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Synthesis, Characterization, and Cure Chemistry of High Performance Phosphate Cyanate Ester Resins

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Abstract

Three thermosetting cyanate ester resins with phosphate cores have been synthesized from chlorophosphates by a straightforward, three-step approach. A *p*-substituted bis(cyanate) ester generated by this route (PhosCy) was cured to give a thermoset material with a T_g of 223 °C and a char yield of 47% in air, while the *m*-substituted version (MPhosCy) yielded a thermoset with a T_g of only 131 °C and a char yield of 65% in air. The low T_g of the MPhosCy thermoset is attributed to a unique intramolecular cyclization of the cyanate ester groups, while the high char yield is attributed to a high temperature cross-linking reaction involving the phosphate core. To further explore this class of materials, a trifunctional phosphate cyanate ester (PhosCy3) was prepared from POCl₃. This material was cured to generate a thermoset with an impressive T_g of >360 °C and a char yield of 67% in air. All three hybrid resins can potentially be used in fire-resistant composite materials or as protective surface coatings for conventional polymers.

Introduction

Thermosetting polymer composites offer a variety of advantages over metal structures including lighter weight and resistance to corrosion. Despite these advantages, polymer composites are combustible and this leads to concerns when these materials are used in enclosed environments such as aircraft or submarines.¹ Many high temperature polymers are intrinsically fire resistant.² In particular, polymers that contain primarily aromatic groups show excellent fire resistance and high char yields. Incorporating heteroatoms is a proven method to further increase the fire resistance of high temperature polymers. Most fire resistant additives are based on elements including boron, aluminum, phosphorus, antimony, chlorine, and bromine.² Halogenated additives are the most prevalent and act via formation of gas phase radicals that scavenge hydrogen radicals and result in formation of non-flammable HCl or HBr that further dilute flammable oxidants.³ Although halogenated polymers or additives are effective at reducing flammability, the generation of toxic and corrosive byproducts reduces the attractiveness of these materials.⁴ In contrast, phosphorus based flame retardants act through formation of a surface glass that can protect the substrate from oxygen and flame, promote charring, and inhibit free radical propagation. These materials can also act through a vapor phase mechanism in which PO, P, and P₂ species react with H and OH radicals to form HPO.⁵⁻⁷

Cyanate ester resins are a well-known class of thermosetting polymers with high intrinsic fire resistance.⁸ A number of different approaches have been utilized to decrease the flammability of cyanate esters. One method involves the use of bisphenols that incorporate more rigid aromatic structures. For example, a cyanate ester with a 4,4'-biphenylene structure has been prepared with a char yield of 64% and a UL-94 rating approaching V-O.⁹ Another approach is to increase the crosslink density by increasing the number of crosslinking sites per molecule. For example,

recently reported tris(cyanate) esters derived from resveratrol resulted in char yields >70% and heat release capacities as low as 3 J/(g•K).^{10,11} Taking advantage of halogen-based materials, a cyanate ester derived from bisphenol C has been extensively studied.⁴ Other researchers have decreased the flammability of cyanate esters by incorporating nitrogen heterocycles. For example, Emrick synthesized a novel triazole containing cyanate ester that was non-flammable and had a heat release capacity of only 10 J/(g•K).¹²

Combining a high temperature thermosetting resin with phosphorus-based flame retardants is another common route to the preparation of fire resistant composite materials. Polyphosphates and diphosphates prepared from bisphenol A have been blended with epoxy resins.¹³ Other researchers have prepared cyanate ester resins containing cyclic phosphinates that can be blended with conventional cyanate esters to generate V-0 grade composites.¹⁴⁻¹⁶ Phosphinated cyanate esters have also been prepared from phenylphosphine oxides,¹⁷ while self-curing phosphine adducts of BADCy and blends with epoxy resins were studied by Lin.¹⁸ Although many of these materials have applications as fire-resistant materials that can be used as standalone resins or blended with conventional materials, there are currently no known examples of cyanate esters with a simple phosphate core. An average P-O bond has a bond dissociation energy about 82 kJ/mol greater than an average P-C bond.¹⁹ The higher average bond dissociation energy of a phosphate should translate into greater stability to thermal degradation than related phosphinates. Phosphates are also straightforward precursors to acids and can readily cross-link to form network structures.⁵ In addition, the valency of phosphorus readily lends itself to the synthesis of either bis or tris(cyanate) esters. Finally, the increased flexibility of the bridging phosphate group compared to an sp³ hybridized carbon atom would be expected to result in a high degree of

cure. To explore this new class of cyanate ester resins, this paper describes the synthesis, characterization, and cure chemistry of three cyanate ester resins with phosphate cores.

Experimental

General. All solvents and chemicals were purchased from Sigma Aldrich and used as received except for triethylamine which was distilled from sodium/benzophenone under nitrogen. NMR spectra were collected with a Bruker Avance II 300 MHz NMR spectrometer. ^1H and ^{13}C NMR chemical shifts are reported versus the deuterated solvent peak [Acetone- d_6 : δ 2.05 (^1H), 29.9 (^{13}C)]. A cif file for PhosCy3 has been deposited with the Cambridge Structural Database. The deposition number is CCDC 1406404. Selected crystallographic data are included in the supporting information. Elemental analysis was performed by Atlantic Microlabs Inc. Norcross, GA.

bis(4-(benzyloxy)phenyl) ethyl phosphate (1): To a solution of 4-benzyloxyphenol (10.0 g, 50 mmol) in THF (200 mL) was added 95% NaH (1.26 g, 50 mmol). After the reaction was complete, ethyl dichlorophosphate (3.0 mL, 25 mmol) was added dropwise. The mixture was refluxed overnight then cooled to ambient temperature. 100 mL water was then added. The layers were separated and the aqueous layer was extracted with ether (200 mL). The combined organic layers were dried (MgSO_4) and concentrated under reduced pressure to give 11.20 g (91%) of a brown oil.

Ethyl bis(4-hydroxyphenyl) phosphate (3): A mixture of **1** (11.20 g, 22.8 mmoles) and 10% Pd/C (0.5 g) in methanol (250 mL) was hydrogenated at 50 psi overnight. The solution took up approximately 51 mmol H_2 . The mixture was filtered through Celite then concentrated under reduced pressure to give 7.14 g (100%) of a yellow oil. The oil was chromatographed on silica

gel using 3:1 EtOAc/hexanes to give 5.67 g (85%) of a crystalline solid. ^1H NMR (acetone- d_6): δ 8.38 (s, 2H), 7.07 (dd, $J = 1.3, 9.1$ Hz, 4H), 6.81 (dd, $J = 0.6, 9.2$ Hz, 4H), 4.28 (dq, $J = 1.5, 7.1$ Hz, 2H), 1.31 (dt, $J = 1.1, 7.1$ Hz, 3H). ^{13}C NMR (Acetone- d_6): δ 154.72 (d, $J = 1.6$ Hz), 143.49 (d, $J = 7.2$ Hz), 120.90 (d, $J = 4.4$ Hz), 115.92 (d, $J = 0.9$ Hz), 65.0 (d, $J = 6.2$ Hz), 15.43 (d, $J = 6.6$ Hz).

bis(4-cyanatophenyl) ethyl phosphate (PhosCy): A solution of **3** (4.78 g, 16.4 mmol) and cyanogen bromide (3.65 g, 34.5 mmol, 2.1 eq) in THF (100 mL) was cooled to -30°C and triethylamine (5.0 mL, 36.1 mmoles, 2.2 eq) was then added dropwise. The mixture was allowed to warm to room temperature and stirred for one hour. The mixture was washed with saturated aqueous NaCl then dried and concentrated under reduced pressure to give 5.66 g (96%) of a clear tan liquid. The oil was chromatographed on silica gel using 3:1 EtOAc:hexanes to give 3.88 g (66%) of a colorless oil which slowly crystallizes on standing. mp: 51°C (DSC). ^1H NMR (acetone- d_6): 7.48 (s, 8H), 4.40 (dq, $J = 7.1, 8.7$ Hz, 2H), 1.36 (dt, $J = 1.1, 7.1$ Hz, 3H). ^{13}C NMR (acetone- d_6): 150.00 (d, $J = 1.7$ Hz), 148.75 (d, $J = 7.1$ Hz), 122.26 (d, $J = 4.9$ Hz), 117.04, 108.44, 66.05 (d, $J = 6.2$ Hz), 15.40 (d, $J = 6.3$ Hz). GC/MS: 360 (M^+). Anal. Calcd for $\text{C}_{16}\text{H}_{13}\text{N}_2\text{O}_6\text{P}$: C, 53.34%; H, 3.64%; N, 7.78%. Found: C, 53.43%; H, 3.54%; N, 7.62%.

bis(3-(benzyloxy)phenyl) ethyl phosphate (2): To a solution of 3-benzyloxyphenol (8.36 g, 41.8 mmol) in THF (150 mL) was added 95% NaH (1.05 g, 41.8 mmoles). After the reaction was complete, ethyl dichlorophosphate (2.5 mL, 20.9 mmoles, 0.5 eq) was added dropwise. The mixture was refluxed overnight and then cooled to ambient temperature. 100 mL water was then added. The layers were separated and the aqueous layer was extracted with 100 mL ether. The combined organic layers were dried (MgSO_4) and concentrated under reduced pressure to give 10.06 g (98%) of a thick yellow oil.

Ethyl bis(3-hydroxyphenyl) phosphate (4): A mixture of **2** (10.06 g, 20.5 mmol) and 10% Pd/C (0.5 g) in methanol (250 mL) was hydrogenated at 50 psi overnight. The mixture was filtered through Celite and then concentrated under reduced pressure to give 7.62 g (100%) of a clear tan liquid. The oil was chromatographed on silica gel using 1:1 EtOAc:hexanes to give 4.23 g (67%) of a thick colorless oil. ^1H NMR (acetone- d_6): 8.65 (s, 2H), 7.20 (t, $J = 8.2$ Hz, 3H), 6.74 (m, 6H), 4.30 (q, $J = 7.5$ Hz, 2H), 1.33 (t, $J = 7.5$ Hz, 3H). ^{13}C NMR (acetone- d_6): 151.71, 131.87, 128.75, 112.54, 110.84, 107.35, 65.20, 15.40.

bis(3-cyanatophenyl) ethyl phosphate (MPhosCy): A solution of **4** (4.23 g, 13.6 mmol) and cyanogen bromide (3.23 g, 30.5 mmoles, 2.2 eq) in THF (100 mL) was cooled to -30 °C and then triethylamine (4.5 mL, 32.3 mmoles, 2.3 eq) was added dropwise. The mixture was allowed to warm to room temperature and stirred for one hour. The mixture was washed with saturated aqueous NaCl then dried and concentrated under reduced pressure to give 4.75 g (100%) of a yellow oil. The oil was chromatographed on silica gel using 1:1 EtOAc:hexanes to give 2.56 g (52%) of a colorless oil. ^1H NMR (acetone- d_6): 7.62 (m, 2H), 7.35 (m, 6H), 4.42 (q, $J = 7.1$, 8.8 Hz, 2H), 1.38 (t, $J = 1.2$, 7.1 Hz, 3H). ^{13}C NMR (acetone- d_6): 153.32, 151.50, 131.92, 118.70, 112.37, 108.16, 107.99, 66.40 (d, $J = 6.6$ Hz), 15.40 (d, $J = 6.6$ Hz). Anal. Calcd for $\text{C}_{16}\text{H}_{13}\text{N}_2\text{O}_6\text{P}$: C, 53.34%; H, 3.64%; N, 7.78%. Found: C, 53.59%; H, 3.76%; N 7.64%.

tris(4-(benzyloxy)phenyl) phosphate (5): To a solution of 4-(benzyloxy)phenol (10.0 g, 50 mmol) in THF (200 mL) was added 95% NaH (1.26 g, 50 mmoles). When the reaction was complete, trichlorophosphate (1.56 mL, 16.6 mmoles, 0.33 eq) was added dropwise. The mixture was refluxed for four hours then cooled to ambient temperature. Water (200 mL) was then added. The layers were separated and the aqueous layer was extracted with ether (200 mL). The combined organic layers were dried (MgSO_4) and concentrated under reduced pressure to

give 9.26 g (86%) of an off white solid. This was recrystallized from ethanol (200 mL) to give 8.11 g (76%) of white crystals. mp: 78-79°C. ^1H NMR (acetone- d_6): 7.36 (m, 15H), 7.20 (bd, 6H), 7.02 (bd, 6H), 5.10 (s, 6H). Anal. Calcd for $\text{C}_{39}\text{H}_{33}\text{O}_7\text{P}$: C, 72.66%; H, 5.16%. Found: C, 72.88%; H, 5.15%.

tris(4-hydroxyphenyl) phosphate (6): A mixture of **5** (8.02 g, 12.4 mmol) and 10% Pd/C (0.5 g) in 300 mL methanol was hydrogenated at 55 psi overnight. The solution took up approximately 45 mmoles H_2 . The mixture was then filtered through Celite and concentrated under reduced pressure to give 4.73 g (100%) of a tan glassy solid. This was dissolved in about 30 mL ethanol and poured into 700 mL ice water. The solids were filtered off, washed with water, and then dried to give 4.19 g (90%) of a white solid. ^1H NMR (acetone- d_6): δ 8.43 (s, 3H), 7.08 (dd, $J = 1.2, 9.0$ Hz), 6.84 (dd, $J = 0.3, 8.7$ Hz). ^{13}C NMR (acetone- d_6): 154.91 (d, $J = 1.7$ Hz), 143.37 (d, $J = 7.8$ Hz), 120.95 (d, $J = 4.7$ Hz), 115.99. Anal. Calcd for $\text{C}_{18}\text{H}_{15}\text{O}_7\text{P}$: C, 57.76%; H 4.04%. Found: C, 57.99%; H 4.12%.

tris(4-cyanatophenyl) phosphate (PhosCy3): A solution of **6** (3.68 g, 9.8 mmol) and cyanogen bromide (3.33 g, 31.5 mmol, 3.2 eq) in THF (200 mL) was cooled to -30°C and then triethylamine (4.5 mL, 32.4 mmoles, 3.3 eq) was added dropwise. The mixture was allowed to warm to ambient temperature and stirred for one hour. The mixture was washed with brine (100 mL) and the organic layer was separated. The organic fraction was dried (MgSO_4) and concentrated under reduced pressure to give 4.08 g (93%) of a white solid. The crude material was recrystallized from EtOAc (150 mL) to give 3.38 g (77%) of white crystals. mp: 123°C (DSC). ^1H NMR (acetone- d_6): δ 7.37(bs). ^{13}C NMR (acetone- d_6): 150.17 (d, $J = 1.6$ Hz), 148.14 (d, $J = 7.0$ Hz), 122.04 (d, $J = 5.0$ Hz), 117.10, 108.41. Anal. Calcd for $\text{C}_{21}\text{H}_{12}\text{N}_3\text{O}_7\text{P}$: C, 56.14%; H, 2.69%; N, 9.35%. Found: C, 56.18%; H, 2.83%; N 9.25%.

X-ray crystallographic analysis. A specimen of PhosCy3, approximate dimensions 0.192 mm x 0.225 mm x 0.425 mm, was used for the X-ray crystallographic analysis. A total of 1464 frames were collected. The total exposure time was 8.13 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a trigonal unit cell yielded a total of 12418 reflections to a maximum θ angle of 26.37° (0.80 Å resolution), of which 1431 were independent (average redundancy 8.678, completeness = 100.1%, $R_{int} = 2.33\%$) and 1378 (96.30%) were greater than $2\sigma(F_2)$. The final cell constants of $a = 12.5995(9)$ Å, $b = 12.5995(9)$ Å, $c = 7.5587(5)$ Å, volume = $1039.16(16)$ Å³, are based upon the refinement of the XYZ-centroids of 6378 reflections above $20 \sigma(I)$ with $5.389^\circ < 2\theta < 54.30^\circ$. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.929. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9270 and 0.9660. The final anisotropic full-matrix least-squares refinement on F_2 with 113 variables converged at $R_1 = 2.55\%$, for the observed data and $wR_2 = 5.91\%$ for all data. The goodness-of-fit was 1.010. The largest peak in the final difference electron density synthesis was $0.147 \text{ e}/\text{Å}^3$ and the largest hole was $-0.108 \text{ e}/\text{Å}^3$ with an RMS deviation of $0.028 \text{ e}/\text{Å}^3$. On the basis of the final model, the calculated density was $1.436 \text{ g}/\text{cm}^3$ and $F(000)$, 460 e⁻.

Mold preparation. To prepare cured resin bars for TMA analysis, silicone molds were prepared using Silpak Inc. R2374A silicone mixed with R2374B curing agent in a 10:1 weight ratio. The mixture was degassed for 90 min at ambient temperature under reduced pressure and cured overnight at room temperature followed by 150°C for 60 min.

Preparation of test articles from PhosCy and MPhosCy. Cyanate esters were transferred into the mold, and placed into an oven at 110 °C under reduced pressure for 30 min to degas. Degassed samples were placed under a nitrogen atmosphere and heated to 150 °C for 3 h and then 210 °C for 24 h. Samples were then cooled to ambient temperature over a 5 h period and removed from the silicone mold. MPhosCy samples were further post-cured at 240 °C for 18 h followed by 3 h at 270 °C. Sample bars were 20 mm x 2 mm x 2 mm in dimension and weighed ~200 mg. Bars were cut to 10 mm in length and were shaved to a height of ~ 2 mm prior to TMA analysis.

Preparation of test articles from PhosCy3. The cyanate ester crystals were crushed into a fine powder with a mortar and pestle, packed into the mold, and placed into an oven at 130 °C under N₂. The sample was heated to 180 °C and then placed under reduced pressure for 30 min to degas. The samples were then placed under a nitrogen atmosphere and heated to 230 °C for 24 hr. Samples were cooled to room temperature over a 4 h period and then removed from the silicone mold. Samples were post-cured by slowly heating (over a 60 min period) to 240 °C for 60 min, and then heating to 270 °C for 3 h. The size and shape of the bars was similar to those described above.

Differential Scanning Calorimetry (DSC). 5-10 mg pieces of the cyanate ester resins were hermetically sealed in aluminum DSC pans. Samples were then ramped under 50 mL/min of flowing nitrogen at 5 °C / min, from -40 °C to 400 °C using a TA Instruments Q100 DSC. The melting points for PhosCy and PhosCy3 were obtained from these experiments and are simply the temperatures corresponding to the maximum endothermic heat flows.

Dynamic-mode TMA. Dynamic-mode TMA was performed using a TA Instruments Q400-0537 analyzer under 100 mL/min N₂. The bars were placed in contact with a flat, cylindrical probe under a force of 0.10 N. Samples were cooled to -50 °C then heated at 5 °C/min to 250-395 °C depending on the sample. The force was modulated ± 0.04 N at a frequency of 0.05 Hz during the cycle.

Thermogravimetric Analysis Fourier Transform Infrared Spectroscopy (TGA-FTIR).

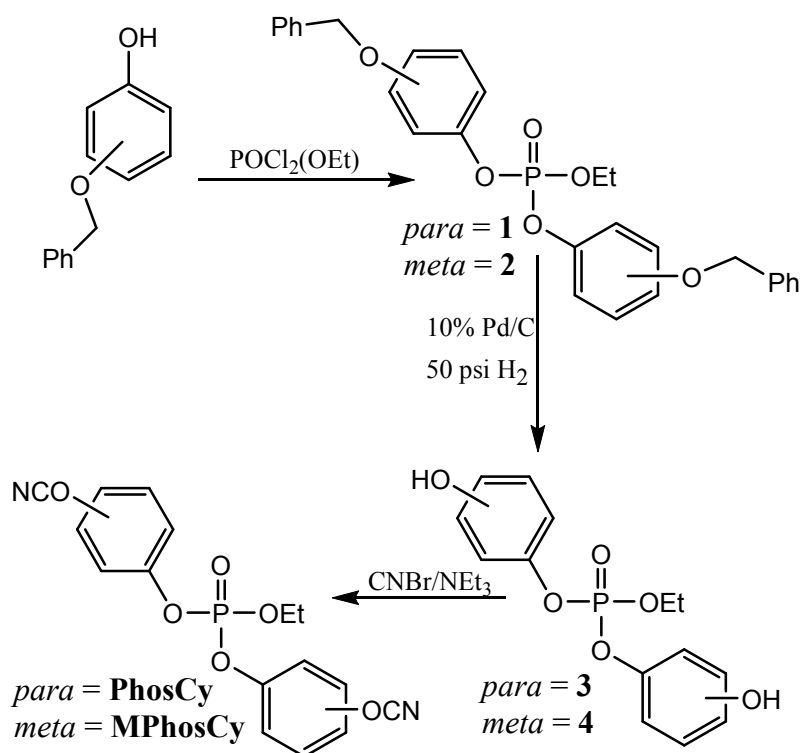
Samples were analyzed using a Thermo Nicolet Nexus 870 FTIR interfaced via a heated gas cell and transfer line (held at 150 °C) to a TA Instruments Q50 TGA. The TGA was set to ramp from ambient temperature to 600 °C at a rate of 10 degrees per min. FTIR spectra are an average of 32 scans at 4 cm⁻¹ resolution. A liquid nitrogen cooled MCTA detector was used. Spectra were background corrected with the gas cell heated and under a nitrogen purge.

DFT Calculations

DFT calculations were conducted using Gaussian03 with the basis set 6-31G(d,p) and the B3LYP functional. All compounds were first fully optimized and then a frequency calculation was performed to obtain total energies.

Results and Discussion

To synthesize a hybrid resin that combined aromatic cyanate esters bridged by a phosphate group, PO(OEt)Cl₂ was allowed to react with two equivalents of p-benzyloxyphenoxide (Scheme 1) to generate compound **1** in excellent yield (91%). Reductive elimination of the benzyl groups (10% Pd/C/50 psi H₂) then yielded bisphenol **3**. Subsequent reaction with cyanogen bromide in the presence of triethylamine generated the bis(cyanate) ester (PhosCy) in near quantitative yield. PhosCy was stable to column chromatography and was isolated as a thick oil that slowly solidified over time. To expand the scope of these materials, an isomer of PhosCy with the cyanate ester group in the position *meta* to the bridging group (MPhosCy) was prepared by an analogous route (Scheme 1).



Scheme 1. Synthesis of PhosCy and MPhosCy

MPhosCy was also stable to chromatography and the *meta*-substitution of the aromatic rings resulted in a liquid resin at room temperature. The low melting points of both PhosCy and MPhosCy make them interesting materials for the fabrication of composites.

PhosCy and MPhosCy were characterized by NMR and FTIR spectroscopy (Figures S1-4, S10, S11). PhosCy only exhibited 3 discernable resonances in the ^1H NMR spectrum with all 8 of the aromatic protons appearing as a singlet at 7.48 ppm. The methylene of the ethoxy group appeared at 4.40 ppm as a doublet of quartets due to the splitting of the adjacent methyl group and the phosphorus atom. Similarly, the methyl group appeared upfield at 1.36 ppm as a doublet of triplets. The ^{13}C NMR spectrum exhibited 7 resonances. The 4 downfield resonances are attributed to the aromatic carbons, while the low intensity peak at 108.4 ppm is due to the quaternary carbon of the cyanate ester group. The ethoxy carbons are found as peaks at 66.1 and 15.4 ppm. The ^1H NMR spectrum of MPhosCy was more complicated than that of PhosCy due to the *meta*-substitution of the aromatic ring. The aromatic hydrogens were observed as two multiplets appearing at 7.62 and 7.35 ppm and integrating as 2 and 6 hydrogens, respectively, while the methylene of the ethoxy group was observed as a doublet of quartets at 4.42 ppm and the methyl group as a doublet of triplets centered at 1.38 ppm. The ^{13}C NMR spectrum exhibited 9 resonances. The six peaks from 153.3 to 108.2 ppm are attributed to the aromatic carbons, while the low intensity peak at 108.0 ppm is assigned as the quaternary carbon of the cyanate ester group. The ethoxy carbons are found at 66.4 and 15.4 ppm.

The cure chemistry of PhosCy and MPhosCy was probed by DSC. Due to the very slow crystallization of pure PhosCy, we initially believed the resin was a liquid. After purification, the thick oil often remains unchanged for days to weeks. However, DSC analysis showed that the monomer is actually present as a super-cooled liquid which exhibited a freezing transition at

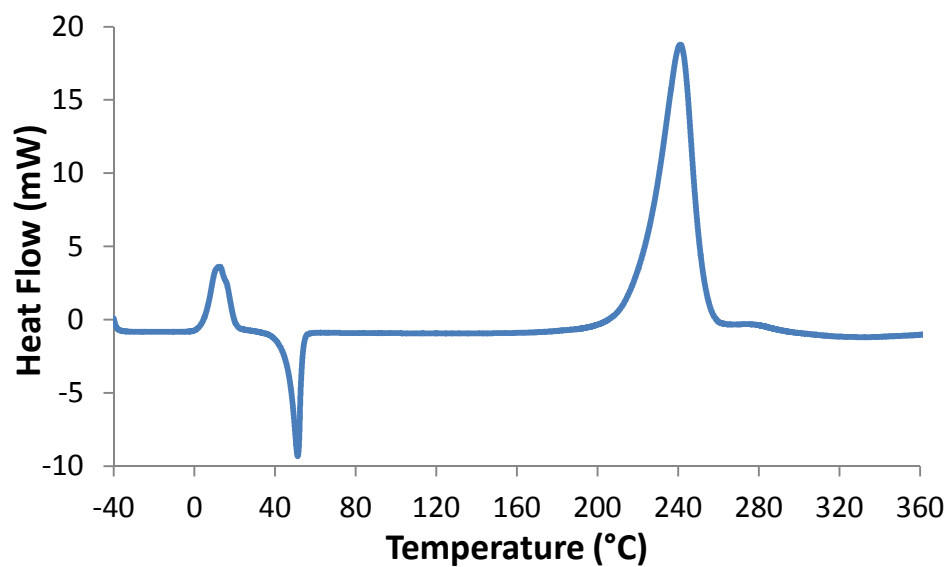


Figure 1. DSC data for PhosCy

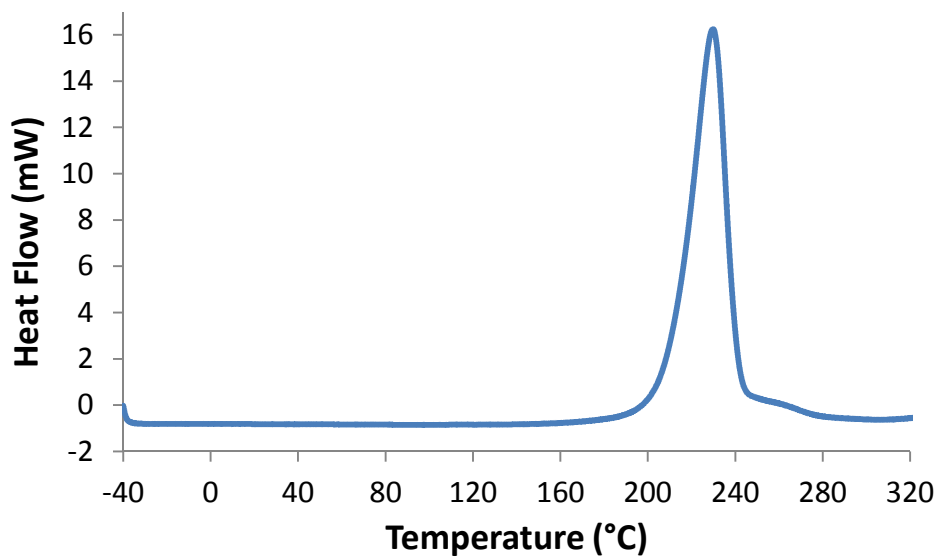


Figure 2. DSC data for MPhosCy

12.6 °C followed by a sharp melt transition at 51 °C (Figure 1). The sample was then stable up to ~200 °C at which point the material underwent cyclotrimerization to form a polycyanurate network. The peak of the exotherm was at 241 °C and the change in enthalpy for the trimerization was 110 kJ/(mol -OCN) which is consistent with the typical literature value of 100 kJ/(mol -OCN).²⁰ MPhosCy showed no low temperature transitions suggesting that it is a permanent liquid at room temperature (Figure 2). The onset of cyclotrimerization began at a similar temperature compared to PhosCy, with a peak exotherm observed at 230 °C. The enthalpy of cyclotrimerization was 105 kJ/(mol equiv. cyanate ester).

To further examine the cure chemistry of the resins and measure the T_g s of the cured thermosets, samples of each resin were thermally cured without addition of a catalyst to generate test articles that were evaluated by FTIR and TMA. An initial cure cycle of 150 °C for 3 h followed by 210 °C for 24 h was employed for both PhosCy and MPhosCy. To ensure complete cure, the samples were then post-cured at 240 °C for 18 h, followed by 270 °C for 3 h. TMA showed that the post-cure actually decreased the T_g of the PhosCy derived thermoset material, but improved the T_g of cured MPhosCy. On this basis, test articles prepared from PhosCy were only cured under the low temperature protocol, while test articles prepared from MPhosCy underwent the high temperature post-cure. FTIR spectra taken before and after the respective heating cycles confirmed that both resins cured completely (Figures S10 and S11). TMA revealed a T_g ($\tan \delta$) of 223 °C for PhosCy (low temperature cure, Figure S16). In contrast, MPhosCy with its *meta*-substitution exhibited a maximal T_g (high temperature post-cure) of only 131 °C (Figure S17). Interestingly, the T_g of the MPhosCy thermoset after the low temperature cure protocol was only 112 °C, despite the cure proceeding well above the T_g . This suggests that MPhosCy undergoes a subtle high-temperature secondary cure mechanism during the post-cure, likely through

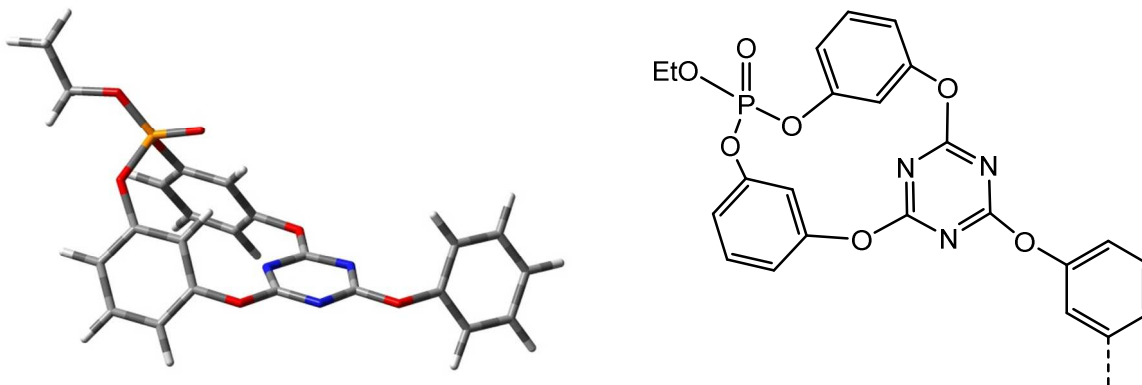


Figure 3. Potential endcap structures for MPhosCy. The structure on the left was generated by GaussView

phosphate crosslinking. Some evidence for this is observed in the DSC trace for MPhosCy which exhibits a modest secondary exotherm starting at approximately 240 °C (Figure 2).

The T_g s of both these resins are significantly lower than conventional cyanate ester resins prepared from bisphenol A or bisphenol E (as cured T_g s of 291 and 275 °C, respectively).²¹ However, unlike these conventional cyanate ester resins bridged by isopropylidene or ethylidene groups, the current molecules have a much more flexible (O-P-O) bridging structure combined with a flexible ethoxide group. The T_g of MPhosCy is 92 °C lower than PhosCy, suggesting that the *meta*-substitution may allow for both cyanate ester groups in a single molecule to combine in the same cyanurate ring system, which lowers the effective cross-link density. A number of researchers have reported the intramolecular cyclization of aromatic dicyanates.²²⁻²⁴ To explore this possibility for MPhosCy, a surrogate molecule was modeled in which two cyanate esters from one molecule of MPhosCy were incorporated into a cyanurate ring system. To mimic the actual network, the remaining carbon in the ring system was functionalized with a phenoxide group. An optimized structure representing a true minimum was successfully refined with

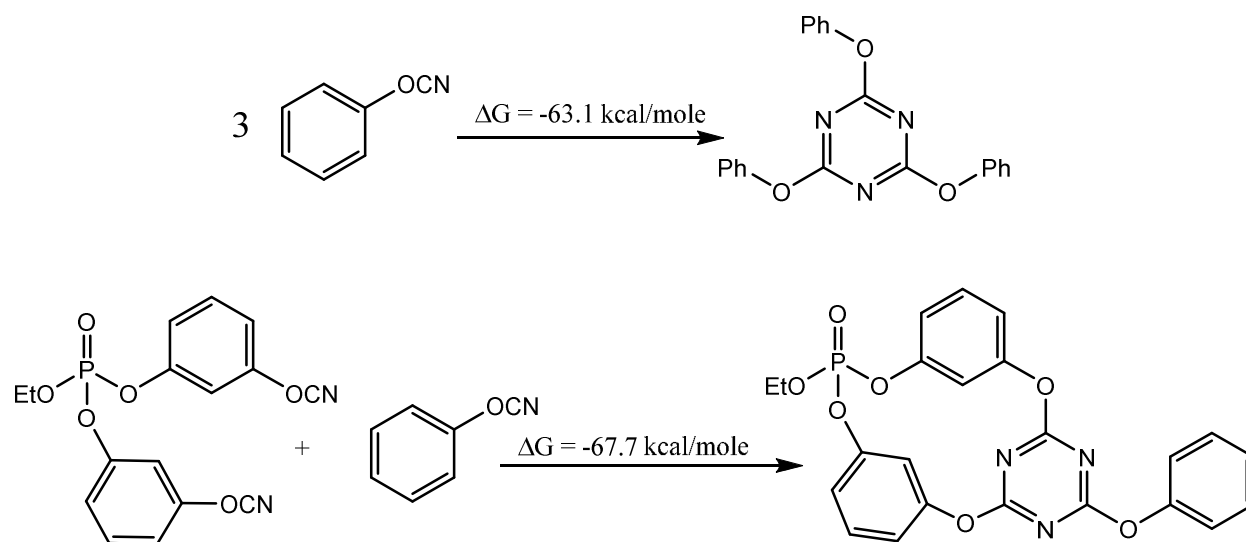


Figure 4. Comparison of different reaction pathways for **MPhosCy**

Gaussian03 (Figure 3). To provide further evidence for the intramolecular cyclization, ΔG was calculated for the gas phase cyclotrimerization of 3 equivalents of phenyl cyanate and compared to the cyclotrimerization of MPhosCy and one equivalent of phenyl cyanate (Figure 4). The latter reaction was favored by 4.6 kcal/mol suggesting that this is a key mechanism occurring during thermal polymerization of MPhosCy.

After gaining some insight into the cure chemistry of MPhosCy, the thermal stability and thermal decomposition pathways of PhosCy and MPhosCy were then probed by TGA-FTIR. Under N_2 , PhosCy lost 5% of its mass at 328 °C and 10% by 368 °C. The char yield at 600 °C was 45% under N_2 and 47% in air (Figure 5). Gas phase FTIR data showed that the initial weight loss was due to evolution of isocyanic acid, carbon dioxide, and ethylene. Mass loss at 450 °C was due primarily to isocyanic acid and ammonia, while the mass loss at 520 °C was dominated by phenol. MPhosCy showed slightly higher thermal stability with 5% mass loss by 343 °C and

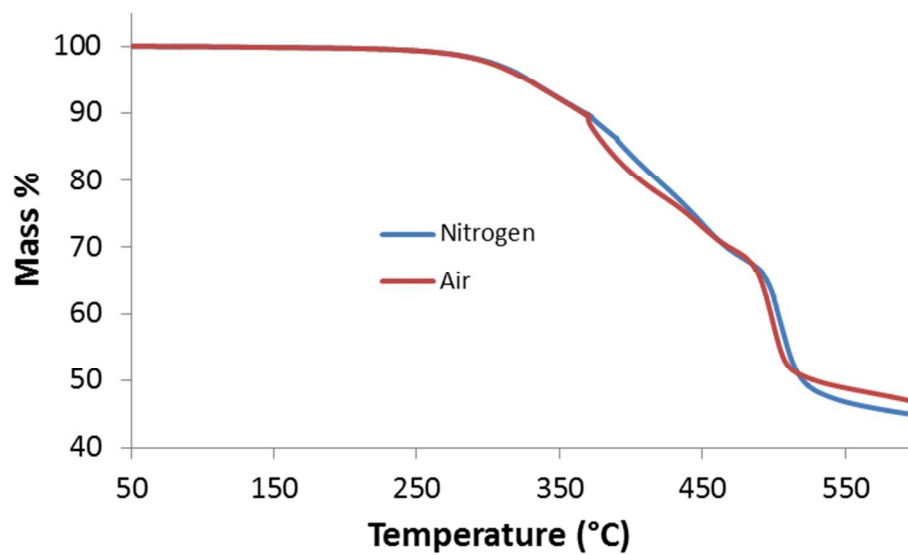


Figure 5. TGA data for PhosCy

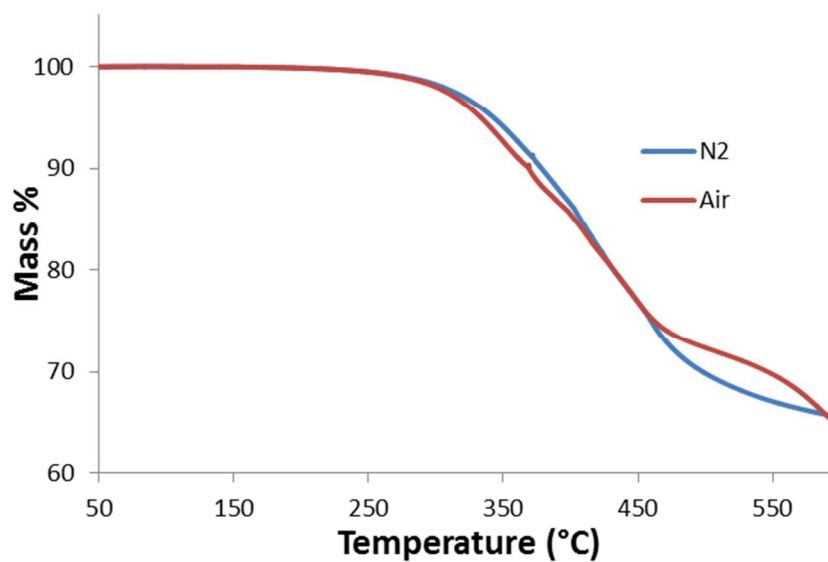
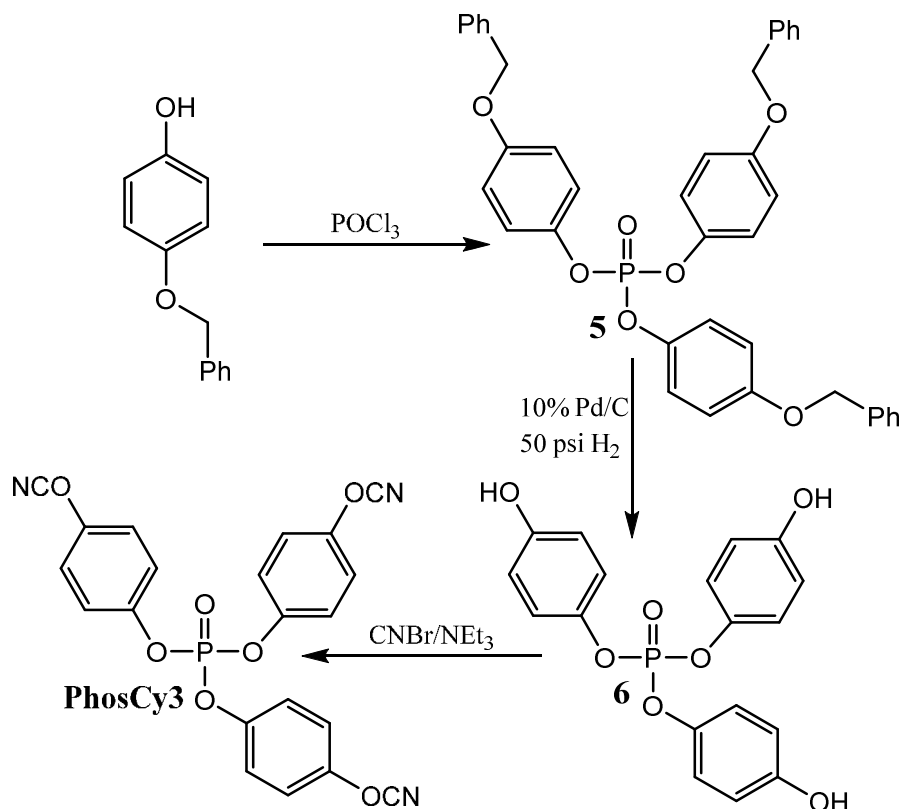


Figure 6. TGA data for MPhosCy

10% mass loss by 379 °C. The char yield at 600 °C was an impressive 66% in N₂ and 65% in air (Figure 6). The decomposition products of MPhosCy were similar to PhosCy.

The higher thermal stability and char yield of MPhosCy is puzzling, but a potential explanation is that the low T_g of the material provides a larger window in which intermolecular interactions can occur. Cross-linking between phosphate groups at elevated temperature is an important char forming mechanism for phosphate containing polymers.^{2,5} Both the TMA and TGA results suggest that thermal curing of MPhosCy results in end-capped structures that then cross-link through loss of the ethoxy group. Although PhosCy undergoes the same cross-linking reaction, as evidenced by a secondary exotherm in the DSC at 270 °C (Figure 1), the higher T_g and greater cyanurate cross-link density of PhosCy significantly reduces the ability of the network to reorganize as phosphate cross-linking proceeds.

Based on the TMA and TGA data for PhosCy and MPhosCy and the evolution of ethylene in the FTIR experiment, it was clear that the ethoxy group bound to the central phosphorus atom decreased the utility of these resins by lowering their T_gs, thermal stability, and char yields. To eliminate the ethoxy group and generate a thermosetting resin with a higher T_g, a tris(cyanate) ester (PhosCy3) was prepared from POCl₃ (Scheme 2). PhosCy3 was characterized by both NMR and FTIR spectroscopies (Figures S5, S6, and S12). The ¹H NMR spectrum exhibited a broad single resonance at 7.37 ppm. The ¹³C NMR was similarly straightforward, exhibiting 5 peaks. The 4 downfield peaks from 150.2 to 117.1 ppm are attributed to the aromatic carbons, while the low intensity peak at 108.4 ppm is assigned as the carbon of the cyanate ester group. Recrystallization of PhosCy3 from ethyl acetate resulted in crystals suitable for a single crystal X-ray diffraction study. PhosCy3 crystallized in a highly symmetric trigonal space group with one-third of the molecule in the asymmetric unit. PhosCy3 has a trigonal pyramidal structure



Scheme 2. Synthesis of PhosCy3

with an O-P=O bond angle of $116.73(8)^\circ$ and O-P-O bond angles of $101.34(9)^\circ$. In the solid state PhosCy3 is chiral and has C_3 symmetry (Figure 7). Key crystallographic information is listed in Table 1 and additional X-ray data is included in the supporting information.

The cure chemistry of PhosCy3 was first explored by DSC. The resin melted cleanly at 119°C . Although this is somewhat high for a cyanate ester, it is not prohibitive in regard to processing and is similar to the melting point of a recently reported tris(cyanate) ester based on dihydroresveratrol.¹⁰ The onset of cure for PhosCy3 begins at a lower temperature than for PhosCy or MPhosCy, starting at about 135°C and continuing up to about 300°C with a peak exotherm at 248°C (Figure 8). The broadness of the exotherm is likely due to the trifunctional

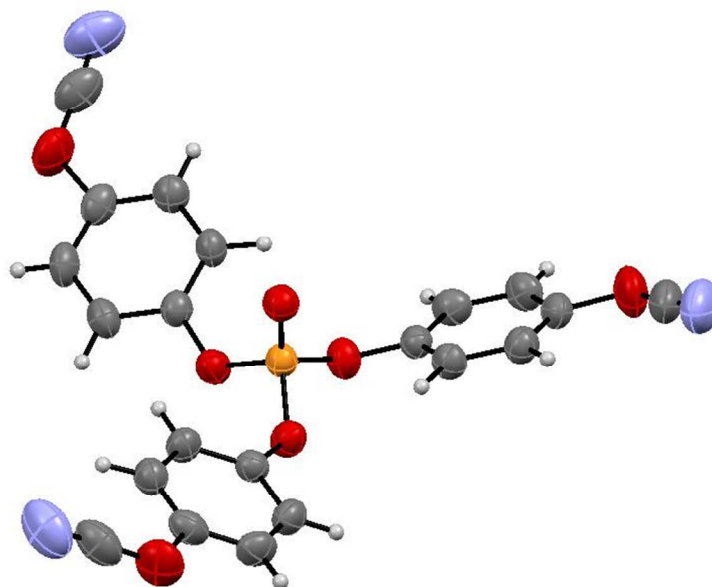


Figure 7. Solid state structure of PhosCy3

Table 1. X-ray Crystallographic Data for PhosCy3

empirical formula	C ₂₁ H ₁₂ N ₃ O ₇ P
formula weight	449.31
temperature	296(2) K
wavelength	0.71073 Å
crystal size	0.192 x 0.225 x 0.425 mm
crystal system	trigonal
space group	P 3 1 c
unit cell dimensions	a = 12.5995(9) Å, α = 90° b = 12.5995(9) Å, β = 90° c = 7.5587(5) Å, γ = 120°
volume	1039.16(16) Å ³
Z	2
density (calculated)	1.436 g/cm ³
θ range for data collection	1.87 to 26.37°
reflections collected	12418
independent reflections	1431 [R(int) = 0.0233]
data / restraints / parameters	1431 / 1 / 113
goodness-of-fit on F ²	1.010
final R indices [I > 2σ(I)]	R1 = 0.0255, wR2 = 0.0580

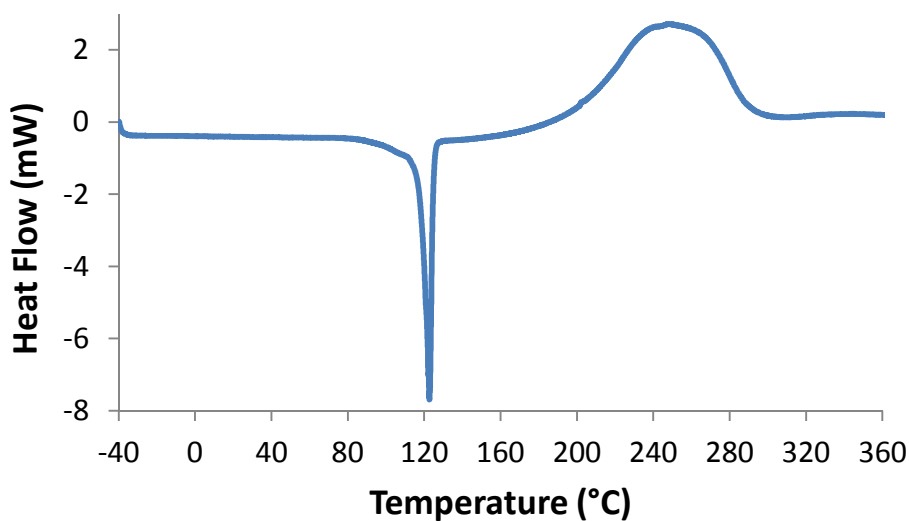


Figure 8. DSC data for **PhosCy3**

nature of the resin and suggests that full cure is more difficult for PhosCy3 compared to PhosCy and MPhosCy. Despite this, the enthalpy of trimerization was 101 kJ/(mol -OCN), consistent with a high degree of cure. A cured resin bar was prepared under conditions similar to those utilized for MPhosCy and FTIR confirmed that complete cure had taken place (Figure S12). A cured bar was then subjected to TMA. The loss peak and $\tan \delta$ peaks were still increasing even at 390 °C, while the storage trace suggested a T_g of >360 °C. This is a remarkable T_g for a cyanate ester, nearly 90 °C higher than BADCy.²¹

As expected, PhosCy3 showed significantly higher thermal stability compared to PhosCy and MPhosCy. TGA/FTIR analysis showed 5% weight loss at 428 °C, while 10% weight loss was observed at 443 °C. The thermal stability in air was remarkably similar with 5% weight loss at 423 °C and 10% weight loss at 437 °C (Figure 9). The initial decomposition starting at about 400 °C generated primarily ammonia and CO₂ due to degradation of the cyanurate ring system.

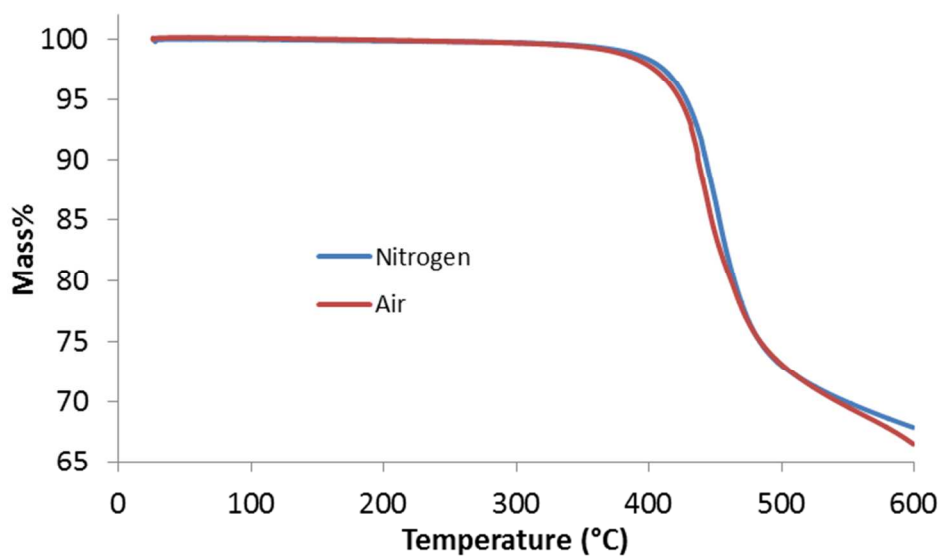


Figure 9. TGA data for **PhosCy3**

At 550 °C the primary decomposition product observed was phenol. At 600 °C PhosCy3 exhibited a remarkable char yield of 68% in nitrogen and 67% in air. The key properties of all three phosphate cyanate esters are compared in Table 2.

Table 2. Key properties of phosphate cyanate esters

Resin	T_g (°C)	T_m (°C)	Char Yield (N ₂)	Char Yield (air)	ΔH_{cure} (kJ/mol)	%P
PhosCy	223	51	45%	47%	110	8.5
MPhosCy	131	<RT	66%	65%	105	8.5
PhosCy3	>360	119	68%	67%	100	6.9

Conclusions

A series of cyanate ester resins with bridging phosphate groups has been synthesized. The T_g s of these materials varied between 131 and >360 °C depending on the number of cyanate ester groups per phosphate and the substitution pattern of the aromatic rings. The low T_g for MPhosCy is attributed to intramolecular cyclization which is supported by DFT calculations. The high char yields of these resins coupled with the phosphate core suggests that these materials will have applications as fire-resistant polymers. Alternatively, these materials can potentially be blended with conventional cyanate esters or other compatible thermosetting resins to improve the fire resistance of composite materials. Other applications may include use in fire-resistant circuit boards, or as surface coatings to reduce flammability of conventional composite materials or thermoplastics. Studies along these lines are currently being undertaken in our laboratory.

Acknowledgements

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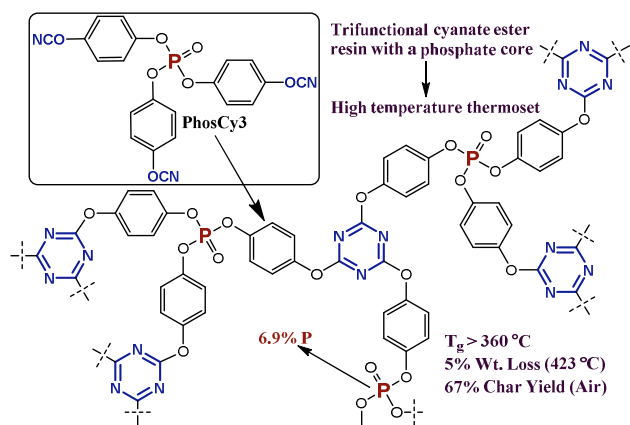


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