Synthesis and Testing of Nonhalogenated Alkyne-Containing Flame-Retarding Polymer Additives

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ABSTRACT: In this paper, the synthesis and thermal properties of several alkyne-containing materials are discussed. The materials were synthesized using palladium/copper- or palladium/zinc-mediated cross-coupling reactions between multibrominated aromatics and phenylacetylene. Therefore, in one step, commercially available brominated flame retardants can be converted into nonhalogenated high-char materials using transition metal catalysis. The materials synthesized included polymers, oligomers, carbonates, and diphenyl ethers. 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 the synthesized materials were all high-char-yielding materials. Further, DSC data showed that the materials which had *o*-dialkyne substitutions (enediyne systems) generally cross-linked at lower temperatures than materials that had *m*-dialkynes. However, TGA showed that the materials with *ortho* substitutions, especially those with multiple *ortho* substitutions, generally had higher char yields than those with *meta* substitutions. The materials were blended into polycarbonate and tested for ignition resistance using the UL-94 flame test. Alkyne-containing oligomer **9**, used in conjunction with 0.5 wt % of a bromide-containing flame retardant, provided flame retardancy in polycarbonate according to the UL-94 test. This indicates that alkyne-containing materials, acting as condensed phase flame retardants, can substantially lower the amount of halogen content needed for flame retardancy in polycarbonate.

Introduction

A precise mechanism for polymer combustion is difficult to discern, but there is some existing information on fire propagation in polymers.[1] Polymer combustion can be retarded in three ways: (1) Create a nonflammable atmosphere or flame front "poison". This can be done by using a material that forms CO_2, N_2, H_2O, or a similar noncombustible species when the polymer is ignited or thermally decomposed. Halogen-based compounds are the most commonly used flame front poisons.[2] (2) Prevent depolymerization of the plastic, which then retards flammable monomer release. (3) Block the source of fuel by covering the outer layer of the plastic with a nonflammable coating such as carbon from a high-char material. While brominated flame retardant additives are extremely common and highly effective, their attractiveness is declining due to environmental concerns that are dictating the use of nonhalogenated materials. Since there is an abundance of inexpensive brominated flame retardants available, we show here simple, one-pot procedures for the conversion of the brominated compounds into nonhalogenated alkyne-containing materials. Therefore the focus of this paper is on the synthesis of potential alkyne-bearing aromatic flame retardants that may use the latter two methods of retarding flame propagation, namely, depolymerization retardation and char formation. The efficacy of this flame-retardation methodology is demonstrated with commercial-grade polycarbonate.

Alkynes are known to thermally and photolytically initiate cross-linking, which can be used to increase the thermal stability of a polymer.[1] Upon heating, alkynes are known to form cross-linked alkenes and/or cyclotrimerize.[3] Alkyne end groups for polymers and oligomers have also been used to produce high-performance polymers and composite matrixes after thermal curing.[4] This cross-linking creates a network polymer that has higher thermal stability than the starting polymer. Enediynes are a special class of dialkynes and are more reactive than typical alkynes. *cis*-1,2-Enediynes, upon heating, undergo a Bergman cyclization to form a benzene-1,4-diradical compound, which is a very reactive system.[5] Cross-linking via this diradical at elevated temperatures is a possible method of defeating two flame propagation sources at once. While cross-linking prevents radical depolymerization, which slows fuel release and oxidative degradation, it also converts a thermoplastic polymer into a thermoset polymer. Preventing a polymer from melting and flowing, by converting it into a thermoset polymer, impedes the feed of fuel into the flame. Also, highly cross-linked materials can lead to high char, which blocks fuel molecules from reaching the flame. Char is a carbon-based residue that undergoes slow oxidative degradation. Thick char becomes a thermally insulating layer, which prevents heat from reaching the remaining plastic, thus preventing further melt, flow, and thermal decomposition.[6] Therefore, either alkynes or enediynes, by forming a char, could prevent depolymerization of the plastic, thus slowing the rate of fuel release.

Results and Discussion

Due to the wide variety of brominated starting materials commercially available, we used the palladium/copper-mediated cross-coupling reaction[14] between the aromatic bromides and phenylacetylene to afford several different alkynylated materials. Therefore, in one step, commercially available brominated flame retardants can be converted into nonhalogenated high-char materials using transition metal catalysis. Previously in our laboratory, alkynes were used to synthesize glassy carbon thermoset precursors.[7] Also enediynes were synthesized in our group as monomers

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Table 1. Thermal Characteristics of the Synthesized Alkyne-Based Materials

	TGA data			DSC data	
compound	dec onset (°C)	10 wt % loss (°C)	char yield[a] at 900 °C (wt %)	cross-link range[b] (°C)	cross-link peak[c] (°C)
1	200	300	12	270−350	320
2	300	526	74	220−400	275, 325, 375
3	300	530	71	200−400	275, 325, 375
4	300	410	78	200−300	260
5	300	540	78	200−300	230
6	300	395	65	200−350	275
7	400	480	73	>300	350
8	300	390	58	>350	395
9	300	500	70	300−400	375
10	300	470	69	300−400	375

[a] See Experimental Section for calculations. [b] Exothermic event temperature range. [c] Maximum heat release temperature of exothermic event.

for preparing substituted polyphenylenes.[8] The end groups for the alkynes on each of these enediynes affected the Bergman cyclization onset, eventual cross-linking temperature, and the char yield of the final polymers. Due to phenylacetylene's high cross-linking temperature and enhanced char yields in the previous systems mentioned, we chose phenylacetylene as the alkyne of choice for all of our reactions. We synthesized a wide variety of compounds, ranging from small molecules to oligomers and polymers. The materials synthesized fall into two categories: those with *o*-dialkyne (1,2-enediyne) substitutions on the aromatic ring, and those with *m*-dialkyne (1,3-dialkyne) substitutions on the aromatic ring. Thermogravimetric analysis (TGA) was used to investigate the thermal stability of the materials synthesized. Initial and major onsets of decomposition were noted as well as final weight percent loss at 900 °C. Final percent weight loss was converted into char yields, and the data are recorded in Table 1. Differential scanning calorimetry (DSC) was used to determine the cross-linking temperatures for each of the synthesized materials. Exothermic features were identified as cross-linking events, with the overall range and peak of the exothermic event being noted. The list of TGA and DSC data for each of the compounds synthesized is shown in Table 1. 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 with the scanning window set from 50 to 400 °C. The synthesis and thermal properties of each of the synthesized compounds are discussed according to alkyne substitution type.

***Ortho* (1,2-Enediyne) Materials.** We synthesized six *o*-dialkyne-substituted materials. One was a substituted aromatic, two were diphenyl ethers, two were polymers, and one was an anhydride. The synthesis of these compounds is shown in Scheme 1.

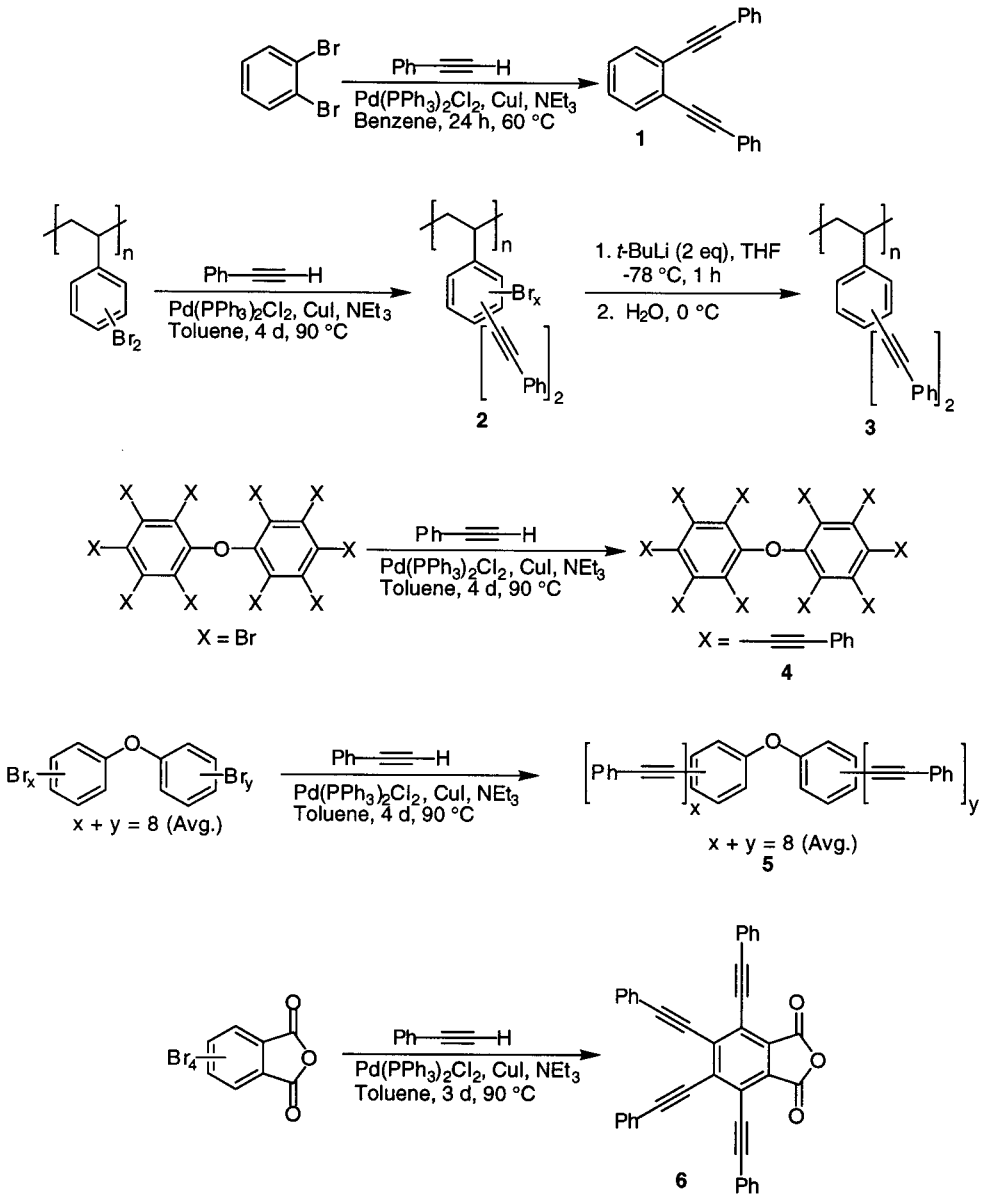
The data from the DSC analysis of **1** showed a high cross-linking event peaking at 320 °C. However, TGA data showed that the compound, while thermally stable according to DSC, was too volatile due to its low molecular weight. Testing was done with a cone calorimeter, which measures the rate of heat release during burning. We found that **1**, blended into a poly(ether imide), gave a higher rate of heat release upon ignition than for the poly(ether imide) without **1**, possibly indicating a flashpoint.[9] Thus we preparedhigher molecular weight enediyne materials. A polymeric enediyne material was synthesized, poly(bis(phenylethynyl)styrene) (**2**). The starting material for **2** was poly(dibromostyrene), which is a mixture of isomers: 43% 3,4-dibromo isomer, 28% 2,4-dibromo isomer, 15% 4-monobromo isomer, 10% 2,5-dibromo isomer, and 5% 2,4,5-tribromo isomer.[10] All of these percents are accurate to ±1%. Thus 48% of the polymer would contain the 1,2-enediyne unit, and the remainder would contain cross-linking phenylethynyl units and some remaining unreacted bromides *ortho* to the polymer chain. Analysis of this compound showed that about 15 wt % bromide remained unreacted, which was more than expected, and this was probably due to the sterically inhibited reactions near the polymer backbone. We then attempted to remove the remaining bromide by the use of a lithium−halogen exchange followed by quenching with water to give debrominated poly(bis(phenylethynyl)styrene) (**3**), which left only 1.2 wt % bromide unreacted. TGA results for both **2** and **3** showed that they were both high-char materials, with very good thermal stability. Close inspection of the DSC data showed three cross-linking events. Since there is a mixture of isomers with this polymer, it is not surprising that there are three cross-linking events, each occurring at a different temperature for each of the three major isomers.

Three nonpolymeric materials that contained enediyne units were also synthesized. They were decakis(phenylethynyl)diphenyl ether (**4**), octakis(phenylethynyl)diphenyl ether (**5**), and tetrakis(phenylethynyl)phthalic anhydride (**6**). All of these materials, after reactions, had a small amount of unreacted bromide (1−3 wt %) that would not react further. These compounds had to be subjected to long reaction times due to the high insolubility of these brominated starting materials in organic solvents as well as the sterically crowded environment for placing the phenylacetylenes. These multialkynylated materials have multiple enediynes in place, which should allow a great amount of cross-linking when used as a flame retardant. Purification of **4** and **5** was difficult. Chromatographic separations, distillations and crystallizations all failed to afford single components; therefore a simple product precipitation from MeOH was often utilized to yield product mixtures. This resulted in ~25% occluded 1,4-diphenyl-1,3-butadiyne (caused by homocoupling of the phenylacetylene), which could not be removed due to solubility properties similar to those of the desired product. This impurity does not seem to hinder the thermal resistance properties of the bulk material.

Compounds **4**−**6** gave good char yields and were very thermally stable, especially **4** and **5**. There is some concern regarding their low cross-linking temperatures, which may limit the plastics with which these high-char compounds can be used. The low cross-linking temperature is most likely responsible for the very high char yields because it causes the materials to form glassy carbon very quickly at a relatively low temperature, preventing much thermal decomposition.

***Meta* (1,3-Dialkyne) Materials.** We also synthesized high molecular weight materials that did not have *o*-dialkyne substitution patterns, but instead had *m*-dialkyne substitutions on the aromatic ring. *Meta*-substituted phenylethynylated materials have been shown to cross-link at higher temperatures than *ortho*-substituted materials.[11] The synthesis of these compounds is shown in Scheme 2.

Scheme 1

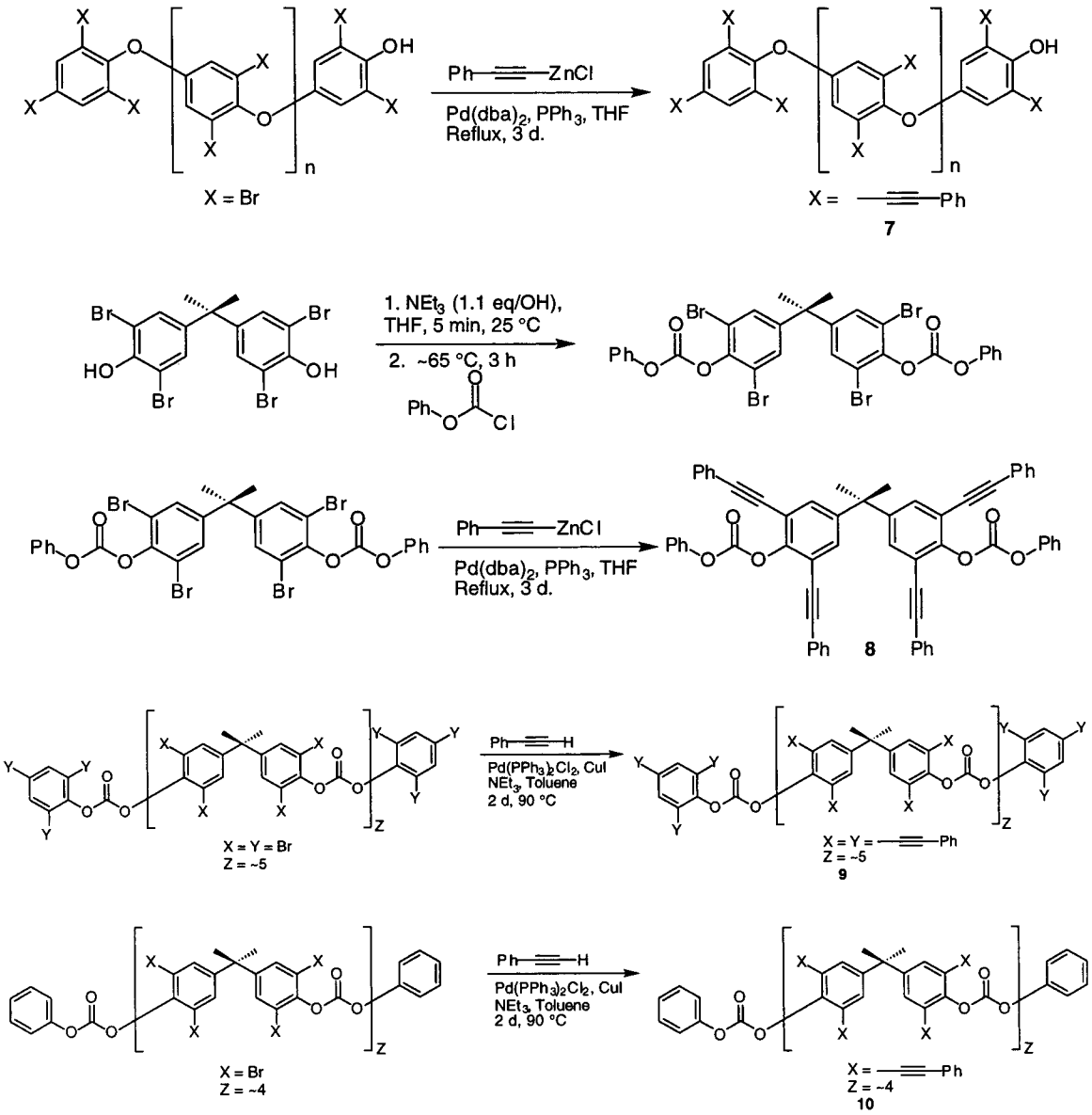


The synthesis of **7** was originally attempted with Pd/Cu cross-coupling conditions, but a large amount of the bromide remained unreacted. Thus a different reaction protocol, the Pd/Zn cross-coupling reaction was used. The Pd/Zn process was a cleaner reaction and resulted in easier purification, but again, not all the Br was reacted. This likely occurs because the phenolic site on each material becomes deprotonated during the reaction, leading to an electron rich ring that inhibits oxidative addition. **7** had about 9 wt % unreacted Br. This polymer has the highest onset of decomposition temperature out of all the materials described in this paper. Poly(phenylene oxide)s are thermally stable engineering plastics; thus it is not surprising that this material has such a high thermal stability. Also, the *m*-dialkyne substitution on the aromatic ring shows a higher cross-linking temperature by DSC than the *ortho*-substituted material, as expected.

Due to the problems seen with the free phenol on the previously mentioned polymer **7** during either Pd/Cu or Pd/Zn coupling conditions, tetrabromobisphenol A was converted into tetrabromobisphenol A phenyl carbonate (Scheme 2). The phenyl carbonate was synthesized using phenyl chloroformate and triethylamine as a base, which gave the easily purified desired product in high yields.[12] With this compound in hand, coupling with phenylacetylene was attempted; however, the product could not be cleanly isolated using the Pd/Cu conditions. Thus, the typically cleaner Pd/Zn reaction conditions were used. This gave the product tetrakis(phenylethynyl)bisphenol A phenyl carbonate (**8**) with an approximate 1−3% of trisubstituted material that cocrystallized, and this impurity could not be separated from the desired material. Larger scale Pd/Zn reactions between phenylacetylene and the starting brominated carbonate resulted in lower yields (40−50%) of **8**. The reasons for this lowering of yield are unclear.

The other materials synthesized were phenylethynylated oligomeric carbonates, synthesized from brominated oligomeric carbonates. Both phenylethynylated carbonate pentamer (**9**) and phenylethynylated carbonate tetramer (**10**) were easily synthesized and purified in high yields. They had little or no bromide remaining after coupling (<0.5 wt % Br). These two oligomers, along with **8**, have one other flame retardant capability. Polycarbonate is known to expel CO_2 upon thermal

Scheme 2



decomposition.[1,12] Therefore these materials, having carbonate groups, could also release CO_2 and work not only as a cross-linking flame retardant but also as nonflammable gas releasing compounds that would poison the flame. Both the oligomers and the phenyl carbonate showed excellent thermal stability. The high cross-linking temperature seen by DSC is noteworthy, indicating that these materials could be used in a wide range of plastics with no decomposition of the flame retardant while being blended into the plastic.

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.[13] The plastic is subjected to two 10 s ignitions with a calibrated methane-fueled flame in a controlled-sized unit that 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 that could be blended into polycarbonate. The polycarbonate used had a processing, or melting, temperature of 270 °C, so the 1,2-enediynes with their exothermic cross-linking event near or below 270 °C were eliminated from testing. The *meta*-substituted phenylethynylated materials **7**−**10** were tested. Compound **7** would not blend evenly into the polycarbonate and gave varied results due to poor blending, and further investigations on this material were discontinued. Compound **8** did show some effectiveness, but due to the difficulty of scaling up compound **8**, it was eliminated from further testing. Compounds **9** and **10** showed the most effectiveness and were evenly blended into polycarbonate. Oligomer **9** was more effective than **10**, leading to further optimization of additive loading of **9**. Oligomer **9** meets the goals of a simple synthesis, good properties, and low cost. The polycarbonate used for the tests contained the common antidrip additive, fibrillar poly(tetrafluoroethylene) (PTFE). The fibrillar PTFE was blended at 0.1 wt %

Table 2. UL-94 Flame Test Results for Oligomer 9/Polycarbonate Blends

additive	1st ignition[a] (s)	obsd dripping[b]	2nd ignition[a] (s)	obsd dripping[b]	pass UL-94 test
9 (10 wt %)	16, 1	no, no	4, 23	no, no	no
9 (10 wt %) + Br (1 wt %)	1,1	no, no	5, 3	no, no	yes
9 (10 wt %) + Br (0.5 wt %)	3, 2	no, no	9, 5	no, no	yes
9 (5 wt %) + Br (1 wt %)	2, 6	no, no	3, 10	no, no	yes
9 (5 wt %) + Br (0.5 wt %)	2, 2	no, no	7, 8	no, no	yes

[a] Time to self-extinguish after ignition. The two numbers are for two separate tests on separately blended samples. [b] Indicates that the plastic did (yes) or did not (no) drip onto the cotton patch below the test sample. The two observations are for tests number one and two, respectively.

loading into the polycarbonate. Without the antidrip additive, the polycarbonate will drip upon burning, preventing an accurate test of the flame retardants effectiveness. Oligomer **9** was blended into the PTFE-containing polycarbonate in various weight percents. Burn tests were then performed in an HVUL-94 flame test station, and the results of the study are shown in Table 2. After this was accomplished, it was seen that **9**, by itself, did not consistently provide a V-0. However, when a brominated oligomeric carbonate flame retardant (the starting material for **9**, 58 wt % Br) and oligomer **9** were combined in the same blend, they worked very well at 0.5 or 1 wt % Br loadings. Thus, simply 5 wt % of **9** plus 0.5 wt % Br afforded V-0 results. Note that 0.5 and 1 wt % bromide loadings, with 0.1 wt % fibrillar PTFE, will not give this polycarbonate a V-0 unless the alkyne is present in the blend. The alkyne cross-linked materials do seem to assist in char formation judging by the large amounts of char observed during burn experiments. Therefore, although a bromide-free system was not developed, the low bromide loadings were effective when working in concert with the high-char-yielding alkynes.

Conclusion

The synthesis of several thermally stable alkyne-containing materials was achieved from commercially available brominated flame retardants. Due to either the high insolubility of the brominated starting material or the steric crowding on the aromatic rings, it was difficult to react all of the bromide on many of the compounds. Despite this problem, all of the materials synthesized showed high char yields by TGA and high thermal stability by DSC. In general, the materials which contained multiple *o*-dialkyne substitutions on the aromatic ring cross-linked at lower temperatures and had higher char yields. The materials that contained multiple *m*-dialkyne substitutions on the aromatic rings cross-linked at higher temperatures but had slightly lower char yields. Oligomer **9** was successfully blended into polycarbonate, and with the use of a small amount of bromide-containing flame retardant (0.5 wt %), it provided flame retardancy according to the UL-94 test. This indicates that alkyne-containing materials, acting as condensed phase flame retardants, can substantially lower the amount of halogen content needed for flame retardancy.

Experimental Section

Theoretical Yield Determination for Phenylethynylated Materials (Polymers and Oligomers) Made from Brominated Aromatics. X = grams of starting material (SM). xx = weight percent Br in starting material. X' = grams of Br lost upon 100% substitution. X^* = moles of Br from X' grams of Br Y^* = moles of C_8H_5 from X^* moles of Br. Y' = grams of C_8H_5 gained upon 100% substitution. Z = theoretical yield.

$$\text{X g of SM} \times 0.xx\ (xx \text{ wt \% Br}) = X' \text{ g of Br}$$

$$\text{X' g of Br} \times 1 \text{ mol of Br}/79.9 \text{ g of Br} = X^* \text{ mol of Br}$$

$$X^* \text{ mol of Br} = Y^* \text{ mol of } C_8H_5(\text{phenylacetylene} - 1 \text{ hydrogen})$$

$$Y^* \text{ mol of } C_8H_5 \times 101 \text{ g of } C_8H_5/1 \text{ mol of } C_8H_5 = Y' \text{ g of } C_8H_5 \text{ gained}$$

$$X \text{ g of SM} - X' \text{ g of Br} + Y' \text{ g of } C_8H_5 = Z \text{ g (theoretical yield)}$$

Char Yield Calculation From TGA Data at 900 °C.

$$100 \text{ wt \%} - \text{wt \% loss at 900 °C} = \text{char yield at 900 °C}$$

General Procedures. ^{1}H NMR spectra were recorded at 300, 400, and 500 MHz on Brüker AM-300, WH-400, and AM-500 spectrometers, respectively. The ^{13}C NMR spectra at 75, 100, and 125 MHz were recorded on a Brüker AM-300, WH-400, and AM-500 spectrometers, respectively. Proton chemical shifts (δ) are reported in ppm downfield from tetramethylsilane (TMS) and ^{13}C resonances (unless otherwise noted) were recorded using the 77.0 ppm $CDCl_3$ resonance as an internal reference and are reported in ppm downfield from TMS. Infrared (IR) spectra were recorded on a Perkin-Elmer 1600 Series FTIR. Thermal gravimetric analysis (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 THF at 60 °C (flow rate 1.0 mL/min, 700 psi). Molecular weight results were based on five polystyrene standards (M_w = 435 500, 96 000, 22 000, 5050, 580, correlation coefficient >0.997) purchased from Polymer Laboratories Ltd. Melting points were obtained on a Melt-Temp apparatus. A Custom Scientific Instruments CSI-183MMX Mini-Max blender/extruder was used for plastic bar fabrication, and an Atlas Electric HVUL-94 flame test station was used for the flame tests. Reagent grade tetrahydrofuran (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. Decabromodiphenyl ether (Saytex 102E), octabromodiphenyl ether (Saytex 111), tetrabromobisphenol A (Saytex RB-100), and tetrabromophthalic anhydride (Saytex RB-49) were provided by Albemarle Corp. Brominated oligomeric carbonates (Great Lakes BC-58 and BC-52), poly(2,6-dibromophenylene oxide) (Great Lakes PO-64P), and poly(dibromostyrene) (Great Lakes PDBS-80) were provided by Great Lakes Chemical Corp. All other reagents were used as received unless otherwise noted. Gravity column chromatography, silica gel plugs, and flash chromatography were carried out on silica gel (230−400 mesh from EM Science). 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 lab. Elemental analysis was performed by Atlantic Microlab (Norcross, GA). All synthetic operations were carried out under a dry, oxygen-free, nitrogen atmosphere unless otherwise noted.

General Procedure for the Coupling of a Terminal Alkyne with an Aryl Bromide Utilizing a Palladium−Copper Cross-Coupling (Castro−Stephans/Sonogashira Protocol).[14] To a round-bottom flask equipped with a water-cooled West condenser and a magnetic stir bar were added the aryl bromide, bis(triphenylphosphine)palladium(II) dichloride (3 mol % per bromide), and copper(I) iodide (6 mol % per bromide). The vessel was then sealed with a rubber septum under a N_2 atmosphere. A cosolvent of benzene or toluene was sometimes added at this point depending on the solubility of the aryl bromide. The terminal alkyne (2 equiv per bromide) was added and the reaction allowed to stir for 5 min under a N_2 atmosphere. Triethylamine (10 equiv per bromide) was then added and reaction heated until complete.[15] Upon completion of the reaction, the black reaction mixture was filtered through Celite to remove palladium and triethylammonium hydrobromide salts. The reaction mixture was then quenched with water, a saturated solution of NH_4Cl, or brine. The organic layer was diluted with toluene or Et_2O and washed with water, a saturated solution of NH_4Cl, or brine (3×). The combined aqueous layers were extracted with toluene or Et_2O (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 fractional precipitation. Elutants and other slight modifications are described below for each material.

General Procedure for the Coupling of a Terminal Alkyne with an Aryl Bromide Utilizing a Palladium−Zinc Cross-Coupling (Negishi Protocol).[16] To a round-bottom flask equipped with a magnetic stir bar under a N_2 atmosphere were added the terminal alkyne (1.5 equiv per bromide) and THF. The solution was cooled to −78 °C, and *n*-butyllithium (1.1 equiv per bromide) was added dropwise. The reaction was allowed to stir at −78 °C for 30 min and then warmed to 0 °C. To a second round-bottom flask equipped with a magnetic stir bar was added zinc(II) chloride (1.5 equiv per alkyne). The zinc(II) chloride was flame dried under vacuum, then cooled to 23 °C, and placed under a N_2 atmosphere. THF was added to the zinc(II) chloride. This solution was cooled to 0 °C, and the solution containing the lithioalkyne was added dropwise via cannula. This mixture was allowed to stir for 30 min at 23 °C. To a third round-bottom flask equipped with a magnetic stir bar and a West water cooled condenser were added bis(dibenzylideneacetone)-palladium(0) (6 mol % per bromide), triphenylphosphine (5 equiv per palladium(0)), the aryl bromide, and THF. The alkynylzinc(II) chloride solution was then added dropwise via cannula at 23 °C. The solution was allowed to stir for 15 min at 23 °C and then heated to reflux (∼65 °C) for 1 day. Upon completion of the reaction, the black reaction mixture was then quenched with a saturated aqueous solution of NH_4Cl. The organic layer was washed with a saturated aqueous solution of NH_4Cl (2×) and with H_2O (2×). The combined aqueous layers were extracted with CH_2Cl_2 (2×). The combined organic layers were dried over $MgSO_4$, and the solvent was removed in vacuo. The resulting crude product was either purified by fractional precipitation or by flash chromatography (silica gel). Elutants and other slight modifications are described below for each material.

1,2-Bis(phenylethynyl)benzene (1).[17] 1,2-Dibromobenzene (1.21 mL, 10 mmol) was coupled to phenylacetylene (3.29 mL, 30 mmol) as described above using copper(I) iodide (0.23 g, 1.2 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.42 g, 0.6 mmol), benzene (5 mL), and triethylamine (8.5 mL, 60 mmol) in a screw cap tube that was then sealed with a Teflon screw cap. The reaction mixture was stirred at 60 °C for 1 day. Phenylacetylene (1.1 mL, 10 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.21 g, 0.3 mmol), and triethylamine (5 mL) were added, and the tube was resealed again with the same Teflon screw cap as before. The black reaction mixture was stirred at 60 °C for 1 day. The resulting black reaction mixture was then subjected to an aqueous workup as described above, giving a black oil. The black oil was redissolved in a small amount of Et_2O, and Celite was added to the concentrated solution. Hexane was then added in excess, precipitating any polymeric materials. This mixture was then filtered through a fritted funnel (medium frit) containing silica gel. This served as a silica gel plug filtration and removed a great amount of the impurities, which yields a red-brown hexane solution. The solvent was removed in vacuo, resulting in a red-brown oil that was purified by flash chromatography (silica gel/hexane) to give 2.03 g of a yellow oil (73%). FTIR (neat): 3055.6, 3022.2, 2211.1, 1950.0, 1888.9, 1811.6, 1750.0, 1600.0, 1572.2, 1494.4, 1444.4, 1383.3, 1311.1, 1277.8, 1177.8, 1155.8, 1088.9, 1066.7, 1027.8, 950.0, 911.1, 867.7, 833.3, 756.6, 688.9 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.55 (m, 6 H), 7.33 (m, 8 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 131.793, 131.673, 128.420, 128.367, 127.998, 125.840, 123.309, 93.592, 88.307.

Poly(bis(phenylethynyl)styrene) (2). Poly(dibromostyrene) (Great Lakes PDBS-80) (4 g, 29.6 mmol of Br) was coupled to phenylacetylene (6.5 mL, 59.2 mmol) as described above using copper(I) iodide (0.34 g, 1.78 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.62 g, 0.89 mmol), toluene (60 mL), and triethylamine (42 mL, 296 mmol) in a round-bottom flask equipped with a West water-cooled condenser and sealed under a N_2 atmosphere with a rubber septum. Upon addition of the triethylamine, the reaction became black. The reaction was then heated for 4 days at reflux (∼89 °C). After heating, the resulting black reaction mixture was quenched with aqueous NH_4Cl and was diluted with CH_2Cl_2. The resulting thick red-orange oil was redissolved in a minimum amount of THF and precipitated into hexane. The hexane insoluble solid was washed with hexane (3×), MeOH (3×), and EtOH (3×) to give 4.13 g (89%) of a orange-brown solid. FTIR (KBr): 3056.4, 2923.1, 2861.5, 2215.4, 1948.7, 1871.8, 1594.9, 1492.3, 1461.5, 1441.0, 1384.6, 1179.5, 1159.0, 1066.7, 1020.5, 907.7, 892.3, 825.6, 753.8, 687.2 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.6−7.2 (m), 7.2−6.8 (m), 1.8−1.0 (m). Anal. Calcd for $(C_{20}H_{13.6}Br_{0.43})_n$:[18] C, 83.3; H, 4.8; Br, 11.9. Found: C, 80.3; H, 4.6; Br, 15.1. M_w = 23 700, M_n = 10 700, M_w/M_n = 2.2.

Poly(bis(phenylethynyl)styrene) (2). The Negishi protocol was used. Poly(dibromostyrene) (Great Lakes PDBS-80) (2.0 g, 14.8 mmol Br) was coupled to phenylacetylene (2.44 mL, 22.2 mmol) as described above using *n*-butyllithium (24.42 mL, 16 mmol, 1.53 M in hexane), zinc(II) chloride (4.54 g, 33.3 mmol), bis(dibenzylideneacetone)palladium(0) (0.51 g, 0.89 mmol), triphenylphosphine (1.17 g, 4.45 mmol), and THF. The reaction was heated to reflux (∼65 °C) for 3 days. Upon completion of the reaction, the brown-yellow reaction mixture was quenched with a saturated aqueous solution of NH_4Cl and diluted with THF. The resulting red-brown oil was redissolved in THF and the solid was precipitated with an excess of hexane. The light tan solid was washed with hexane (3×) and MeOH (3×) to give 2.08 g (90%) of a light tan solid. FTIR (KBr): 3056.4, 2923.1, 2851.3, 2215.4, 1948.7, 1871.3, 1594.9, 1492.3, 1466.7, 1441.0, 1400.0, 1384.6, 1066.7, 1020,5, 912.8, 892.3, 825.6, 753.8, 687.2 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.8−7.6 (m), 7.6−7.3 (m), 7.3−7.0 (m), 2.0−1.0 (m). Anal. Calcd for $(C_{20}H_{13.6}Br_{0.43})_n$:[18] C, 83.3; H, 4.8; Br, 11.9. Found: C, 78.8; H, 4.6; Br, 15.8. M_w = 57 900, M_n = 21 300, M_w/M_n = 2.7.

Debrominated Poly(bis(phenylethynyl)styrene) (3). To a 250 mL round-bottom flask equipped with a magnetic stir bar was added **2** (3.05 g, 19.22 wt % Br) and THF (100 mL). The flask was sealed with a rubber septum under a nitrogen atmosphere. The solution was cooled to −78 °C. *t*-BuLi (9.79 mL, 14.68 mmol, 1.5 M in pentane) was added and the resulting black solution was stirred at −78 °C for 1 h. After 1 h, the reaction was warmed to 0 °C and quenched with H_2O (15 mL). The organic layer was diluted with CH_2Cl_2 and washed with H_2O (3×). The combined aqueous layers were extracted with CH_2Cl_2 (2×). The combined organic layers were dried over $MgSO_4$ and the solvent removed in vacuo. The resulting brown oil was redissolved in THF, and the polymer was precipitated with hexane to give 2.31 g (94%) of a light tan solid. FTIR (KBr): 3056.4, 3025.6, 2923.1, 2861.5, 2215.4, 1948.7, 1871.8, 1594.9, 1492.3, 1441.0, 1384.6, 1179.5, 1159.0, 1097.4, 1066.7, 1025.6, 907.7, 892.9, 830.8, 794.9, 753.8, 692.3

cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.6−7.3 (m), 7.2−6.2 (m), 1.8−1.0 (m). Anal. Calcd for $(C_{20}H_{14}Br_0)_n$: C, 94.4; H, 5.5. Found: C, 90.2; H, 5.8; Br, 1.2. M_w = 58 600, M_n = 22 700, M_w/M_n = 2.6.

Decakis(phenylethynyl)diphenyl Ether (4). Decabromodiphenyl ether (Albemarle Saytex 102E) (4.8 g, 50 mmol Br) was coupled to phenylacetylene (11 mL, 100 mmol) as described above using copper(I) iodide (0.57 g, 3 mmol), bis(triphenylphosphine)palladium(II) dichloride (1.05 g, 1.5 mmol), toluene (100 mL), and triethylamine (70 mL, 500 mmol). Upon addition of the triethylamine, the reaction became black. The reaction was then heated for 4 days at reflux (∼89 °C). After heating, the resulting black reaction mixture was quenched with a saturated aqueous solution of NH_4Cl and was diluted with CH_2Cl_2. The resulting black tarlike solid was redissolved in a minimum amount of CH_2Cl_2 and precipitated into MeOH. The MeOH insoluble solid was washed with MeOH (3×) and then subjected to a Soxhlet extraction with EtOH for 4 days to give 7.36 g of a dark brown solid. The mass balance was high by 26% due to occluded 1,4-diphenyl-2,3-butadiyne. FTIR (KBr) 3056.4, 2923.1, 2851.3, 2215.4, 1948.7, 1871.3, 1594.9, 1492.3, 1466.7, 1441.0, 1400.0, 1384.6, 1066.7, 1020,5, 912.8, 892.3, 825.6, 753.8, 687.2 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.0−6.0 (m). Anal. Calcd for $C_{92}H_{50}O$: C, 94.3; H, 4.3. Found: C, 87.6; H, 4.85, Br, 2.36. LRMS Calcd for $C_{92}H_{50}O$: 1170 (97%), 1171 (100%), 1172 (52%). Found: 1171 (25%), 1172 (38%), 1173 (43%).

Octakis(phenylethynyl)diphenyl Ether (5). Octabromodiphenyl ether (Albemarle Saytex 111) (5 g, 49.4 mmol Br) was coupled to phenylacetylene (10.9 mL, 98.8 mmol) as described above using copper(I) iodide (0.57 g, 2.96 mmol), bis(triphenylphosphine)palladium(II) dichloride (1.04 g, 1.48 mmol), toluene (100 mL), and triethylamine (69 mL, 494 mmol). Upon addition of the triethylamine, the reaction became black. The reaction was then heated for 4 days at reflux (∼89 °C). After heating, the resulting black reaction mixture was quenched with a saturated aqueous solution of NH_4Cl and was diluted with CH_2Cl_2. The resulting black tarlike solid was redissolved in a minimum amount of CH_2Cl_2 and precipitated into MeOH. The MeOH insoluble solid was washed with MeOH (3×) and then subjected to a Soxhlet extraction with EtOH for 4 days to give 4.4 g (73%) of a tan-brown solid. FTIR (KBr): 3056.4, 2923.1, 2851.3, 2215.4, 1948.7, 1871.3, 1594.9, 1492.3, 1466.7, 1441.0, 1400.0, 1384.6, 1066.7, 1020,5, 912.8, 892.3, 825.6, 753.8, 687.2 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.8−6.8 (m). Anal. Calcd for $C_{76}H_{42}O$: C, 94; H, 4.4. Found: C, 90.9; H, 5.0; Br, 0.65. LRMS Calcd for $C_{76}H_{42}O$: 970 (100%), 971 (86%), 972 (37%), 973 (10%), 974 (2%), 975 (0.4%). Found: 971 (68%), 972 (60%), 973 (69%), 974 (47%), 975 (35%).

Tetrakis(phenylethynyl)phthalic Anhydride (6). Tetrabromophthalic anhydride (Albemarle Saytex RB-49) (6.96 g, 60 mmol Br) was coupled to phenylacetylene (13.2 mL, 120 mmol) as described above using copper(I) iodide (0.69 g, 3.6 mmol), bis(triphenylphosphine)palladium(II) dichloride (1.26 g, 1.8 mmol), toluene (150 mL), and triethylamine (67 mL, 480 mmol). Upon addition of the triethylamine, the reaction became black. The reaction was then heated for 3 days at reflux (∼89 °C). After heating, the resulting black reaction mixture was quenched with a saturated solution of NH_4Cl and was diluted with CH_2Cl_2. The resulting dark brown viscous oil was redissolved in a minimum amount of CH_2Cl_2 and precipitated into hexane. The hexane insoluble solid was washed with hexane (3×) and then subjected to a Soxhlet extraction with hexane for 3 days, giving 0.78 g (57%) of a light brown solid. FTIR (KBr) 3433.3, 3055.6, 3022.2, 2200.0, 1944.4, 1772.2, 1633.3, 1594.4, 1561.1, 1544.4, 1488.9, 1438.9, 1383.3, 1350.0, 1266.7, 1216.7, 1177.8, 1155.5, 1105.5, 1066.7, 1027.8, 972.2, 911.1, 838.9, 755.5, 688.9 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 8−6.8 (m). Anal. Calcd for $C_{40}H_{20}O_3$: C, 87.6; H, 3.7. Found: C, 86.7; H, 4.8; Br, <0.5.

Poly(2,6-bis(phenylethynyl)phenylene oxide) (7). Poly(2,6-dibromophenylene oxide) (Great Lakes PO-64P) (6.44 g, 50.0 mmol Br) was coupled to phenylacetylene (8.24 mL, 75 mmol) as described above using *n*-butyllithium (56.9 mL, 82.5 mmol, 1.45 M in hexane), zinc(II) chloride (15.33 g, 112.5 mmol), bis(dibenzylideneacetone)palladium(0) (1.44 g, 2.5 mmol), triphenylphosphine (3.28 g, 12.5 mmol), and THF. The reaction was heated to reflux (∼65 °C) for 3 days. Upon completion of the reaction, the brown-black reaction mixture was quenched with deionized water and the organic layer diluted with CH_2Cl_2. The organic layers were washed with deionized water (3×). The aqueous layer was extracted with CH_2Cl_2 (3×). Organic layers were evaporated to a minimum and the product was precipitated into hexane from CH_2Cl_2. The precipitate was then filtered and washed with hexane (3×) and MeOH (3×) and dried to give 1.03 g (89%) of a brownish-gray solid. FTIR (KBr) 3435.9, 3148.7, 3056.4, 2205.1, 2102.6, 1948.7, 1871.8, 1600.0, 1487.2, 1466.7, 1430.8, 1384.6, 1353.8, 1282.1, 1205.1, 1142.8, 1097.4, 1066.7, 1025.6, 994.9, 912.8, 876.9, 753.8, 687.2 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.75 (m), 7.6−6.8 (m), 6.3 (m). Anal. Calcd for $C_{30}H_{17}O(C_{22}H_{12}O)_n$-$C_{22}H_{13}O$: C, 90.8; H, 4.3. Found: C, 77.9; H, 3.81; Br, 9.93. M_w = 15 420, M_n = 5233, M_w/M_n = 2.9.

Tetrabromobisphenol A Phenyl Carbonate. To a 250 mL round-bottom flask equipped with a water-cooled West condenser and a magnetic stir bar was added the tetrabromobisphenol A (Albemarle Saytex RB-100) (10.88 g, 20 mmol). The vessel was then sealed with a rubber septum under a N_2 atmosphere. THF (100 mL) and triethylamine (6.13 g, 44 mmol) were added, and the reaction was allowed to stir for 5 min under a N_2 atmosphere. Phenylchloroformate (5.52 mL, 44 mmol) was then added and reaction became a cloudy white. The reaction was then heated to reflux (∼65 °C) for 3 h. Upon completion of the reaction, the THF was removed via rotary evaporator, and the clear oil was redissolved with Et_2O and washed with water (3×). The combined aqueous layers were extracted with CH_2Cl_2 (2×). The combined organic layers were dried over $MgSO_4$ and the solvent removed *in vacuo* to afford a white solid. Any remaining phenylchloroformate and phenol was removed by heating the white solid under vacuum (∼75 °C) to give 14.96 g (95%) of a white solid. Mp: 173−175 °C. FTIR (KBr): 3128.2, 3087.2, 2944.1, 2882.1, 1794.9, 1656.4, 1584.6, 1548.7, 1492.3, 1456.4, 1384.6, 1220.5, 1189.7, 1102.6, 1061.5, 994.9, 984.9, 907.7, 871.8, 835.9, 784.6, 733.3, 687.2 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.41 (m, 8 H), 7.27 (m, 6 H), 1.64 (s, 6 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 151.032, 149.979, 149.816, 144.319, 130.950, 129.672, 126.599, 120.806, 117.492, 42.852, 30.555. HRMS Calcd for $C_{29}H_{20}{}^{79}Br_2$-$^{81}Br_2O_6$: 783.7952. Found: 783.7957.

Tetrakis(phenylethynyl)bisphenol A Phenyl Carbonate (8). Tetrabromobisphenol A phenyl carbonate (1 g, 1.275 mmol) was coupled to phenylacetylene (0.84 mL, 7.65 mmol) as described above using *n*-butyllithium (5.43 mL, 8.42 mmol, 1.55 M in hexane), zinc(II) chloride (1.56 g, 11.48 mmol), bis(dibenzylideneacetone)palladium(0) (0.15 g, 0.255 mmol), triphenylphosphine (0.33 g, 1.28 mmol), and THF. The reaction was heated to reflux (∼65 °C) for 2 days. Upon completion of the reaction, the THF was removed via rotary evaporator and the brown-black reaction mixture was quenched with deionized water (3×). The organic oil was redissolved and diluted with Et_2O and washed with a saturated solution of NH_4Cl (1×) and water (3×). The resulting yellow-brown oil was purified by column chromatography (silica gel, 2:1 hexane/CH_2Cl_2) to give 0.83 g (75%) of a light yellow solid. FTIR (KBr): 3056.4, 2964.1, 2215.4, 1779.5, 1594.9, 1579.5, 1492.3, 1446.2, 1405.1, 1384.6, 1293.2, 1220.5, 1184.6, 1143.6, 1066.7, 1025.6, 1005.1, 912.8, 876.9, 784.6, 753.8, 682.1 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 7.55−7.52 (m, 8 H), 7.44 (s, 4 H), 7.32−7.28 (m, 16 H), 7.22−7.17 (m, 6 H), 1.74 (s, 6 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 151.217, 150.738, 150.092, 147.856, 131.839, 131.233, 129.523, 128.887, 128.434, 126.278, 122.545, 120.929, 117.831, 95.388, 83.370, 42.711, 30.656. HRMS Calcd for $C_{61}H_{40}O_6$: 868.2795. Found: 868.2825.

Phenylethynylated Carbonate Pentamer (9). Brominated carbonate pentamer (Great Lakes BC-58) (6.0 g, 44.1 mmol Br) was coupled to phenylacetylene (9.7 mL, 88.2 mmol) as described above using copper(I) iodide (0.51 g, 2.65 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.93 g, 1.32 mmol), toluene (80 mL), and triethylamine (61.5 mL, 441

mmol). Upon addition of the triethylamine, the reaction became black. The reaction was then heated for 2 days at reflux (~89 °C). After heating, the resulting black reaction mixture was quenched with a saturated solution of NH_4Cl and was diluted with CH_2Cl_2. The resulting dark brown viscous oil was redissolved in a minimum amount of CH_2Cl_2 and precipitated into hexane. The hexane insoluble solid was washed with hexane (3×) and MeOH (3×) giving 7.3 g (100%) of a light brown solid. FTIR (KBr): 3145.3, 3059.8, 2963.7, 2931.6, 2867.5, 2215.8, 1958.3, 1872.9, 1792.7, 1728.6, 1600.4, 1579.1, 1488.2, 1445.5, 1368.8, 1263.9, 1221.2, 1183.8, 1141.0, 1071.6, 1023.5, 975.4, 911.3, 879.3, 841.3, 751.1, 687.0, 585.5, 537.4 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.7 (s), 7.6−7.2 (m), 7.2−7.0 (m), 1.8−1.6 (m). Anal. Calcd for $C_{31}H_{17}O_3$-$(C_{48}H_{30}O_3)_5C_{30}H_{17}$: C, 88.4; H, 4.6. Found: C, 87.5; H, 5.1; Br, 0.0. $M_w = 5300$, $M_n = 3200$, $M_w/M_n = 1.7$.

Phenylethynylated Carbonate Tetramer (10). Brominated carbonate tetramer (Great Lakes BC-52) (6.0 g, 38.5 mmol Br) was coupled to phenylacetylene (8.5 mL, 77 mmol) as described above using copper(I) iodide (0.44 g, 2.31 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.81 g, 1.16 mmol), toluene (80 mL), and triethylamine (53.7 mL, 385 mmol). Upon addition of the triethylamine, the reaction became black. The reaction was then heated for 2 days at reflux (~89 °C). After heating, the resulting black reaction mixture was quenched with a saturated solution of NH_4Cl and was diluted with CH_2Cl_2. The resulting dark brown viscous oil was redissolved in a minimum amount of CH_2Cl_2 and precipitated into hexane. The hexane insoluble solid was washed with hexane (3×) and MeOH (3×), giving 6.57 g (96%) of a light brown solid. FTIR (KBr): 3145.3, 3059.8, 2963.7, 2931.6, 2867.5, 2215.8, 1953.0, 1878.2, 1792, 7, 1728.6, 1600.4, 1579.1, 1488.2, 1445.5, 1386.8, 1221.2, 1189.1, 1141.0, 1066.2, 1023.5, 995.8, 975.4, 911.3, 879.3, 841.9, 751.1, 687.0, 537.4 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.6−7.2 (m), 7.2−7.0 (m), 1.8−1.6 (m). Anal. Calcd for $C_7H_5O_3(C_{48}H_{30}O_3)_4C_6H_5$: C, 86.9; H, 4.6. Found: C, 87.2; H, 4.9; Br, 0.0. $M_w = 5100$, $M_n = 2900$, $M_w/M_n = 1.8$.

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 % of additive per 3.6 g batch of polymer.[19] The amount of Br added to the blend was determined from the weight percent Br present in the brominated oligomeric carbonate.[20] 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 × $^1/_2$ 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 bunsun burner to the bottom of the test bar was 70 mm. 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.

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(19) Polycarbonate (3.6 g) was used since this was the minimum amount necessary to fill the test bar mold ($^1/_8$ in. thick × $^1/_2$ in. long × 3 in. long).

(20) The brominated oligomeric carbonate used was 58 wt % bromide in content. The calculated weight of bromide was multiplied by 58% to give the amount of brominated oligomeric carbonate that was to be added to the blend.

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