and upon cooling, the phosphate precipitated. The first crop was collected, and the acetone solution was evaporated to approximately 50 mL and more white solid precipitated and the solid was collected by filtration. It was then dried in a vacuum oven (75°C, 0.1 in.Hg) to give 2.22 g (73%) of a light orange solid.

FTIR (KBr): 3111.5, 3053.8, 1719.2, 1551.9, 1430.8, 1373.1, 1309.6, 1257.7, 1223.1, 1113.5, 1055.8, 992.3, 946.2, 911.5, 853.8, 790.4, 738.5, 709.6, 646.2, 617.3, 553.8, 473.1, 455.8, 415.4, 365.5 cm^{-1}. ^{1}H-NMR (300 MHz, CDCl$_3$): δ 7.69 (d, J = 0.84 Hz, 6 H). ^{13}C-NMR (100 MHz, CDCl$_3$): δ 145.4 (d, J_{C-P} = 8.5 Hz), 135.4, 119.7, 117.7 (d, J_{C-P} = 4.3 Hz). ^{31}P-NMR (162 MHz, CDCl$_3$): δ −24.0. HRMS: Calcd for C$_{18}$H$_6$^{79}Br$_4$^{81}Br$_5$O$_4$P: 1037.2552. Found: 1037.2533.

Tri[4-(phenylethynyl)phenyl]phosphate (4)

Phenol **5** (9.32 g, 48.0 mmol) was treated with phosphorus oxychloride (1.49 mL, 16.0 mmol) as described above using benzene (150 mL) and triethylamine (6.8 mL, 48.5 mmol). Upon addition of the phosphorus oxychloride, the reaction became a cloudy light yellow color. The reaction was allowed to stir at room temperature for 30 min and then was heated to reflux for 1 day. After workup, the crude material was purified by recrystallization from hexane to give 8.18 g (82%) of small white needlelike crystals.

FTIR (KBr): 3056.4, 2215.4, 1892.3, 1589.7, 1502.6, 1441.0, 1384.6, 1307.7, 1230.8, 1189.7, 1159.0, 1097.4,

1066.7, 1015.4, 964.1, 835.9, 748.7, 687.2, 661.5, 635.9 cm^{-1}. ^{1}H-NMR (300 MHz, CDCl$_3$): δ 7.51 (m, 12 H), 7.33 (m, 9 H), 7.21 (d, J = 11.7 Hz, 6 H). ^{13}C-NMR (100 MHz, CDCl$_3$): δ 149.9 (d, J_{C-P} = 8.3 Hz), 133.28, 131.60, 128.45, 128.37, 122.91, 121.12, 120.2 (d, J_{C-P} = 5.5 Hz), 89.91, 88.10. ^{31}P-NMR (162 MHz, CDCl$_3$): δ −18.24. HRMS: Calcd for C$_{42}$H$_{27}$O$_4$P: 626.1647. Found: 626.1633.

4-Iodophenyl Acetate

To a 500-mL round-bottom flask equipped with a magnetic stirbar was added 4-iodophenol (77.0 g, 350.0 mmol). The vessel was then sealed with a rubber septum under a N$_2$ atmosphere. THF (150 mL) followed by triethylamine (73.0 mL, 525.0 mmol) was then added, and the reaction was allowed to stir for 5 min under a N$_2$ atmosphere, giving a dark orange solution. Acetic anhydride (33.5 mL, 357 mmol) was then added and the reaction became a light orange color. The reaction was then heated to 50°C for 2 h. After cooling to room temperature, the THF was removed via rotary evaporation to give an orange oil. The oil was dissolved and diluted with Et$_2$O and washed with water (2×). The combined aqueous layers were extracted with Et$_2$O (2×). The combined organic layers were dried over MgSO$_4$ and the solvent removed via rotary evaporation to afford the crude product which was an orange oil. The oil was then redissolved in Et$_2$O, transferred to a 500-mL Erlenmeyer flask equipped with a magnetic stirbar, and decolorized with Norit A while stirring for 20 min. The Norit A was removed by filtration and then washed with Et$_2$O (2×) to give a colorless Et$_2$O solution. The Et$_2$O was removed via rotary evaporation to give a light yellow oil, which, upon standing in a freezer, crystallized to give 88.0 g (96%) of a white solid.

Mp: 31–33°C. FTIR (KBr): 3076.9, 2841.0, 2759.0, 1887.2, 1769.2, 1651.3, 1600.0, 1579.5, 1476.9, 1430.8, 1389.7, 1374.4, 1287.2, 1271.8, 1194.9, 1164.1, 1097.4, 1051.3, 1010.3, 938.5, 907.7, 835.9, 794.9, 702.6, 666.7 cm^{-1}. ^{1}H-NMR (300 MHz, CDCl$_3$): δ 7.66 (dd, J = 6.7, 2.1 Hz, 2 H), 6.84 (dd, J = 6.7, 2.1 Hz, 2 H), 2.26 (s, 3H). ^{13}C-NMR (100 MHz, CDCl$_3$): δ 168.98, 150.46, 138.45, 123.81, 89.96, 21.30. HRMS: Calcd for C$_8$H$_7$IO: 261.9491. Found: 261.9489.

General Procedure for the Coupling of a Terminal Alkyne with an Aryl Halide Utilizing a Palladium—Copper Cross-coupling (Castro–Stephans/Sonogoshira Protocol)[14]

To a round-bottom flask equipped with a water-cooled West condenser and a magnetic stirbar were added the aryl halide, bis(triphenylphosphine)palladium(II) dichloride, and copper(I) iodide. The vessel was then sealed with a rubber septum under a N$_2$ atmosphere. A cosolvent of toluene or THF was sometimes added at this point depending on the solubility of the aryl halide. Triethylamine was added and the reaction allowed to stir for 5 min under a N$_2$ atmosphere. The terminal alkyne was then added and reaction heated until complete.* Upon completion of the reaction, the reaction mixture was filtered through Celite to remove palladium and triethylammonium salts. The salts were washed once with THF, toluene, or Et$_2$O. The reaction mixture was then quenched with either water, a saturated solution of NH$_4$Cl, or brine. The organic layer was diluted with toluene or Et$_2$O and washed with either a saturated solution of NH$_4$Cl, or brine (3×). The combined aqueous layers were extracted with toluene or Et$_2$O (2×). The combined organic layers were dried over MgSO$_4$ and the solvent removed *in vacuo* to afford the crude product that was purified by column chromatography (silica gel) or by recrystallization. Elutants for chromatography, purification procedures, and other slight modifications to reactions are described below for each material.

4-(Phenylethynyl)phenol (5)[15]

4-Iodophenyl acetate (26.2 g, 100.0 mmol) was coupled to phenylacetylene (12.1 mL, 110.1 mmol) as described above using copper(I) iodide (0.38 g, 2.0 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.71 g, 1.0 mmol), triphenylphosphine (0.52 g, 2.0 mmol), THF (150 mL), and triethylamine (70.0 mL, 500.0 mmol). The reaction was heated for 20 h at reflux. After workup, the crude product was dissolved in CH$_2$Cl$_2$ and passed through a plug of silica gel. The solvent was removed and the crude yellow–orange solid was dissolved 100 mL of THF and 400 mL of MeOH and then transferred to a 1000-mL Erlenmeyer flask equipped with a magnetic stirbar. Two hundred fifty milliliters of a 3*M* KOH aqueous solution was added and the organic layer became black. The reaction mixture was allowed to stir for 4 h at room temperature. The THF and MeOH were then removed, leaving behind the dark brown–green aqueous layer. The aqueous layer was extracted with Et$_2$O (1×). The aqueous layer

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* Triethylamine was used for all reactions. Diisspropylamine and *N,N*-diisopropyl ethylamine (Hünig's base) has been used previously and can also be used for these reactions.

was then acidified with 130 mL of 6M HCl, which resulted in the precipitation of a dark brown solid. The reaction mixture was then allowed to cool to room temperature. The aqueous layer was extracted with Et$_2$O (3×) and the combined organic layers were dried over MgSO$_4$. The Et$_2$O solution was decolorized thoroughly with Norit A while stirring for 1 h in a 500-mL magnetic stirbar Erlenmeyer flask. The Norit A was removed by filtration and the filter cake washed with Et$_2$O. The Et$_2$O solution was passed through a plug of silica gel. The Et$_2$O was removed and the yellow solid was redissolved in a minimum of CH$_2$Cl$_2$. The yellow solution was poured into an excess of hexane and the product was then recrystallized from hexane to give 15.7 g (81%) of white plate and needle crystals. If the product was still colored after the initial recrystallization, the product was decolorized again with Norit A in Et$_2$O and recrystallized again following the above procedure.

Mp: 121–122°C. FTIR (KBr): 3415.4, 3179.5, 2215.4, 1605.1, 1584.6, 1507.7, 1435.9, 1379.5, 1292.3, 1246.2, 1169.2, 1133.3, 1097.4, 1066.7, 1020.5, 938.5, 907.7, 830.8, 800.0, 748.7, 687.2 cm^{-1}. ^{1}H-NMR (300 MHz, CDCl$_3$): δ 7.51–7.48 (m, 2 H), 7.42 (dd, J = 6.6, 2.1 Hz, 2 H), 7.35–7.29 (m, 3 H), 6.79 (dd, J = 6.7, 2.1 Hz, 2 H), 4.87 (s, 1 H). ^{13}C-NMR (100 MHz, CDCl$_3$): δ 155.62, 133.26, 131.44, 128.30, 127.97, 123.50, 115.65, 115.48, 89.17, 88.04. HRMS: Calcd for C$_{14}$H$_{10}$O: 194.0731. Found: 194.0726.

Oligo[(4,4′-isopropylidenediphenyl-4-(phenylethynyl)phenyl phosphate)-*co*-(4,4′-isopropylidenediphenyl-4-bromophenylphosphate)] (12)

9 (1.00 g, 2.23 mmol Br) was coupled to phenylacetylene (0.49 mL, 4.46 mmol) as described above using copper(I) iodide (0.03 g, 0.134 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.05 g, 0.067 mmol), toluene (50 mL), and triethylamine (3.11 mL, 22.3 mmol). Upon addition of the triethylamine, the reaction became black. The reaction was then heated for 2 days at reflux. Workup gave a dark brown viscous oil that was redissolved in a minimum amount of CH$_2$Cl$_2$ and precipitated into hexane. The hexane-insoluble solid was washed with hexane (3×), giving 0.70 g (66%) of a light brown solid.

FTIR (KBr): 3065.4, 2961.5, 2692.2, 2211.5, 1892.3, 1598.1, 1500.0, 1482.7, 1401.9, 1378.8, 1381.5, 1303.8, 1234.6, 1194.2, 1165.4, 1101.9, 1067.3, 1015.4, 963.5, 836.5, 755.8, 692.3, 634.6, 571.2, 525.0, 363.5 cm^{-1}.

^{1}H-NMR (300 MHz, CDCl$_3$: δ 7.6–7.2 (m, 14 H), 7.2–7.0 (m, 20 H), 6.9 (m, 4 H), 1.7–1.5 (m, 18 H).

ANAL. Calcd for (C$_{29}$H$_{23}$O$_4$P)$_n$: C, 74.6%; H, 5.0%. Found: C, 63.38%; H, 4.65%; Br, 11.75%. M_w = 4000, M_n = 1900, M_w/M_n = 2.1

General Procedure for the Synthesis of Alkyne-containing Diphosphates

To a 250-mL round-bottom flask equipped with a magnetic stirbar and a West water-cooled condenser sealed with a rubber septum under a N$_2$ atmosphere was added phosphorus oxychloride and THF. This is referred to as flask A. To a 100-mL round-bottom flask equipped with a magnetic stirbar was added the aromatic diol (0.5 equivalents per phosphorus oxychloride) and the flask was sealed with a rubber septum under a N$_2$ atmosphere. THF and triethylamine (1.1 equivalents per OH) were then added and the reaction was allowed to stir for 10 min at room temperature. This is referred to as flask B. To a second 100-mL round-bottom flask equipped with a magnetic stirbar was added phenol **6** (2.0 equivalents per phosphorus oxychloride) and the flask was sealed with a rubber septum under a N$_2$ atmosphere. THF and triethylamine (1.1 equivalents per OH) were then added and the reaction was allowed to stir for 10 min at room temperature. This is referred to as flask C. The solution in flask B was then transferred via a cannula to flask A (while the contents of flask A were stirring) and a white gas was released upon contact along with the eventual precipitation of a white solid, presumably triethylammonium salts, in flask A. Flask B was rinsed with THF (10 mL) and the contents were added to flask B via a cannula to flask A. The reaction mixture in flask A was allowed to stir at room temperature for 30 min. The contents of flask C were then transferred to flask A via a cannula. Flask C was rinsed with THF (10 mL) and the contents were added via a cannula to flask A. The resulting reaction mixture in flask A was allowed to stir at room temperature for an additional 30 min and then was heated to reflux for 1 day. Upon completion of the reaction, the amine salts were removed by filtration and washed with toluene or THF (3×). Solvent was removed via rotary evaporator, and the resulting crude product was purified by column chromatography (silica gel) or by recrystallization. Elutants for chromatography, recrystallization solvents, and other slight modifications to reactions are described below for each material.

Tetrakis[4-(phenylethynyl)phenyl]-1, 3-benzenediphosphate (6)

The following compounds were treated using the procedure for synthesis of alkyne-containing diphosphates listed above: Phosphorus oxychloride (0.37 mL, 4.0 mmol) and THF (10 mL)—flask A. Resorcinol (0.22 g, 2.0 mmol), THF (30 mL), and triethylamine (0.62 mL, 4.4 mmol)—flask B. Phenol **5** (1.55 g, 8.0 mmol), THF (30 mL), and triethylamine (0.91 mL, 8.9 mmol)—flask C. After workup, complete removal of the solvent under a vacuum gave the crude product which was purified by flash chromatography (silica gel/CH_2Cl_2/ hexane: 2/1) to give a light yellow oil. The oil was then dissolved in a minimum of CH_2Cl_2 and added to an excess of MeOH. The product was then recrystallized from MeOH, filtered, and washed with MeOH ($1\times$) to give 0.88 g (45%) of small white needlelike crystals.

Mp: 133–135°C. FTIR (KBr): 3138.5, 2219.2, 1594.9, 1502.6, 1441.0, 1384.6, 1307.7, 1261.5, 1189.7, 1159.0, 1133.3, 1097.4, 1066.7, 969.2, 835.9, 810.3, 779.5, 748.7, 692.3, 635.9 cm^{-1}. ^{1}H-NMR (400 MHz, CDCl$_3$): δ 7.51 (d, J = 8.4 Hz, 16 H), 7.38 (m, 1 H), 7.33 (m, 12 H), 7.22 (d, J = 9.2 Hz, 8 H), 7.17 (d, J = 8 Hz, 3 H). ^{13}C-NMR (100 MHz, CDCl$_3$): δ 150.5 (d, J_{C-P} = 7.5 Hz), 149.5 (d, J_{C-P} = 7.5 Hz), 133.1, 131.4, 130.7, 128.2, 128.1, 122.7, 121.0, 119.9 (d, J_{C-P} = 5.2 Hz), 117.4 (d, J_{C-P} = 5.2 Hz), 112.5 (t, J_{C-P} = 11.2, 5.9 Hz). ^{31}P-NMR (162 MHz, CDCl$_3$): δ −18.39. HRMS: Calcd for C$_{62}$H$_{40}$O$_8$P$_2$: 974.2198. Found: 974.2207.

Tetrakis[4-(phenylethynyl)phenyl]−1, 4-benzenediphosphate (7)

The following compounds were treated using the procedure for the synthesis of alkyne-containing diphosphates listed above. Phosphorus oxychloride (0.37 mL, 4.0 mmol) and THF (10 mL)—flask A. Hydroquinone (0.22 g, 2.0 mmol), THF (30 mL), and triethylamine (0.62 mL, 4.4 mmol)— flask B. Phenol **5** (1.55 g, 8.0 mmol), THF (30 mL), and triethylamine (0.91 mL, 8.9 mmol)—flask C. After workup, complete removal of the solvent under a vacuum gave the crude product which was purified by flash chromatography (silica gel/ CH_2Cl_2/ hexane: 2/1) to give a light yellow oil. The oil was then dissolved in a minimum of CH_2Cl_2 and added to an excess of MeOH. The product was then recrystallized in MeOH, filtered, and washed with MeOH ($1\times$) to give 0.95 g (48%) of small white needlelike crystals.

Mp: 160–162°C. FTIR (KBr): 3046.2, 2215.4, 1589.7, 1502.6, 1441.0, 1384.6, 1287.2, 1189.7, 1159.0, 1097.4,

1071.8, 964.1, 928.2, 851.3, 830.8, 753.8, 692.3, 666.7, 635.9 cm^{-1}. ^{1}H-NMR (400 MHz, CDCl$_3$): (7.52 (m, 20 H), 7.32 (m, 8 H), 7.25 (s, 4 H), 7.22 (d, J = 8.4 Hz, 8 H). ^{13}C-NMR (100 MHz, CDCl$_3$): (149.6 (d, J_{C-P} = 7.5 Hz), 147.4 (d, J_{C-P} = 6.7 Hz), 133.1, 131.4, 128.2, 128.1, 122.7, 121.3 (d, J_{C-P} = 4.5 Hz), 121.0, 119.9 (d, J_{C-P} = 5.3 Hz), 89.8, 87.9. ^{31}P-NMR (162 MHz, CDCl$_3$): δ −18.05. HRMS: Calcd for C$_{62}$H$_{40}$O$_8$P$_2$: 974.2198. Found: 974.2244.

Tetrakis[4-(phenylethynyl)phenyl]-1, 1′-(4,4′-isopropylidene diphenyl)diphosphate (8)

The following compounds were treated using the procedure for the synthesis of alkyne-containing diphosphates listed above. Phosphorus oxychloride (0.37 mL, 4.0 mmol) and THF (10 mL)—flask A. Bisphenol A (0.46 g, 2.0 mmol), THF (30 mL), and triethylamine (0.62 mL, 4.4 mmol)—flask B. Phenol **5** (1.55 g, 8.0 mmol), THF (30 mL), and triethylamine (0.91 mL, 8.9 mmol)—flask C. After workup, complete removal of the solvent under a vacuum gave the crude product which was prepurified by flash chromatography (silica gel/CH_2Cl_2/ hexane: 2/1) to give a light yellow oil. Complete removal of the solvent under a vacuum gave 1.30 g (60%) of a fluffy white solid.

Mp: 52–62°C. FTIR (KBr): 3138.5, 2964.1, 2215.4, 1594.9, 1502.6, 1441.0, 1384.6, 1307.7, 1194.9, 1164.1, 1102.6, 1015.4, 964.1, 835.9, 748.7, 687.2, 635.9 cm^{-1}. ^{1}H-NMR (400 MHz, CDCl$_3$): (7.50 (m, 16 H), 7.32 (m, 12 H), 7.21 (d, J = 8.8 Hz, 8 H), 7.17 (d, J = 9.2 Hz, 4 H), 7.11 (d, J = 8.8 Hz, 4 H), 1.63 (s, 6 H). ^{13}C-NMR (100 MHz, CDCl$_3$): δ 149.9 (d, J_{C-P} = 7.5 Hz), 148.1 (d, J_{C-P} = 7.5 Hz), 147.75, 133.18, 131.54, 128.38. 128.32, 128.25, 122.89, 120.94, 120.1 (d, J_{C-P} = 4.4 Hz), 119.5 (d, J_{C-P} = 5.2 Hz), 89.85, 88.16, 42.53, 30.98. ^{31}P-NMR (162 MHz, CDCl$_3$): δ −17.86. HRMS: Calcd for C$_{71}$H$_{50}$O$_8$P$_2$: 1092.2981. Found: 1092.3033.

General Procedure for the Synthesis of Oligophosphates

To a 250-mL round-bottom flask equipped with a magnetic stirbar and a West water-cooled condenser sealed with a rubber septum under a N$_2$ atmosphere was added phosphorus oxychloride and benzene or toluene. This is referred to as flask A. To a 100-mL round-bottom flask equipped with a magnetic stirbar was added the phenol (1.0 equivalents per phosphorus oxychloride) and the flask was sealed with a rubber septum under a N$_2$ atmosphere. Benzene or toluene (30 mL) and triethylamine (1.1 equivalents per phenol) were then added and the reaction was allowed to stir

for 10 min at room temperature. This is referred to as flask B. To a second 100-mL round-bottom flask equipped with a magnetic stirbar was added the aromatic diol and the flask was sealed with a rubber septum under a N_2 atmosphere. Benzene or toluene (30 mL) and triethylamine (1.1 equivalents per OH) were then added and the reaction was allowed to stir for 10 min at room temperature. This is referred to as flask C. The solution in flask B was then transferred via a cannula to flask A (while the contents of flask A was stirring) and a white gas was released upon contact along with the eventual precipitation of a white solid, presumably triethylammonium salts, in flask A. Flask B was rinsed with benzene (10 mL) and the contents were added via a cannula to flask A. The reaction mixture in flask A was allowed to stir at room temperature for 10 min. The contents of flask C were then transferred to flask A via a cannula. Flask C was rinsed with benzene or toluene (10 mL) and the contents were added via a cannula to flask A. The resulting reaction mixture in flask A was allowed to stir at room temperature for 30 min and then was heated to reflux for 1 day. Upon completion of the reaction, the triethylammonium salts were removed by filtration and washed with toluene or THF ($3\times$). The solvent was removed via a rotary evaporator and the product was collected. Modifications to this general procedure are included with each of the compounds below.

Oligo(4,4′-isopropylidenediphenyl-4-bromophenylphosphate) (9)

The following compounds were treated using the procedure for synthesis of polyphosphates listed above. Phosphorus oxychloride (0.93 mL, 10.0 mmol) and benzene (10 mL)—flask A. 4-Bromophenol (1.73 g, 10.0 mmol), benzene (30 mL), and triethylamine (1.53 mL, 11.0 mmol)—flask B. Bisphenol A (2.28 g, 10.0 mmol), benzene (30 mL), and triethylamine (3.1 mL, 22.0 mmol)—flask C. After workup, complete removal of the solvent under a vacuum gave 3.83 g (86%) of a white fluffy solid.

FTIR (KBr): 3100.0, 3065.4, 2857.7, 1598.1, 1588.5, 1505.8, 1482.7, 1384.6, 1367.3, 1309.6, 1194.2, 1165.4, 1101.9, 1067.3, 1015.4, 963.5, 836.5, 773.1, 634.6, 576.9, 553.8, 525.0, 490.4, 392.3 cm^{-1}. ^{1}H-NMR (300 MHz, CDCl$_3$): (7.6–7.4 (m, 4 H), 7.2–7.0 (m, 8 H), 1.7−1.5 (m, 6 H).

ANAL. Calcd for (C$_{21}$H$_{18}$BrO$_4$P)$_n$: C, 56.60%; H, 4.10%; Br, 17.90%. Found: C, 56.75%; H, 4.14%; Br, 17.85%.

$M_w = 5500$, $M_n = 2900$, $M_w/M_n = 1.9$.

Oligo(1,4-dioxophenyl-4-bromophenylphosphate) (10)

The following compounds were treated using the procedure for synthesis of polyphosphates listed above. Phosphorus oxychloride (0.93 mL, 10.0 mmol) and benzene (10 mL)—flask A. 4-Bromophenol (1.73 g, 10.0 mmol), benzene (30 mL), and triethylamine (1.53 mL, 11.0 mmol)—flask B. Hydroquinone (1.10 g, 10.0 mmol), benzene (30 mL), and triethylamine (3.1 mL, 22.0 mmol)—flask C. After workup, complete removal of the solvent under a vacuum gave 3.24 g (98%) of a red–pink translucent solid.

FTIR (KBr): 3100.0, 1580.8, 1494.2, 1482.7, 1378.8, 1309.6, 1171.2, 1096.2, 1067.3, 963.5, 830.8, 761.5, 692.3, 634.6, 605.8, 542.3, 501.9, 403.8 cm^{-1}. ^{1}H-NMR (300 MHz, CDCl$_3$): (7.5–7.4 (m, 2 H), 7.2–7.0 (m, 4 H), 6.9 (m, 2 H).

ANAL. Calcd for (C$_{12}$H$_8$BrO$_4$P)$_n$: C, 44.00%; H, 2.50%; Br, 24.40%. Found: C, 45.30%; H, 2.78%, Br, 22.29%. $M_w = 2100$, $M_n = 1200$, $M_w/M_n = 1.8$.

Oligo(1,3-dioxophenyl-4-bromophenylphosphate) (11)

The following compounds were treated using the procedure for synthesis of polyphosphates listed above. Phosphorus oxychloride (0.93 mL, 10.0 mmol) and benzene (10 mL)—flask A. 4-Bromophenol (1.73 g, 10.0 mmol), benzene (30 mL), and triethylamine (1.53 mL, 11.0 mmol)—flask B. Resorcinol (1.10 g, 10.0 mmol), benzene (30 mL), and triethylamine (3.1 mL, 22.0 mmol)—flask C. After workup, complete removal of the solvent under a vacuum gave 3.23 g (98%) of a viscous yellow translucent oil.

FTIR (Neat): 3088.5, 3030.8, 2973.1, 2926.9, 2857.7, 2626.9, 2488.5, 2096.2, 1967.3, 1944.2, 1880.8, 1598.1, 1482.7, 1448.1, 1396.2, 1303.8, 1125.0, 1067.3, 1009.6, 865.4, 830.8, 788.8, 732.7, 680.8, 634.6, 432.7 cm^{-1}. ^{1}H-NMR (300 MHz, CDCl$_3$): (7.5–7.2 (m, 3 H), 7.2–7.0 (m, 5 H).

ANAL. Calcd for (C$_{12}$H$_8$BrO$_4$P)$_n$: C, 44.00%; H, 2.50%; Br, 24.40%. Found: C, 45.03%; H, 2.93%; Br, 22.60%. $M_w = 3500$, $M_n = 1800$, $M_w/M_n = 2.0$.

Oligo(4,4′-isopropylidenediphenyl-4-(phenylethynyl)phenyl) phosphate) (13)

The following compounds were treated using the procedure for synthesis of polyphosphates listed

above. Phosphorus oxychloride (0.93 mL, 10.0 mmol) and toluene (10 mL)—flask A. Phenol **5** (1.94 g, 10.0 mmol), toluene (30 mL), and triethylamine (1.53 mL, 11.0 mmol)—flask B. Bisphenol A (2.28 g, 10.0 mmol), toluene (30 mL), and triethylamine (3.1 mL, 22.0 mmol)—flask C. After workup, complete removal of the solvent under a vacuum gave 3.94 g (85%) of a fluffy white solid.

FTIR (KBr): 3056.4, 2964.1, 2871.8, 2215.4, 1953.8, 1892.3, 1594.9, 1502.6, 1441.0, 1405.1, 1384.1, 1307.7, 1235.9, 1200.0, 1164.1, 1097.4, 1015.4, 964.1, 835.9, 753.8, 687.2, 635.9 cm^{-1}. ^{1}H-NMR (400 MHz, CDCl$_3$): δ 7.58 (d, J = 7.6 Hz, 2 H), 7.55–7.45 (bs, 4 H), 7.4–7.28 (m, 4 H), 7.25–7.0 (m, 5 H), 6.78 (t, J = 13.2, 6.0 Hz, 2 H), 1.63−1.55 (bs, 6 H).

ANAL. Calcd for (C$_{29}$H$_{23}$O$_4$P)$_n$: C, 74.66%; H, 4.98%. Found: C, 74.49%; H, 5.01%. M_w = 2400, M_n = 1500, M_w/M_n = 1.5.

General Blending and Extruding Procedure for Flame-retardant Additive/Polycarbonate Blends

The additive and polycarbonate (Dow, Calibre 301-15) were weighed out in their respective amounts according to the weight percent of the additive per 3.6 g batch of polymer.† The polycarbonate/additive blend was then placed in the heated blending cup of the CSI blender. Heating temperatures for the blending cup and the extrusion mold varied depending on the material involved. The processing temperatures for polycarbonate blends in the blender included a blending cup temperature of 270°C and mold temperature of 71–93°C. The blend was allowed to equilibrate to 270°C before extrusion. Extrusion into the mold gave one 1/8-in.-thick × 1/2-in.-wide × 3-in.-long plastic bar.
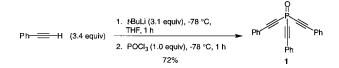
General Procedure for Modified UL-94 Burn Test

Two 1/8-in.-thick × ½-in.-wide × 3-in.-long plastic (polymer + additive) bars were used for this test. All flame tests were done in an UL-94 flame test station. The setting on the methane tank pressure regulator was set to 23 psi. The pressure regulator on the HVUL-94 test station was set to 5 psi. The Bunsen burner flame height was 125 mm, and the height from the top of the Bunsen burner to the bottom of the test bar was 70 mm.

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† Polycarbonate, 3.6 g, was used since this was the minimum amount necessary to fill the test bar mold 1/8 in.-thick × ½ in.-long × 3 in.- long.

All test bars underwent two trials, each trial consisting of ignition for 10 s, followed by flame removal, and the time for self-extinguishing and dripping characteristics were recorded.

RESULTS AND DISCUSSION

All the phosphorus-containing compounds synthesized here utilized 1-metalloalkynes or phenolic groups as nucleophiles toward phosphorus oxychloride to yield a variety of alkyne and/or phosphorus-containing materials. After the materials were synthesized, TGA was used to investigate their thermal stabilities. Initial and major onsets of decomposition were noted as well as their final percent weight losses at 900°C. The final percent weight loss at 900°C was converted into the calculated char yields listed in Table I. Differential scanning calorimetry (DSC) was used to determine the endothermic and exothermic events for each of the synthesized materials. Exothermic events were identified as crosslinking events with the overall range and peak of the event noted. Some materials showed two exothermic events: one for the alkyne-induced crosslinking and a second one for the phosphorus-induced crosslinking. The list of TGA and DSC data for each of the compounds synthesized is shown in Table I. All TGA experiments were conducted under nitrogen at 10°C/min from 30 to 900°C. All DSC analyses were conducted under nitrogen at 10°C/min from 50 to 400°C. The synthesis and thermal properties of each of the compounds are discussed below.

Tri(4-phenylethynyl)phosphine Oxide

Phosphine oxide **1** was synthesized from phosphorus oxychloride and phenylacetylene:

DSC showed two exothermic events; the lower-temperature exothermic event caused the compound to form a network polymer before the phosphine oxide could volatilize, thus giving a high char yield (Table I). The higher-temperature crosslink event was assigned to phosphorus crosslinking, and the lower-temperature event

Table I   Thermal Characteristics of the Synthesized Alkyne-containing Phosphorus Materials

	TGA Data			DSC Data	
Compound	Decomposition Onset (°C)	10 wt % Loss (°C)	Char Yield[a] at 900°C (wt %)	Crosslink Range[b] (°C)	Crosslink Peak[c] (°C)
1	400	450	71	200–280	250, 425
2	200	300	0[d]	None[e]	None[e]
3	200	400	0[f]	None[e]	None[e]
4	300	490	65	300–400	370
6	300	490	59	325–380	370
7	300	490	60	325–380	370
8	300	480	55	300–400	375
9	300	490	23	400–450	425
10	100	300	24	400–450	425
11	100	375	28	400–450	440
12	300	470	34	380–450	400, 425
13	300	450	37	340–450	380, 430

[a] See experimental section for the calculation.
[b] Exothermic event temperature range.
[c] Maximum heat-release temperature of the exothermic event.
[d] 100 wt % lost at 375°C.
[e] No exothermic events were observed for this compound.
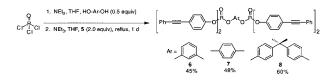[f] 100 wt % lost at 450°C.

corresponded to the alkyne crosslinking event. This analysis is based upon DSC data on phosphorous-free alkynes that we have prepared previously. Interesting liquid crystalline properties were observed for this compound by DSC which showed two melting events: one at 103–107°C (peak 105°C) and a second at 120–123°C (peak 122°C). These two melting points were repeatedly observed by thermal cycling between 50 and 150°C.
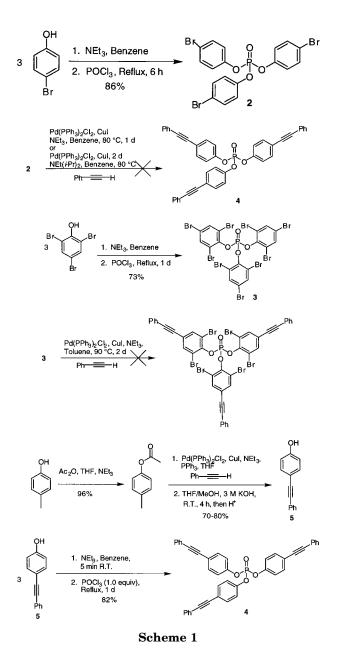
Trisubstituted Aryl Phosphates

Three different trisubstituted aryl phosphates were easily synthesized using three equivalents of substituted phenols which were added to one equivalent of phosphorus oxychloride as shown in Scheme 1. Triethylamine was used to scavenge the HCl that formed during the course of the reaction. Unfortunately, the Pd/Cu-catalyzed methods used to substitute the *para*-bromides on **2** and **3** with alkynes were unsuccessful. Therefore, phosphate **4** was synthesized from 4-(phenylethynyl)phenol (**5**), which required no subsequent alkyne cross-coupling step. **5** was synthesized using a Pd/Cu-mediated cross-coupling reaction between phenylacetylene and 4-iodophenyl acetate.

Interestingly, the nonalkyne bearing compounds **2** and **3** had 0% char yields, a remarkable contrast to the alkyne-containing systems. **4** showed excellent thermal stability (Table I) and some interesting melt properties, similar to **1**. DSC showed two melting points, one at 85–95°C (peak 90°C) and a second at 105–115°C (peak 110°C), although these two phases could not be detected upon a second scan between 50 and 150°C. DSC showed a broad crosslinking event for the alkyne, although no discrete second exothermic event for phosphorus crosslinking was noted.

Aryl Diphosphates

The diphosphates were synthesized in one pot by first adding 0.5 equivalents of an aromatic diol, in the presence of triethylamine, to 1.0 equivalent of phosphorus oxychloride. This generated the aryl-diphosphoro tetrachloride *in situ*. Two equivalents of substituted phenol **5** were then added to give diphosphates **6–8**.
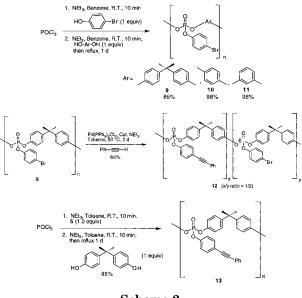
Scheme 1

The lower than expected yields of **6–8** occurred from failing to cleanly generate the aryldiphosphoro tetrachloridate; 1–5% of **4** was found in the crude products. The thermal stabilities and moderately high char yields of these three diphosphates (**6**, **7**, and **8**) were similar to each other (Table I). None of the three compounds showed independent phosphorus-induced crosslinking events. The diphosphates, having an alkyne to phosphorus ratio of 2:1, had lower char yields than that of phosphate **4**, which has an alkyne to phosphorus ratio of 3 : 1.

Oligophosphates

Several oligophosphates were synthesized in a similar manner to the diphosphates. *para*-Substituted phenol derivatives (**5** or 4-bromophenol) were added to phosphorus oxychloride in the presence of triethylamine. Then, the aromatic diol was added, with triethylamine as an acid scavenger, to synthesize the desired oligophosphates shown in Scheme 2.

An attempt to synthesize oligomer **13** from **9** was made using a Pd/Cu-mediated cross-coupling with phenylacetylene as shown in Scheme 2. This failed to give **13** and instead gave oligomer **12**. According to the elemental analysis, the ratio of reacted bromide to unreacted bromide was approximately 1 : 2. Despite the incomplete reaction, TGA of **12** showed an improvement in thermal stability over **9**. Due to the difficulty in exhaustively alkynylating the brominated oligomers, with phenylacetylene, via a Pd/Cu-mediated cross-coupling, these oligomers were of little value. The desired oligomer **13** was synthesized using phenol derivative **5** and bisphenol A. Interestingly, **13** had the lowest char yield of all the alkyne-containing materials prepared. The alkyne-to-phosphorus ratio for **14** was 1 : 1. DSC showed independent exothermic events which were assigned to the alkyne and phosphorus crosslinking events. The large peak at 380°C corresponds to the alkyne, and the smaller peak at 430°C corresponds to the phosphorus moiety decompositions.

Scheme 2

Table II   UL-94 Flame Test Results for Oligomers 4 and 13/Polycarbonate Blends

Additive	First Ignition[a] (s)	Observed Dripping[b]	Second Ignition[a] (s)	Observed Dripping[b]	UL-94 Rating
4 (10 wt %)	7, 2	No, No	6, 5	No, Yes	V-0
4 (5 wt %)	13, 3	No, No	17, 6	Yes, Yes	V-1
13 (10 wt %)	3, 3	No, No	3, 8	Yes, Yes	V-0
13 (5 wt %)	4, 2	No, No	14, 13	No, No	V-1

[a] Time to self-extinguishing after ignition. The two numbers are for two separate tests on two separate blended samples.
[b] Indicates that molten plastic did (Yes) or did not (No) drip onto the cotton patch underneath the bar during the UL-94 test. In the samples that dripped, no ignition of the cotton ensued throughout this test.

Flame-retardant Testing in Polycarbonate

Flame-retardant testing of the materials synthesized was accomplished using the UL-94 flame test wherein the plastic sample is suspended above cotton.[7] The plastic is subjected to two 10-s ignitions with a calibrated methane-fueled flame in a controlled-sized unit which is free of passing air currents. After the first ignition, the flame is removed, and the time for the polymer to self-extinguish is recorded. Cotton ignition is noted if polymer dripping ensues. Then, the second ignition is performed on the same sample and the self-extinguishing time/dripping characteristics are recorded. If the plastic self-extinguishes in less than 10 s with no dripping, it is considered to be a V-0 material, an industry standard for flame retardancy. Dripping is permissible if no cotton ignition results.

TGA and DSC were used to screen compounds which could be blended into polycarbonate. The polycarbonate used had a processing, or melting, temperature of 270°C, so compounds with an exothermic crosslinking event near or below 270°C were eliminated from testing. Brominated phosphates and oligophosphates were eliminated as they were not condensed-phase but vapor-phase-flame retardants.[8] This left phosphate **4**, diphosphates **6–8,** and oligophosphate **13**. Diphosphates **6–8** did show some effectiveness, but due to the difficulty of scaling up these compounds, they were eliminated from further testing. The polycarbonate used for the tests contained an antidrip additive, fibrillar polytetrafluoroethylene (PTFE). The fibrillar PTFE was blended at 0.1 wt % loading in the polycarbonate. Without the antidrip additive, the polycarbonate will drip upon burning, preventing an accurate test of the flame retardant's effectiveness. Compounds **4** and **13** were evenly blended into the PTFE-containing polycarbonate in various weight percents and then ex-

truded into test molds. Burn tests were then performed in an HVUL-94 flame test chamber. The results of the flame-retardant study are shown in Table II.

Compounds **4** and **13** in 10 wt % loadings gave the UL-94 V-0 result. Neither sample passed the test at 5 wt % loadings, giving V-1 results instead. These materials do assist in char formation judging by the large amounts of char observed during the burn experiments. Materials containing both alkynes and phosphorus are superior to alkyne-containing materials which were reported previously.[9] These previously reported alkyne-containing materials gave UL-94 V-1 ratings for polycarbonate at 10 wt % loadings.[9] To obtain a UL-94 V-0 result in polycarbonate with the 10 wt % loading of the alkyne-containing material, an additional amount of aromatic bromide, about 1–0.5 wt %, was needed.[9] The results obtained from this study and the previous study[9] indicate that the two flame-retardant mechanisms of alkynes and phosphorus work together in the condensed phase to provide flame retardancy for polycarbonate without the need for a brominated additive. Further, this combined condensed phase mechanism may provide an additional advantage of lowered smoke production during burning when these materials are used in place of halogenated flame retardants.

CONCLUSIONS

The syntheses of several thermally stable alkyne/phosphorus-containing materials were accomplished. The materials synthesized showed good to fair thermal stabilities. The higher the alkyne-to-phosphorus ratio, the higher the char yields. Comparison of materials containing both alkynes and phosphorus to the materials containing just

phosphorus and halogen showed that the alkynes were more reactive crosslinking agents than was phosphorus. The halogen-free compounds **4** and **13**, with their dual alkyne/phosphorus crosslinking mechanisms, are condensed-phase flame retardants that can be easily blended into polycarbonate at 10 wt % loadings to afford blends that pass the UL-94 flame test.

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