Flame Retardant Polycyanurate Thermosets from the Cyanate Esters of Triphenylphosphine Oxide

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ABSTRACT: Three cyanate esters containing phosphorus are synthesized in good overall yields starting from bromoanisoles. Di- and tricyanates with *meta* configuration are most stable while *para* is less so. The *para* dicyanate ester isomer is particularly affected by water from the atmosphere. The *meta* dicyanate ester 2 has good thermal properties with glass transition at 268 °C and char yield of 65% in air at 600 °C. All three phosphorus-containing cyanate esters are low flammability in an open flame. They make highly combustible cyanate esters resins less flammable simply by blending. Mixing 10 wt% dicyanate ester 2 into bisphenol A or E dicyanate esters makes them rate V-0. Published 2018. This article is a U.S. Government work and is in the public domain in the USA. J. Polym. Sci., Part A: Polym. Chem. **2018**, *00*, 000–000

KEYWORDS: composites; cyanate ester; flame resistant; high performance; phosphorus; thermosets

INTRODUCTION Polymer matrix composites (PMCs) are increasing in usage for aerospace structures due to their excellent strength to weight ratio, resulting in better fuel economy (e.g., Boeing 787, Airbus A350 XWB).[1–4] The matrix resins of PMCs are primarily composed of hydrocarbon and therefore are susceptible to oxidation and combustion. For example, bisphenol A diglycidyl ether, a prototypical epoxy resin used in the manufacture of a wide range of PMCs, is highly flammable with a heat release capacity (HRC) of over 650 J g^{-1} K^{-1}.[5] In addition, epoxy resins tend to have glass transition temperatures (T_g) below 150 °C leading to dimensional stability issues when used for structures that experience elevated temperatures, for example adjacent an engine. Matrix resins and their PMC are referred to as high-performance when their T_g values are greater than 150 °C. A relatively new member of this category are cyanate esters (aryl-O—C≡N; $T_g > 200$ °C), discovered in the 1960s, Chart 1.[6–9] Cyanate esters are thermosetting materials which undergo an irreversible trimerization reaction when heated to ~200 °C resulting in an infusible polycyanurate plastic.

Although cyanate esters have greater thermal stability than epoxy, they are still flammable. For example, the heat release capacity for the dicyanate ester of bisphenol A (BADCy) was found to be 283 J g^{-1} K^{-1}.[5] An excellent method to decrease the flammability of epoxies, as shown by Hergenrother et al., was to incorporate phosphorus into their structure.[10–13] A standard and inexpensive method to test the flammability of plastics is the Underwriters Laboratory UL94 test. Small samples of a plastic are suspended in an open flame for a specified time period to observe how quickly they burn. Owing to its simplicity, there is a wide body of published UL94 data for all types of plastics. Typical epoxy fails the UL94 testing protocol with a sustained burn, but after blending the same with small amounts (<10 wt%) of phosphorus-containing epoxy gave the desired V-0 rating.[14] We wondered whether this striking effect of phosphorus would occur in cyanate ester resins as well. A survey of the literature found few reports of phosphorus-containing cyanate esters. One of the first attempts at their synthesis, a tricyanate ester of triphenylphosphine, was made by Casares but the final cyanation step failed.[15] Around the same time, the *para* dicyanate **1** was reported by Abed et al. but they did not completely purify or fully characterize the compound, nor study the flammability of their product, Chart 2.[16] More recently, cyanates of dihydrooxaphosphaphenanthrene (DOPO) were made such as Lonza's **FR-300** whose polycyanurate had $T_g = 225$ °C and V-0 flammability rating, supporting the above hypothesis.[17–19]

Additional Supporting Information may be found in the online version of this article.

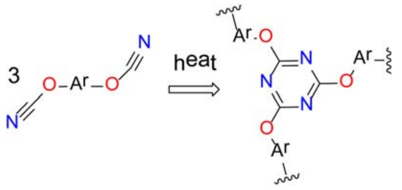


CHART 1 Thermal cyclotrimerization and polymerization process of cyanate ester resins. [Color figure can be viewed at wileyonlinelibrary.com]

Although **FR-300** appears promising as a flame retardant additive for common cyanate esters, it may be an expensive product owing to the complexity in its manufacture which is only now becoming commercially available.[20,21]

To begin our study in this area, we decided to reevaluate the older synthetic routes owing to such rapid methods of preparing triarylphosphines. It was hypothesized that the difficulties in obtaining pure **1** were due to the electron withdrawing nature of the phosphine oxide in conjugation with the *para* cyanate groups, causing the resin to undergo oligomerization at a much lower temperature than ordinarily observed (~200 °C) in common arylalkyl cyanate esters. Thus, it was proposed that the *meta* isomer **2** would be more desirable since it might significantly decrease, if not eliminate, this undesirable electronic effect. Furthermore, with the cyanates in *meta* positions, the melting point of **2** would likely be lower than **1**, making processing easier and solubility better.[22–24] This brief report will describe the successful synthesis and characterization of isomers **1** and **2** as well as tricyanate ester **3**, all derivatives of triphenylphosphine oxide. Preliminary thermal characterization of the resins was made by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and thermomechanical analysis (TMA). Finally, we show that commercial arylalkyl cyanate esters resins had greatly improved flame resistant when blended with any of the phosphorus-containing cyanate esters **1**–**3**. By a method similar to the UL94 test, both bisphenol E dicyanate ester (LeCy) and BADCy achieved a V-0 rating when mixed with as little as 10 wt% monomer **2**.

EXPERIMENTAL

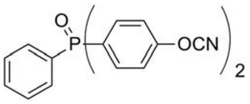
Materials

Cyanogen bromide (BrCN), trimethylamine (TEA), and anhydrous tetrahydrofuran (THF) were purchased from Sigma-Aldrich (Milwaukee) and used as received. Commercial resins bisphenol E (LeCy) and bisphenol A (BADCy) dicyanate esters were obtained from Lonza (Basel). All other reagents and solvents were obtained commercially and used as received. CAUTION! The procedures employing BrCN are hazardous due to the toxic nature of this reagent.[25–27] Although BrCN is a solid (mp 52 °C), it has a low vapor pressure and the risk of inhalation is high. All handling of this reagent as well as the reactions involving it must be done in a fume hood with the sash down as far as possible.

General Methods

The melting points were collected on a Mel-Temp II from Laboratory Devices (Holliston, MA) and are not corrected. All NMR data were collected on a Bruker Avance II 300 MHz spectrometer (^{1}H at 300 MHz, ^{13}C at 75 MHz, ^{31}P at 121.5 MHz) and referenced to solvent or tetramethylsilane. All ^{31}P NMR was performed with 85% H_3PO_4 as external standard and the phosphoric acid signal was designated as 0 ppm. Nuclear magnetic resonance data (free-induction decay's) were processed using NUTS software from Acorn NMR (Livermore, CA). Elemental analyses were performed by Atlantic Microlab, Inc. (Norcross, GA). Complete details for the chemical synthesis of the intermediates of cyanates **1**–**3**, figures of their NMR spectra and those of monomers **1**–**3**, can be found in the Supporting Information.

Synthesis of Monomers 1–3



Synthesis of Phenylbis(4-Cyanatophenyl)Phosphine Oxide (1)

A round-bottomed flask equipped with magnetic stirring bar, addition funnel and N_2-bubbler was filled with phenylbis(4-hydroxyphenyl)phosphine oxide (1 g, 3.2 mmol) and anhydrous THF (15 mL). Anhydrous DMF (3 mL) was added until all the solids completely dissolved. The mixture was then cooled in a −20 °C bath before BrCN (883 mg, 8.3 mmol, 2.5 equiv) was added in one portion and allowed to dissolve completely. Next, the addition funnel was filled with TEA (700 mg, 6.9 mmol, 2.1 equiv) which was then added to the reaction mixture dropwise over 15 min. A fine white precipitate formed during this addition. Afterwards, the cooling

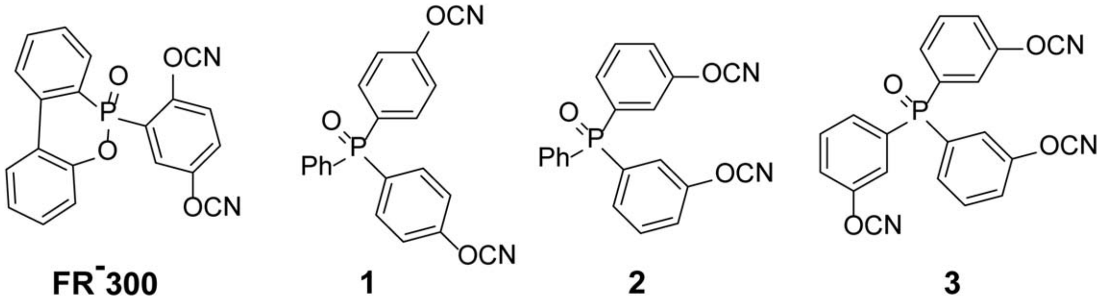
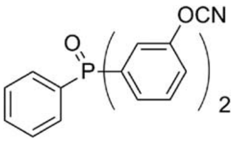


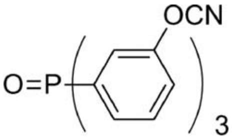
CHART 2 Chemical structures of **FR-300** and the three phosphorus-containing cyanate esters synthesized and studied in this report.

bath was removed and the mixture was stirred at rt for 1 h. The mixture was diluted with H_2O (25 mL) but no immediate precipitate formed. The mixture was extracted with toluene. The organic layer was washed with H_2O (2 × 25 mL) followed by brine (25 mL). The organic layer was then dried over anhydrous $MgSO_4$ and rotary evaporated (bath $T = 40$ °C) leaving a viscous and colorless oil which slowly solidified. The crude solid was recrystallized from a mixture of EtOAc/hexanes (1:3) to obtain **1** as small, colorless needles (1.07 g). Yield: 92%. Mp 101–103 °C. ^1H $\{^{13}C\}$ NMR ($CDCl_3$, δ, ppm): 7.78 (dd, $J = 11.6$ and 11.1 Hz, 4H), 7.67–7.58 (m, 3H), 7.57–7.49 (m, 2H), 7.45 (dd, $J = 8.2$ and 2.1 Hz, 4H). ^{13}C $\{^1H\}$ NMR ($CDCl_3$, δ, ppm): 155.53 (d, $J_{\mathrm{PC}} = 3.5$ Hz), 134.95 (d, $J_{\mathrm{PC}} = 11.7$ Hz), 133.11 (d, $J_{\mathrm{PC}} = 2.3$ Hz), 132.11 (d, $J_{\mathrm{PC}} = 10.0$ Hz), 131.64 (d, $^1J_{\mathrm{PC}} = 104.9$ Hz), 131.18 (d, $^1J_{\mathrm{PC}} = 107.3$ Hz), 129.27 (d, $J_{\mathrm{PC}} = 12.3$ Hz), 116.13 (d, $J_{\mathrm{PC}} = 13.5$ Hz), 107.9 (OCN). ^{31}P $\{^1H\}$ NMR ($CDCl_3$, δ, ppm): +26.63 (m). Anal. calcd. for $C_{20}H_{13}N_2O_3P$: C, 66.67; H, 3.64; N, 7.77. Found for the crude product: C, 66.37; H, 3.64; N, 7.57. Found for the recrystallized product: C, 65.24; H, 3.89; N, 7.68.



Synthesis of Phenylbis(3-Cyanatophenyl)Phosphine Oxide (2)

A round-bottomed flask equipped with magnetic stirring bar and addition funnel was charged with anhydrous THF (500 mL) followed by phenylbis(3-hydroxyphenyl)phosphine oxide (22 g, 71 mmol). After all the solids dissolved, the mixture was cooled in a −20 °C bath and then BrCN (22.6 g, 3 equiv) was added and allowed to dissolve completely. The addition funnel was then charged with TEA (20.7 mL, 15.03 g, 149 mmol, 2.1 equiv) which was then added dropwise to the reaction mixture over 30 min. A copious white precipitate began to appear shortly after the addition was started. After the addition was complete, the cooling bath was removed and the mixture was allowed to stir at rt for 1 h. The reaction mixture was partitioned between H_2O (500 mL) and toluene (500 mL). The organic phase was washed with H_2O (3 × 500 mL) and then brine (500 mL). The organic layer was separated and dried over anhydrous $MgSO_4$ and then treated with decolorizing charcoal for several hours. After filtration through celite, the solvent was rotary evaporated (bath $T = 40$ °C) leaving a colorless oil which was stored under dynamic vacuum (0.1 torr) for 24 h to remove residual solvent and traces of diethylcyanamide (from von Braun degradation of TEA). After storing the crude product for several weeks at room temperature, the product began to crystallize from the melt. The white crystalline solid **2** was washed with toluene and filtered on filter paper (20.4 g). Yield: 80%. Mp: 89–91 °C. ^1H $\{^{13}C\}$ NMR ($CDCl_3$, δ, ppm): 7.8–7.5 (m, 13H). ^{13}C $\{^1H\}$ NMR ($CDCl_3$, δ, ppm): 153.01 (d, $J_{\mathrm{PC}} = 16.6$ Hz), 135.66 (d, $^1J_{\mathrm{PC}} = 102$ Hz), 133.27 (d, $J_{\mathrm{PC}} = 3$ Hz), 131.99 (d, $J_{\mathrm{PC}} = 10$ Hz), 131.45 (d, $J_{\mathrm{PC}} = 13$ Hz), 130.45 (d, $J_{\mathrm{PC}} = 9.5$ Hz), 130.05 (d, $^1J_{\mathrm{PC}} = 107$ Hz), 129.27 (d, $J_{\mathrm{PC}} = 13.1$ Hz), 119.23 (d, $J_{\mathrm{PC}} = 17.2$ Hz), 119.14 (d, $J_{\mathrm{PC}} = 25.8$ Hz), 108 (OCN). ^{31}P $\{^1H\}$ NMR ($CDCl_3$, δ, ppm): +26.09 (m). Anal. calcd. for $C_{20}H_{13}N_2O_3P$: C, 66.67; H, 3.64; N, 7.77. Found: C, 66.37; H, 3.65; N, 7.74.



Synthesis of Tri(3-Cyanatophenyl)Phosphine Oxide (3)

A round-bottomed flask (100 mL) equipped with magnetic stirring bar and addition funnel with nitrogen bubbler was charged with tris(3-hydroxyphenyl)phosphine oxide (580 mg, 1.8 mmol) and anhydrous THF (15 mL). The solution was cooled in a −20 °C bath before BrCN (760 mg, 7.2 mmol, 4 equiv) was added in one portion and allowed to dissolve completely. The funnel was charged with TEA (560 mg, 771 μL, 5.58 mmol, 3.1 equiv) which was added dropwise over 15 min. After the addition the reaction mixture was thick with a white precipitate, the cooling bath was removed, and the mixture was stirred at rt for 1 h. The reaction mixture was then diluted with ice water (50 mL) and allowed to stir for several hours. After this time, a white granular precipitate of the product had formed. The crude product was harvested by suction filtration on Fisherbrand® P5 medium filter paper and air-dried under suction for several hours. The crude solid was slurried with isopropanol to give **3** in pure form as a white crystalline powder (550 mg). The solid could be recrystallized from toluene and gave microcrystalline needles. Single crystals were grown from acetone. Yield: 76%. Mp 140–142 °C. ^1H $\{^{13}C\}$ NMR ($CDCl_3$, δ, ppm): 7.77–7.52 (m, 12H). ^{13}C $\{^1H\}$ NMR ($CDCl_3$, δ, ppm): 153.26 (d, $J_{\mathrm{PC}} = 16.4$ Hz), 134.45 (d, $^1J_{\mathrm{PC}} = 104.6$ Hz), 131.85 (d, $J_{\mathrm{PC}} = 13.6$ Hz), 130.37 (d, $J_{\mathrm{PC}} = 9.9$ Hz), 120.03 (d, $J_{\mathrm{PC}} = 2.8$ Hz), 119.08 (d, $J_{\mathrm{PC}} = 10.9$ Hz), 107.91 ($O\underline{C}N$). ^{31}P $\{^1H\}$ NMR ($CDCl_3$, δ, ppm): +24.54 (m). Anal. calcd. for $C_{21}H_{12}N_3O_4P$: C, 62.85; H, 3.01; N, 10.47. Found: C, 63.08; H, 3.10; N, 10.40.

X-Ray Structure Determination of Dicyanates 1–3

Crystals of **1**–**3** were grown as outlined above, removed from their mother liquor solutions, coated with fluorinated oil, and examined under a conventional light microscope. Suitable crystals were mounted in the nitrogen cold stream provided by an Oxford Cryostream low-temperature apparatus on the goniometer head of a Bruker ApexII instrument equipped with a CCD detector and copper ($\lambda = 1.54178$ Å) fine-focused sealed tube. Data were reduced using SAINT, and an empirical absorption correction was applied using SADABS.[28] Structure solutions were determined using SHELXT-2015 and refined using SHELXL-2017.[29,30] Refinement details can be found in the respective CIFs. CCDC numbers 1585416 (**1**), 1585415 (**2**), and 1811120 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif, by e-mailing data_request@ccdc.cam.ac.uk, or by contacting CCDC 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336033.

Thermal Analysis

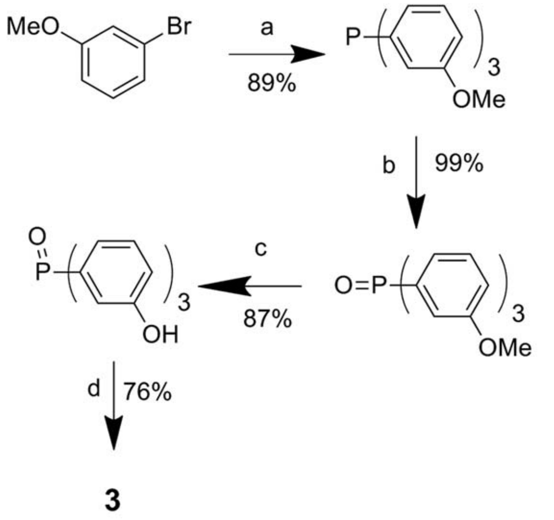
Differential scanning calorimetry (DSC) was performed on ~10 mg of monomers reserved after de-gassing using a TA Instruments Q200 calorimeter under 50 mL min^{-1} of flowing nitrogen. Samples were heated to 350 °C at 10 °C min^{-1}, then cooled at 5 °C min^{-1} to 0 °C and re-heated to 350 °C at 10 °C min^{-1}.

Thermogravimetric analysis (TGA; under both nitrogen and air) was performed on ~10 to 20 mg samples of cured disks, using a TA Instruments Q5000 analyzer, at a gas flow rate of 20 mL min^{-1} (balance) and 20 mL min^{-1} (purge). The samples were equilibrated at 110 °C for 60 min and then heated at 10 °C min^{-1} to 600 or 800 °C.

Cured disks were also tested via oscillatory thermomechanical analysis (OTMA) with a TA Instruments Q400 series analyzer under 50 mL min^{-1} of nitrogen flow. For this experiment, a bulk sample of monomer **2** was cured at 210 °C for 8 h. The disks were initially held in place with a compressive force of 0.05 N using the expansion probe. The sample was equilibrated to −10 °C. The force was then modulated at 0.05 Hz over an amplitude of 0.1 N (with a mean force of 0.1 N) and the temperature was ramped twice (heating and cooling) between −10 °C and 190 °C (to aid in determination of thermal lag) followed by heating to 300 °C, cooling to 100 °C, and re-heating to 300 °C, all at 10 °C min^{-1}.

Flammability Testing Procedure

Cured sample pucks of the monomers and their LeCy and BADCy blends were made in cylindrical aluminum weigh dishes (20 mm × 8 mm, wall thickness ~0.1 mm, volume ~2.5 mL; Wheaton). The cyanate ester blends (1 g total) were loaded into the microdishes and melted on a hotplate (90 °C) and mixed thoroughly with a glass spatula. Immediately afterwards, the molten samples were heated and degassed in a Lab-Line Model 3608-5 vacuum oven (95 °C, 60 torr, 1 h). The samples were then immediately transferred to a Barnstead/Thermolyne 48000 furnace and cured under flowing nitrogen by the following schedule: 1 h at 150 °C then 3 h at 200 °C and finally 1 h at 250 °C. The oven power was shut off and the samples were taken out the next day after cooling to ambient temperature 18 h. The polycyanurate sample pucks were demolded by cutting the exposed edge of the dishes with a razor blade in several places and then carefully peeling away the aluminum from the plastic with a pair of needle-nosed pliers. All of the polycyanurate specimens were tough enough that no cracking or chipping occurred during demolding. The curing process created void free polycyanurate disks by visual inspection. Note that no catalyst was added either to the newly synthesized monomers or to the commercial resins.



Reagents & conditions: a) 1. *n*BuLi, THF, -78 °C; 2. PCl_3, THF, -78 °C to rt; b) 30% H_2O_2, acetone; c) pyridine hydrochloride, reflux; d) BrCN, TEA, THF, -20 °C.

SCHEME 1 Four-step synthesis route to prepare tricyanate **3** in 58% overall yield.

The cured sample disks (five/blend) were held in a blue Bunsen burner flame (natural gas) with a pair of long forceps. The disk was held in a vertical manner so that the flame reached halfway up the side of the disk. The disks were held in the flame for two 10-s periods, with a 10-s period in between to observe the sample, noting the after flame time (t_1 and t_2) with a stopwatch. The total after flame time ($t_1 + t_2$) for each blend of five disks was added together to give the total after flame time in seconds. There was no dripping that occurred when any of the samples were placed in the flame.

RESULTS AND DISCUSSION

Synthesis of the Monomers 1–3

In an attempt to repeat the work of Casares, it was found that addition of cyanogen bromide to a THF solution of tri(4-hydroxyphenyl)-phosphine caused immediate precipitation of an unknown material before any triethylamine base had been added.[15,31] This was likely due to the phosphorus atom (Group V) behaving as a base in the presence of this reagent. This result would explain Casares' difficulty in obtaining the desired product and would indicate complications in forming a cyanate ester of a phosphine, at least by the general cyanation method. Thus, the synthetic scheme used to prepare the tricyanate **3** is shown in Scheme 1. The tri(3-methoxyphenyl)phosphine was made by reaction of the 1-bromo-3-lithiobenzene with phosphorus trichloride in good yield. The phosphine was then oxidized with hydrogen peroxide in quantitative yield. The tri(3-methoxyphenyl)-phosphine oxide

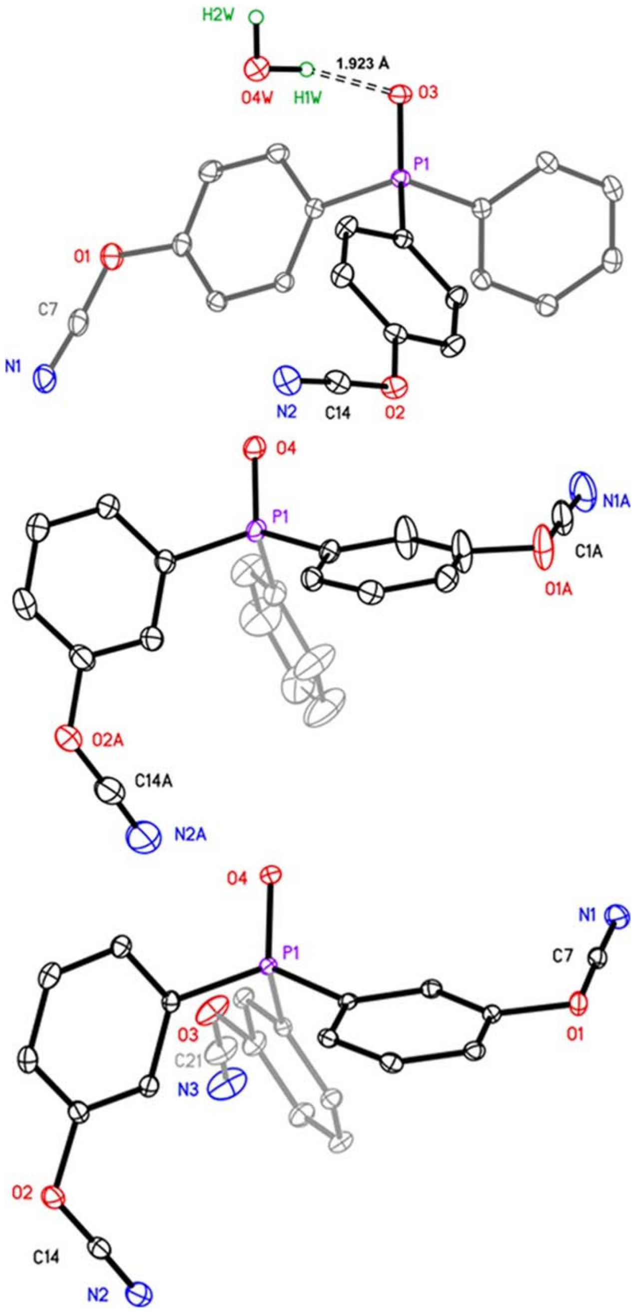
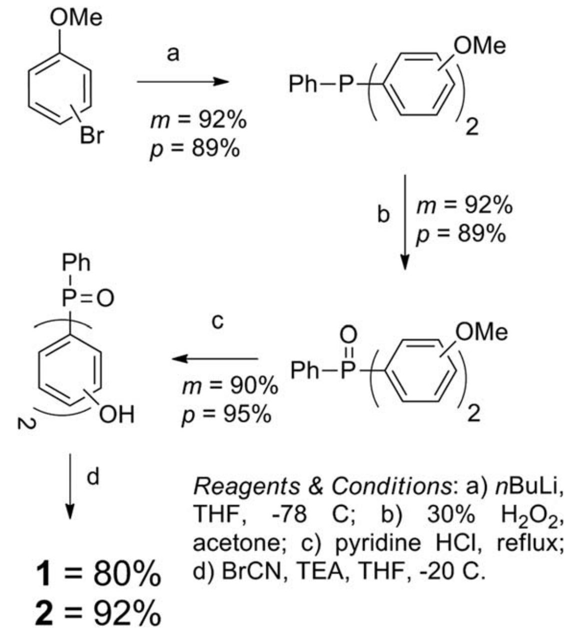


FIGURE 1 X-ray crystal structures of monomers **1** (top), **2** (middle), and **3** (bottom) drawn with 50% thermal contours. Monomer **1** is a hemihydrate and monomer **2** shows disorder in the cyanate groups. Hydrogen atoms and disorder omitted for clarity. [Color figure can be viewed at wileyonlinelibrary.com]

was then deprotected by refluxing in pyridine hydrochloride. ^{1}H NMR was utilized to ensure that complete dealkylation had occurred before workup. Finally, the trihydroxy compound was cyanated without issue by the typical conditions of Grigat and Pütter yielding **3** in 58% overall yield.[6] The crystal structure of monomer **3** is shown in Figure 1.



SCHEME 2 Four-step chemical synthesis route to prepare monomers **1** and **2** in 77% and 65% overall yields, respectively.

The synthesis routes for monomers **1** and **2** are shown in Scheme 2. Adjustment of the pH during work-up in the dealkylation step was important to ensure removal of pyridine from the product phase. However, the phenylbis(4-hydroxyphenyl)phosphine oxide had a melting point (162 °C) which was significantly lower than others reported (~233 °C) suggesting the possibility of polymorphic behavior.[31,32] It was later shown by elemental analysis that our crystalline product, was complexed with either acetic acid (presumably carried through the work-up) or acetonitrile (recrystallization).

Nevertheless, these batches of phenylbis(4-hydroxyphenyl)phosphine oxide underwent routine cyanation and gave dicyanate **1** in 77% overall yield. Monomer **1** could be recrystallized from organic solvents in high purity. X-ray crystallography of **1** showed that it was hemihydrate, although elemental analysis of other batches of this product

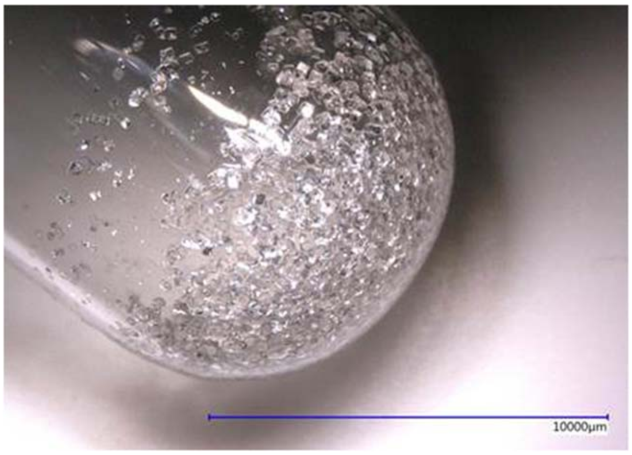


FIGURE 2 Crystals of monomer **2** grown from toluene. [Color figure can be viewed at wileyonlinelibrary.com]

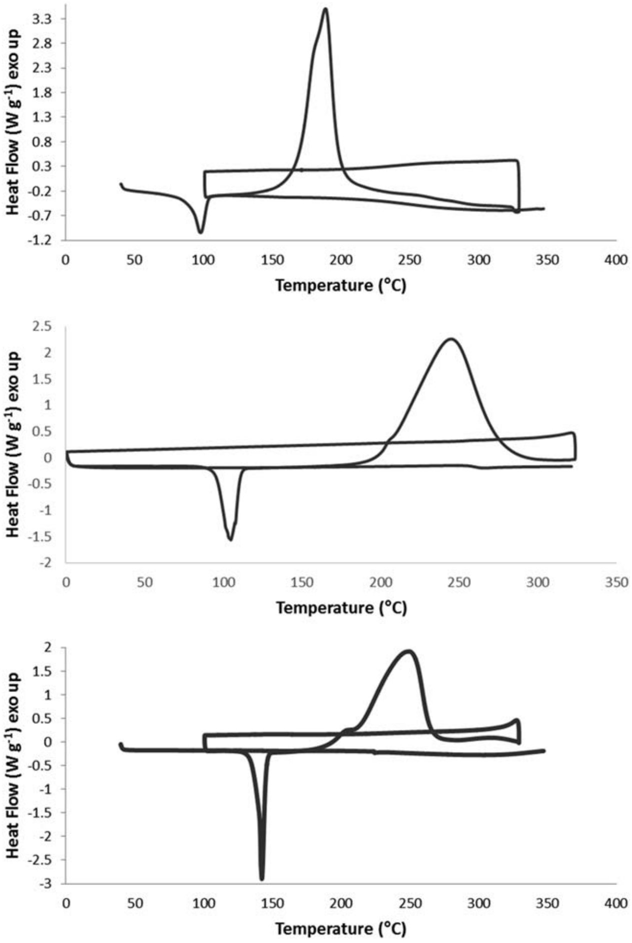


FIGURE 3 DSC thermograms of monomers **1–3** (10 °C min^{-1}).

were apparently free of any solvent, Figure 1.[33] It is hypothesized that the phosphine oxide moiety, a highly polar site, could make the product hygroscopic. It is known that triphenylphosphine oxide can complex water and forms a stable hemihydrate.[34–38] The polar nature of the monomers was noted by the fact that they would elute on silica gel plates only with polar solvents such as ethyl acetate.

The phenylbis(3-methoxyphenyl)phosphine had been reported on three occasions, Keldson and McEwen and Russell and Warren made the compound by Grignard reaction between 3-bromoanisole and phenyldichlorophosphine ($PhPCl_2$) but did not purify the product or provide any spectroscopic data.[39–41] It was found that the lithium salt made by halogen–metal exchange of 3-bromoanisole with *n*-butyllithium would react in the desired manner with dichlorophenylphosphine and gave phenylbis(3-methoxyphenyl) phosphine in excellent yield. The product could be purified by distillation and appeared to be stable on the bench since there was no phosphine oxide impurity present after weeks of storage under ambient conditions. The next step was hydrogen peroxide-mediated oxidation to the phosphine oxide which occurred in nearly quantitative yield. All of the phosphine oxides prepared showed a characteristic large coupling between ring carbon and phosphorus in the phosphorus-coupled ^{13}C NMR spectra ($^{1}J_{PC} \approx 100$ Hz). Another synthetic route briefly explored to prepare phenylbis(3-methoxyphenyl)phosphine oxide was the reaction of 1-lithio-3-methoxybenzene with phenylphosphoryl dichloride ($PhPOCl_2$), eliminating the subsequent oxidation step. Instead, this reaction gave tri(3-methoxyphenyl)phosphine oxide, which is likely due to the fact that three equivalents of the lithium salt was used and that the reaction was heated to reflux.[42] Demethylation to phenylbis(3-hydroxyphenyl)-phosphine oxide was effected in excellent yield by boiling in excess pyridine hydrochloride.[43] Finally, cyanation by the standard conditions (triethylamine/BrCN) completed the synthesis of dicyanate **2** in 65% overall yield. Dicyanate **2** was initially obtained as an oil that crystallized very slowly. Even after significant effort, high-quality crystals suitable for X-ray analysis could not be obtained from the oil.

However, the crystals by evaporation of a toluene solution of **2** (Fig. 2) were analyzed showing disorder in the cyanate groups. Comparing the crystal structures of isomers **1** and **2**, it was thought there might be a difference in the bond lengths of the cyanate esters, from different levels of phosphine oxide influence, yet they were identical.

Thermal Analysis of the Monomers 1–3

DSC heating curves of monomers **1–3** are shown in Figure 3 with significant data points collected in Table 1. Based on the hydration issues uncovered during the X-ray crystallographic studies, the low melting enthalpy (38.9 J g^{-1}) in the thermogram for monomer **1** may be attributed to the poor crystal properties associated with its hygroscopic nature. A $T_g = 250$ °C could be observed for **1** by this method which was significantly higher than reported by Abed et al. (195 °C), which could be due to impurities present in their

TABLE 1 Thermal Data from DSC Analysis of Monomers 1–3

Monomer	Melting Range (°C)	Melting Endotherm (J g^{-1})	Melting Max (°C)	Cure Onset (°C)	Exotherm Max (°C)	ΔH_{cure} (J g^{-1})	ΔH_{cure} (kJ cyanate ester^{-1})	T_g (°C)
1	84–105	38.9	97.8	140	188	477	85.9	250
2	86–110	74.2	102.9	175	246.8	604	108.7	268
3	127–149	81.8	142.3	181	247.6	456	60.9	nd

nd, Not detected.

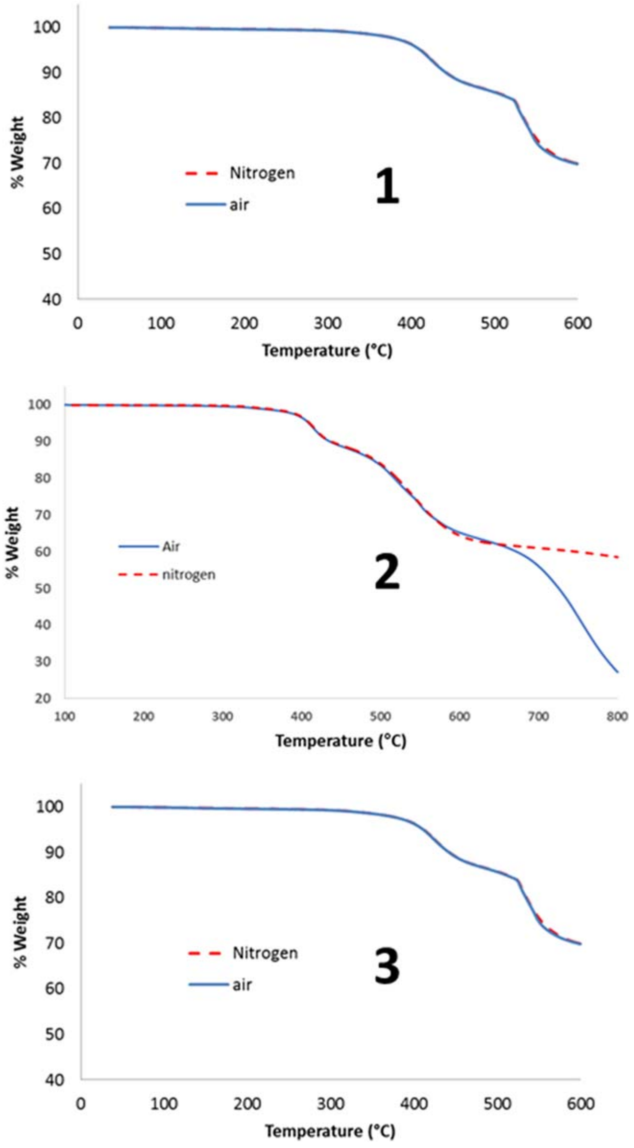


FIGURE 4 TGA curves for **1**–**3** (10 °C $\min^{-1}$). [Color figure can be viewed at wileyonlinelibrary.com]

product.[16] The thermogram shows only 35 °C window between the melt and onset of cure. Cyanate esters ordinarily begin cure at ∼200 °C. The low cure onset temperature (140 °C) of monomer **1** is an indication that the cyanate ester groups are activated, likely from the *para* phosphine oxide moiety. Such an activation by carbonyl was reported by Marcos-Fernández et al. for the *para* isomers in dicyanate esters of benzophenone.[44] The enthalpy of cure (477 J g^{-1}) corresponds to 86 kJ per cyanate ester functionality, which could indicate residual unreacted cyanate ester groups (BADCy, 108 kJ $O{-}C{\equiv}N^{-1}$).[45]

The *meta* dicyanate **2** appeared free from hygroscopic issues and gave consistent DSC thermograms over several months. Monomer **2** had a relatively sharp melting endotherm (74 J g^{-1}). The onset of cure occurs at 175 °C affording a 65 °C processing window. Fortuitously, the *meta* configuration kept the cyanate esters relatively stable since cure began at ∼200 °C. On the second heating trace, which showed the material completely cured in the DSC, the T_g for monomer **2** was clearly seen at 268 °C. The enthalpy of cure for monomer **2** was 108 kJ $O{-}C{\equiv}N^{-1}$ showing that it underwent complete cure reaction. Marcos-Fernández et al. found the *meta* isomer had a slightly lower T_g than para in their study of benzophenone dicyanate esters, however the opposite was found between **1** and **2**.[44] Again, there is a hydration issue associated with monomer **1** that may be at play. Tricyanate **3** had a relatively sharp melting endotherm but only ∼40 °C processing window before cure onset owing to its higher melting temperature. The higher cure onset temperature (∼200 °C) is due to electronic insulation by *meta* orientation between the cyanate esters and the phosphine oxide. The compound exhibits a low enthalpy of cure of 61 kJ per cyanate ester group, which we hypothesize is due to the compact structure of tricyanate **3**, the sterically hindered *meta* cyanates and the resulting high crosslink density which made it difficult for further reaction to take place. Even so, no T_g below 350 °C could be seen in the DSC trace.

The TGA curves and key data for **1**–**3** are shown in Figure 4 and Table 2. The *para* isomer **1** was significantly less stable than *meta* **2** undergoing 5% decomposition ∼30 °C earlier. The T_d for **1** (373 °C) in air was found to be very close to that reported by Abed et al. (371 °C).[16] The char yield for **1** was also approximately 10% less than **2**. The tricyanate **3** showed slightly better stability than **2** with ∼5% higher char yield at 600 °C. Monomer **2** decomposed in air by a three-

TABLE 2 Data from TGA Analysis of Monomers 1–3

Monomer	T_d[a] (°C)		Char Yield 600 °C (%)		Char Yield 800 °C (%)		% Weight Loss @ T (°C) N_2 Air					
	N_2	Air	N_2	Air	N_2	Air	450	550	600	450	550	600
1	382	373	55	57	nd	nd	11	27	7	13	26	4
2	409	408	64	65	58	27	12	16	8	12	16	7
3	412	408	70	70	nd	nd	11	14	5	11	13	4
BADCy[b]	402	400	47	25	nd	nd	35	15	3	37	13	25

[a] T_d = 5% weight loss.
[b] Data from ref. 46.

nd, Not determined.

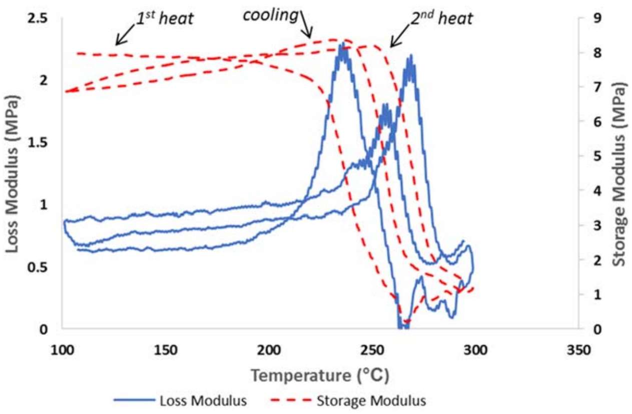


FIGURE 5 TMA data monomer **2** (10 °C min^{-1}). [Color figure can be viewed at wileyonlinelibrary.com]

stage process reaching a char yield of 27% at 800 °C. In nitrogen, monomer **2** closely follows the air curve but plateaus before the third decomposition step ending with a char yield of 58% at 800 °C.

Data included for BADCy shows that monomer **2** compares favorably with more than double the char yield in air at 600 °C.[46]

Unfortunately, complete thermal data for **FR-300** has not been reported yet. But monomer **2** has a T_g of 268 °C which is 40 °C higher than **FR-300**. Lin et al. found their DOPO-tricyanate, another phosphorus-containing cyanate ester, had $T_g = 276$ °C, $T_d = 348$ °C, and char yield of 61% (N_2, 600 °C).[19] So monomer **2** has greater initial thermal stability than the DOPO-tricyanate [$T_d = 409$ °C and char yield of 62% (N_2, 600 °C)] though they both reach a similar end result.

At this juncture, monomer **2** appeared the most interesting of the new resins and with enough material available, it was studied further by TMA (Fig. 5). Taking into account the thermal lag of the instrument, we observe an as-cured T_g of 234 °C, and a fully cured T_g of 264 C by loss modulus. As expected, this fully cured T_g matches the T_g previously determined by DSC.

Such phenomenon is typical in the thermal analysis of thermosetting resins.[47] Analysis by DSC of these same cured pucks (polycyanurate disks) confirmed there was residual heat of cure remaining (~10%), Supporting Information Figure S1. Curiously, both the TMA and latter DSC curves showed a small amount of off-gassing by the sample at ~275 °C. Although monomer **2** appeared to be an anhydrous material, there may be the possibility that it too could absorb water causing this aberration in the thermograms.

Flammability Testing of Cured Cyanate Ester Resins

A convenient, qualitative method to check the flammability of plastics without expensive instrumentation is the UL94 protocol. One drawback of this method, from a materials discovery viewpoint, is the substantial amount of polymer necessary to fulfill the specimen size requirements as defined by the method (5 samples, ~25 mL total). Owing to limited quantities of monomers **1–3** available from this pilot study,

TABLE 3 Flammability Data from UL94 Analysis of Blends of Monomers 1–3 with LeCy and BADCy[a]

Cyanate Ester Blend						Test Specimen and After-Flame Time (s)											
					1		2		3		4		5				
LeCy	BADCy	1	2	3	*P* wt%	t_1	t_2	t_1	t_2	t_1	t_2	t_1	t_2	t_1	t_2	t_1+t_2	Rating[b]
100	0	0	0	0	0	0	60	0	40	0	50	0	22	0	35	207	F
0	100	0	0	0	0	0	100	0	110	4	100	2	66	1	105	488	F
0	90	10	0	0	1.1	0	106	0	46	3	43	0	12	0	80	290	F
0	80	20	0	0	2.2	0	1	2	35	0	5	–	–	–	–	43	–
95	0	0	5	0	0.58	0	20	0	27	0	6	0	10	0	9	72	V1
90	0	0	10	0	1.2	0	9	0	8	0	10	0	8	0	10	45	**V0**
85	0	0	15	0	1.74	0	5	0	4	0	4	0	4	0	2	19	**V0**
80	0	0	20	0	2.32	0	4	0	5	0	4	0	5	0	4	22	**V0**
0	95	0	5	0	0.55	0	9	0	21	0	11	0	16	0	11	68	V1
0	90	0	10	0	1.1	0	2	1	4	1	10	0	5	0	9	32	**V0**
0	85	0	15	0	1.65	0	2	1	5	3	4	0	1	0	7	23	**V0**
0	80	0	20	0	2.2	0	4	0	5	1	2	0	3	1	4	20	**V0**
0	75	0	25	0	2.75	0	2	0	1	0	1	0	1	0	1	6	**V0**
0	0	0	100	0	8.6	0	0	0	0	0	0	0	0	0	0	0	**V0**
90	0	0	0	10	1.1	0	4	0	5	3	2	1	4	0	2	21	**V0**
0	90	0	0	10	1.07	0	44	0	3	2	37	0	8	0	4	98	V1

[a] Bisphenol E (LeCy) and bisphenol A (BADCy) dicyanate esters.

[b] F, failure, sustained combustion.

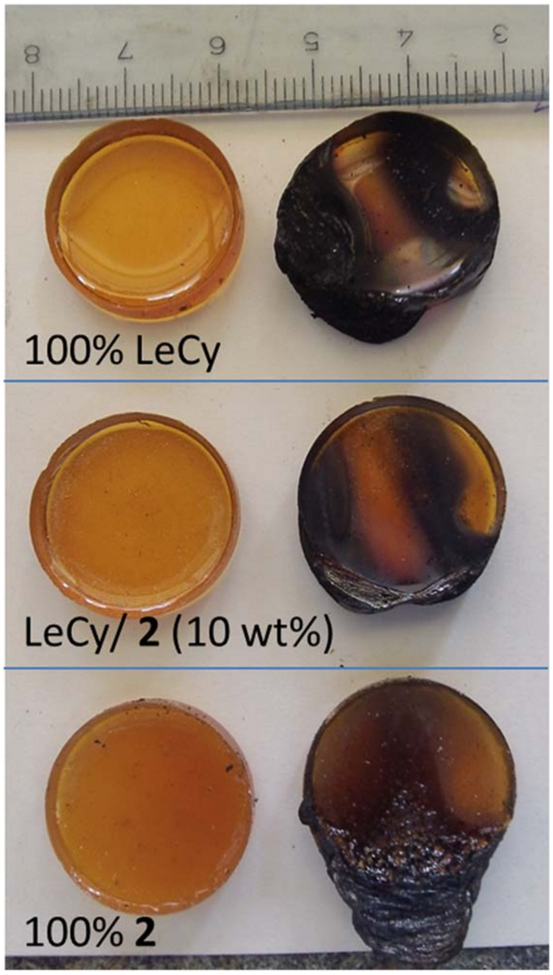


FIGURE 6 Photo of cured sample disks and those after flame testing (millimeters scale). [Color figure can be viewed at wileyonlinelibrary.com]

smaller test specimens were made (~1 mL sample^{-1}). There was no trouble blending monomers **1**–**3**, in up to 25 wt%, with either of the commercial dicyanate esters BADCy and LeCy by gentle heating and mixing.

It was noted that blends formed from LeCy had a tendency to remain liquid when stored at room temperature. The blended resins were cured using a general heat cycle (1h @ 150 °C, 3 h @ 200 °C then 1 h @ 250 °C) in a nitrogen atmosphere.

Apart from the specimen size difference, the UL94 test method was followed accordingly. The least flammable and most desirable rating in this test is known as V-0 where the total after-flame time for the five samples is less than 50 s. The data for the flammability of monomers **1**–**3** with the commercial resins is shown in Table 3. The appearance of the pucks before and after the flame test is shown in Figure 6.

The HRC data for the neat commercial cyanates would lead one to believe that LeCy (316 J g^{-1} K^{-1}) is more flammable than BADCy (283 J g^{-1} K^{-1}).[5] Although neither resin drips, both materials fail the UL94 test but LeCy appears to be significantly less flammable in terms of after-flame time. The propensity for burning of BADCy shown here are in keeping with Zhang et al. and others who also found this material highly flammable.[48–53] The polycyanurate samples did not drip into the flame but simply charred. The other interesting observation was that the polycyanurates generally had very short, if not zero, first after flame times and one could be mistaken regarding flammability of polycyanurates were the second flame test not carried out, as dictated by the UL94 test.

Both LeCy and BADCy could be significantly flame retarded to a V-1 rating by adding just 5 wt% monomer **2**, only ~0.5 wt% phosphorus. But increasing monomer **2** content to 10 wt% got the blends down to the V-0 rating. Samples of pure monomer **2** had zero after-flame time and were V-0. Although these samples did not drip, there was significant creep of the char residue down toward the flame as shown in Figure 6.

Although after-flame time was knocked down nearly one-half, monomer **1** appeared to be less effective in flame retarding since adding 10 wt% to BADCy, ~1 wt% phosphorus, continued to fail the test. From the limited data we could gather, it appears that 20 wt% monomer **1** may be required to achieve low flammability in BADCy. Monomer **3** was effective at the 10 wt% level to achieve V-0 rating in LeCy. But a 10 wt% blend of tricyanate **3** in BADCy only brought down its flammability to the V-1 rating.

CONCLUSIONS

New phosphorus-containing di- and tricyanate esters were prepared by *de novo* chemical synthesis of triphenylphosphine oxide derivatives. By ensuring the penultimate hydroxy-intermediates were pure, the resulting cyanate esters were obtained as homogeneous, recrystallizable solids. The synthetic procedures were uncomplicated and should be amenable to scale-up. The *meta* isomer appears to be the desired configuration in this class of resin for best processing and stability. As such, other synthetic routes to these compounds could be faster. The electron-withdrawing group of triphenylphosphine oxide, an inexpensive starting material, could be leveraged for aromatic *meta*-hydroxylation, for example.

The *meta* dicyanate **2** (T_g 268 °C) had good thermal stability similar to commercial cyanate resins such as LeCy (T_g 296 °C).[52] Dicyanate **2** had more than double the char yield (air, 600 °C) than commercial BADCy and this is likely due the phosphorus present, known to increase charring in polymers.[53] The most striking difference between the phosphorus-containing cyanate esters and commercial non-phosphorus cyanate esters was observed in their reaction to open flame. Cyanate ester with phosphorus in their structure had V-0 flammability using a test similar to the UL94 screen in contradistinction to the highly flammable BADCy and LeCy. However, the latter resins were easily flame retarded to V-0 by blending, requiring only 10 wt% in the case of dicyanate **2**. Our study showed that phosphorus was indeed a suitable heteroatom with which to build intrinsically flame resistant cyanate esters. The only other V-0 rated cyanate esters contained fluorine or sulfur, the dicyanates of bisphenol AF and 4,4′-thiodiphenol, respectively.[54]

The *para* isomer appeared to be hygroscopic and will require more attention to conditions of isolation and storage. The two *meta* configured **2** and **3** did not, or were less prone to, pick up water when stored under ambient conditions. These phosphine oxide containing cyanate esters will likely require more attention to atmospheric moisture during processing and composite construction. This issue with water stems from the polar phosphine oxide moiety and this phenomenon appears not to have been discussed, as it relates to polymers, in any detail until now.[55] This will be important to examine more thoroughly since phosphorus compounds such as triarylphosphate ester are the new, halogen-free additives industry uses to flame retard commodity plastics.[56]

Future work will include more precise water absorption studies of the phosphorus-containing cyanate esters and polycyanurates. Making larger quantities of dicyanate **2** will allow for further testing in flame retarding the various other commercial cyanate ester products. Combustion calorimetry and limiting oxygen index would be good means to quantify the heat release capacity and flammability of the new resins and their blends. The dielectric constant and loss of the phosphorus-cyanate esters should be measured since cyanate ester are often used in the manufacture of radomes and printed circuit boards.

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