Synthesis and characterization of novel cyclotriphosphazene-containing poly(ether imide)s

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Novel cyclotriphosphazene-containing poly(ether imide)s have been developed by nucleophilic displacement of active nitro groups of tris[4-(3'-nitrophthalimido)phenoxy]tris(phenoxy)-cyclotriphosphazene (**I**) or tris[4-(4'-nitrophthalimido)phenoxy]tris(phenoxy)cyclotriphosphazene (**II**) and a bisnitrophthalimido derivative by the dianion of bisphenol A. The synthesized polymers were characterized by Fourier-transform infra-red and ^{1}H, ^{13}C and ^{31}P nuclear magnetic resonance spectroscopy, differential scanning calorimetry (d.s.c.) and thermogravimetric analysis (t.g.a.). The d.s.c. of the polymers demonstrated glass transition temperatures in the range of 179–184°C. The thermal stabilities of the polymers were evaluated in nitrogen and in air by dynamic t.g.a. The synthesized polymers were thermally stable. The dynamic t.g.a. showed thermal decomposition starting at 410–415°C and char yield of 59–42% in nitrogen at 800°C and 30–32% in air at 700°C. Gel permeation chromatography showed a weight-average molecular weight of the polymer of 6.5×10^3. The polymer prepared from cyclotriphosphazene monomer I showed thermoplastic melt processing at 250°C to tough film and moulding.

(Keywords: cyclotriphosphazene; nitrophthalimides; thermoplastic; poly(ether imide)s; nitro displacement; synthesis; characterization; thermal analysis)

INTRODUCTION

There is a growing demand for fire-resistant and heat-resistant polymeric materials for civil and defence applications. However, most commercially available polymers lack structural integrity and fire-retardancy at high temperatures and also give off smoke and toxic gases when burned in air. Phosphazene derivatives have been known to impart fire-retardancy in polymers. The chlorophosphazenes and their derivatives have been used as additives[1] for this purpose, but the additives can leach out or migrate to specific sites, rendering the system unsuitable. The linear poly(phosphazenes)[2], on the other hand, are expensive and may not be suitable for high-temperature applications owing to their known possibility of degradation.

In recent years, our group and others have developed exciting alternative methodologies for incorporating cyclophosphazenes into the structure of commercial polymers. This approach is based on exploiting the reactivity of organofunctional phosphazenes. We have successfully developed cyclotriphosphazene-containing polybismaleimides[3–7], polyimides[8] and epoxy matrix resins[9,10] and have demonstrated that these polymers are better materials than other reported phosphorus-containing polymers[11–14] for use as composites and adhesives. The particular enhanced properties obtained were high char yield of polymers in air and nitrogen and 100% limited oxygen index (*LOI*) of their graphite cloth laminates. These attractive properties of the cyclotriphosphazene-containing polymers prompted our efforts to improve further upon their stability, flexibility and toughness without forfeiture of their fire-resistant characteristics. We have recently synthesized[15] and characterized 3-nitrophthalimido- and 4-nitrophthalimidocyclotriphosphazene monomers and intermediates. In this paper we present the synthesis and characterization of cyclotriphosphazene-incorporated poly(ether imide)s via nitro displacement polymerization. The nitro displacement method has been exploited[16–19] by the investigators of the General Electric Company for the development of Ultem[R], a commercial poly(ether imide). Poly(ether quinoxalines) have also been synthesized[20] using this method. This reaction was discovered earlier[21,22] and a review on the exploitation of aromatic nucleophilic displacement of the activated nitro group has been published[23] by Beck.

EXPERIMENTAL

Equipment

Thermal analysis was performed on a Perkin–Elmer Thermal Analysis Data Station interfaced with a TGS-2 Thermogravimetric System. Glass transition temperatures (T_g) were recorded with the use of a DSC-4 Differential Scanning Calorimeter, heating rate 50°C min^{-1} for d.s.c. and 20°C min^{-1} for t.g.a., gas flow 100 ml min^{-1} and sample weight 2–3 mg. All n.m.r. spectra, in deuterated dimethylsulfoxide (DMSO-d_6), were measured on a Bruker WM-250 spectrometer with

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an Aspect 3000 computer. The operating frequencies were 250.1 (^{1}H), 62.9 (^{13}C) and 101.2 MHz (^{31}P). Tetramethylsilane (Me_4Si) was used as an internal reference for ^{1}H and ^{13}C n.m.r. measurements. For ^{31}P n.m.r. measurements 85% H_3PO_4 was used as an external standard. Chemical shifts downfield of the reference were assigned a positive sign. ^{13}C and ^{31}P n.m.r. spectra were recorded under conditions of broad-band decoupling. Infra-red spectra were recorded on a FT-Nicolet 6000 series spectrophotometer as a KBr disc. Gel permeation chromatography molecular-weight estimates were obtained on a Waters 6000 Å high-performance liquid chromatograph equipped with a refractive-index detector. Three Waters Microstyragel gel columns as a set ($10^3 + 10^4 + 10^5$ Å) were used for the analysis of polymers that are soluble in tetrahydrofuran (THF). The instrument was calibrated against secondary polystyrene standards. Mass spectra were recorded on a Finnigan 4610 spectrometer operating at 80 eV.

Materials

Tris[4-(3′-nitrophthalimido)phenoxy]tris(phenoxy)-cyclotriphosphazene (**I**) and tris[4-(4′-nitrophthalimido)phenoxy]tris(phenoxy)cyclotriphosphazene (**II**) were synthesized by us by the reaction of tris(4-aminophenoxy)tris(phenoxy)cyclotriphosphazene with 3-nitrophthalic anhydride/4-nitrophthalic anhydride, and the details are given elsewhere[15]. 4,4′-Bis(3-nitrophthalimido)diphenyl ether (**IV**), m.p. 306–307°C (lit.[19], m.p. 302–304°C), and 4,4′-bis(4-nitrophthalimido)diphenyl ether (**V**), m.p. 321–323°C (lit.[19], m.p. 322–323°C), were synthesized from 4,4′-diaminodiphenyl ether and 3-nitrophthalic anhydride/4-nitrophthalic anhydride by refluxing in phenol and toluene, and were characterized by i.r., ^{1}H n.m.r. and mass spectroscopy, *N*,*N*′-Dimethylsulfoxide (DMSO) was distilled from CaH_2 before use. Toluene was dried by refluxing over sodium and CaH_2. It was distilled under nitrogen. Bisphenol A (**III**) was recrystallized from methanol and dried, m.p. 158–159°C.

Polymerization by nitro displacement reaction

The polymerization of the active nitro groups containing cyclotriphosphazene derivative and a bisimide aromatic compound by the dianion of bisphenol A was performed under dry conditions. A typical polymerization is described below (see *Scheme 1*).

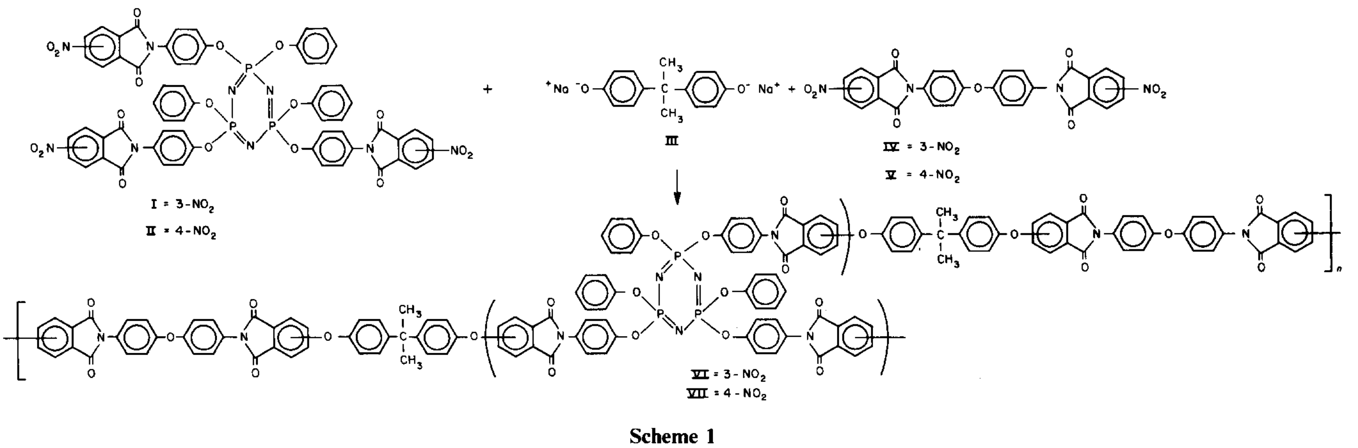
In a flame-dried three-necked flask equipped with a stirrer, thermometer, nitrogen inlet and a condenser with a guard tube, sodium metal (0.46 g, 2×10^{-2} mol) was dissolved in absolute ethanol (30 ml). To this solution, bisphenol A (2.28 g, 1×10^{-2} mol) was added and stirring continued for 0.5 h. The ethanol was removed by distillation and a Dean–Stark condenser was fitted to the flask. Toluene (30 ml) was added to the sodium salt of bisphenol A and the temperature of the reaction was raised to 140°C. The toluene was collected by distillation and the Dean–Stark condenser was replaced by a CaH_2 trap. Toluene (30 ml) and DMSO (20 ml) were added and the temperature of the reaction was increased to 160°C. The toluene was continuously collected to ensure complete removal of water. The reaction mixture was cooled to 40°C and tris[4-(3′-nitrophthalimido)phenoxy]tris(phenoxy)cyclotriphosphazene (**I**) (0.84 g, 6.6×10^{-4} mol) and 4,4′-bis-(3-nitrophthalimido)diphenyl ether (**IV**) (4.95 g, 9×10^{-3} mol) were added along with anhydrous DMSO (20 ml) and toluene (30 ml). The reaction was allowed to stir overnight at 50°C. The reaction mixture was poured into cold water. The brown powder was filtered, washed and dried in vacuum to give polymer **VI** in 90% yield.

Using similar reaction conditions polymer **VII** was synthesized by nucleophilic nitro displacement of tris[4-(4′-nitrophthalimido)phenoxy]tris(phenoxy)-cyclotriphosphazine (**II**) (3.08 g, 2.43×10^{-3} mol) and 4,4′-bis(4-nitrophthalimido)diphenyl ether (**V**) (3.48 g, 6.32×10^{-3} mol) by the disodium salt of bisphenol A (2.60 g, 1×10^{-2} mol) in DMSO at 60°C overnight. The brown polymer **VII** was obtained in 88% yield.

RESULTS AND DISCUSSION

The specific reaction sequence used for the synthesis of cyclotriphosphazene-containing poly(ether imide)s is outlined in *Scheme 1*. The polymer precursors, tris[4-(3′-nitrophthalimido)phenoxy]tris(phenoxy)-cyclotriphosphazene (**I**) and tris[4-(4′-nitrophthalimido)phenoxy]tris(phenoxy)cyclotriphosphazene (**II**) were recently synthesized and characterized by us[15].

The polymerization was conveniently carried out in a dipolar aprotic solvent, such as *N*,*N*′-dimethylsulfoxide (DMSO) under dry conditions. The polymerization of tris[4-(3′-nitrophthalimido)phenoxy]tris(phenoxy)-cyclotriphosphazene (**I**) and 4,4′-bis(3-nitrophthalimido)diphenyl ether (**IV**) with the disodium salt of bisphenol A gave a brown polymer (**VI**) in good yield. Similarly, polymer **VII** was synthesized selecting a



Scheme 1

different stoichiometry of tris[4-(4′-nitrophthalimidophenoxy)]tris(phenoxy)cyclotriphosphazene (**II**) and 4,4′-bis(4-nitrophthalimido)diphenyl ether (**V**) with the disodium salt of bisphenol A. In general, 3-nitro isomers were more reactive than the corresponding 4-nitro isomers under identical conditions. The i.r. spectra of the polymers prepared showed absorption of –P=N– stretching and bending at 1200–1150 cm^{-1}, the imide carbonyl at 1783 and 1717 cm^{-1}, aromatic group at 1493 cm^{-1} and the ether group at 1238 cm^{-1}. A representative i.r. spectrum for polymer **VI** is shown in *Figure 1*. This indicated that the cyclotriphosphazene skeleton was incorporated with the formation of ether imide linkages in the polymers.

A confirmation for the complete nucleophilic displacement of active nitro groups was seen from the ^{1}H n.m.r. and ^{13}C n.m.r. spectra of the polymers. The ^{1}H n.m.r. spectra of the synthesized polymers showed the absence of the downfield aromatic protons at 7.9–8.1 ppm (observed in **I** due to the electron-withdrawing nature of the 3-nitro groups). *Figure 2* shows a ^{1}H n.m.r. spectrum of polymer **VI** in DMSO-d$_6$. The observation of coalescing multiplet due to the aromatic protons at 7.8–7.0 ppm along with the presence of the isopropylidene group at 1.7 and 1.6 ppm of the bisphenol A confirmed the incorporation of the cyclotriphosphazene and bisphenol skeletons with the formation of ether linkages.

The ^{13}C n.m.r. spectrum of the polymers further confirmed the formation of ether imide linkages along with the incorporation of cyclotriphosphazene, bisimide and bisphenol A moieties. The chemical shifts of the carbons for cyclotriphosphazene-containing polymer precursors **I** and **II** and the polymer **VI** are given in *Tables 1* and *2*, respectively. The observation of chemical shifts in polymer **VI** of C-8 at 165.8 ppm and C-12 at 147.3 ppm and the absence of a 162.5 ppm signal (observed for C-8 of polymer precursor **I**) along with the presence of isopropylidene group carbons (C-13 and C-14) at 42.1 and 30.8 ppm, respectively, confirmed the

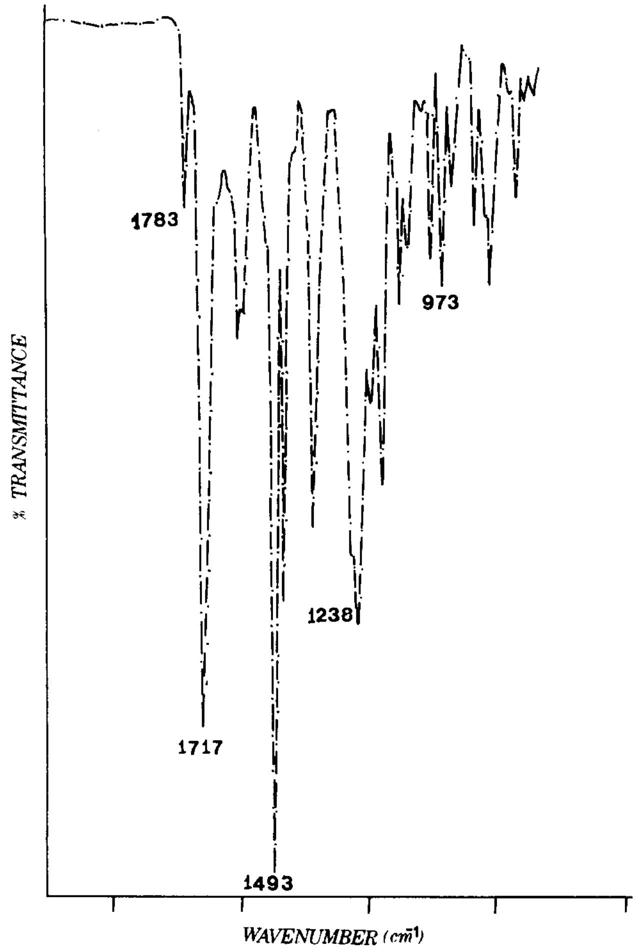


Figure 1 Infra-red spectrum of polymer **VI** on a KBr disc

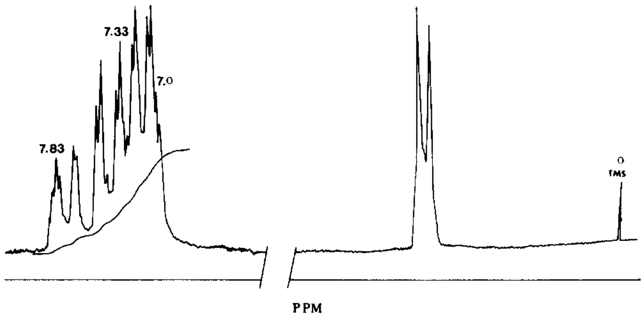
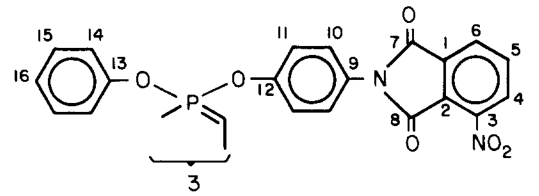
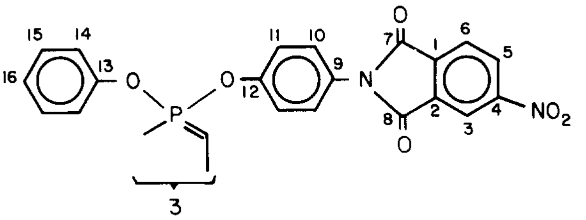


Figure 2 Proton n.m.r. spectrum of polymer **VI** in DMSO-d$_6$ at 250 MHz

Table 1 ^{13}C n.m.r. spectral data for cyclotriphosphazene-containing polymer precursors **I** and **II**[a]



I

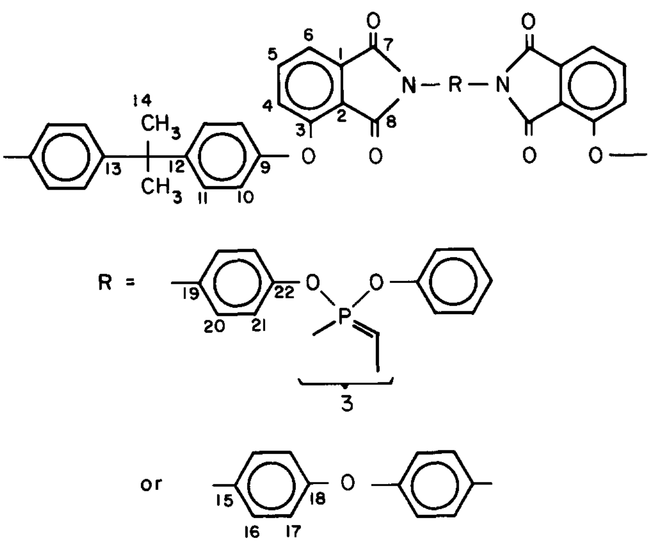


II

Carbon atom	Observed chemical shift of **I** (ppm)	Observed chemical shift of **II** (ppm)
1	133.5	133.6
2	123.1	133.2
3	144.8	118.0
4	127.3	151.7
5	136.6	129.5
6	128.6	125.2
7	165.6	165.5
8	162.5	165.8
9	130.6	130.8
10	127.0	126.6
11	128.8	128.7
12	149.9	149.9
13	150.0	150.1
14	120.8	120.8
15	121.3	121.4
16	128.8	128.5

[a] The observed chemical shifts for carbons 1–12 of **I** and **II** were close to the chemical shifts[18] of 3-nitro-*N*-phenylphthalimide and 4-nitro-*N*-phenylphthalimide, respectively

Table 2 ^{13}C n.m.r. spectral data for cyclotriphosphazene-containing poly(ether imide) **VI**



Carbon atom	Observed chemical shift (ppm)	Carbon atom	Observed chemical shift (ppm)
1	133.9	12	147.3
2	118.5	13	42.1
3	154.8	14	30.8
4	123.1	15	127.5
5	136.9	16	128.5
6	117.9	17	119.5
7	165.4	18	156.3
8	116.8	19	129.6
9	151.8	20	128.7
10	119.4	21	129.5
11	128.5	22	151.2

formation of poly(ether imide) linkages. The ^{31}P n.m.r. spectra of the polymers in DMSO-d_6 showed an A_3 type spin singlet at 14.2 ppm. This confirmed the incorporation of the cyclotriphosphazene ring into the synthesized polymer.

The resulting polymers were soluble in THF, dioxane, DMSO, dimethylacetamide (DMAC), dimethylformamide (DMF) and *N*-methylpyrrolidone (NMP), but insoluble in hydroxylic solvents and stable to atmospheric moisture. The weight-average molecular weight (M_w) of the polymers **VI** was estimated by gel permeation chromatography (g.p.c.) in THF at room temperature using a DRI detector. Based on g.p.c. data (calibrated against polystyrene standards), the weight-average molecular weight (M_w) of the polymer **VI** was 6.5 × 10^3.

Melt processing and thermal characteristics

The polymer **VI** showed thermoplastic melt fusing at 225°C and above. The polymer **VI** on processing at 225–250°C gave tough moulding and film. The polymer **VII** showed poor melt fusing even at 250°C.

The differential scanning calorimetry (d.s.c.) performed on the film of the polymer **VI** showed a glass transition temperature (T_g) at 179°C. On cooling the d.s.c. aluminium pan and rerunning of d.s.c., a glass transition temperature of 184°C was obtained. The nature of the deflection remained the same. The d.s.c. measurements performed on the precipitated polymer samples did not show observable T_g inflections in the d.s.c. curve unless a dense sample, a film or moulding, was used. This is in accordance with the behaviour of known poly(ether imide)s on d.s.c. measurements. The observed moderate T_g value of the polymer **VI** may be principally attributed to the flexible ether linkages in the main chain and to the rotational and flexible freedom of the pendent phenoxy groups of the cyclotriphosphazene moiety.

The thermal stability of the polymers was determined using dynamic thermogravimetric analysis (t.g.a.). The t.g.a. curves were obtained in nitrogen (*Figure 3*) and air (*Figure 4*). The synthesized polymers were stable to 410°C. The polymer **VI** showed a 5% weight loss in air at 425–500°C and a 9% weight loss at 425–555°C. In nitrogen, however, only 1% weight loss was observed at 410–510°C and the thermal stability is comparable to that of conventional poly(ether imide)s. The char yield in nitrogen at 800°C for polymers **VI** and **VII** was 59% and 42%, respectively. The char yield in air at 700°C for polymers **VI** and **VII** was 32% and 30%, respectively. The polymer **VI** thus showed relatively improved thermal stability over polymer **VII**. An explanation for this observation may be sterically restricted rotational freedom around the ether linkage of 3-isomers.

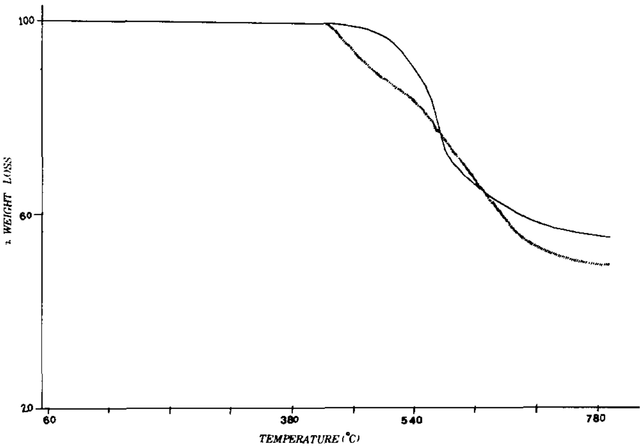


Figure 3 The dynamic thermogravimetric analysis of polymers VI (———) and VII (·····) in nitrogen

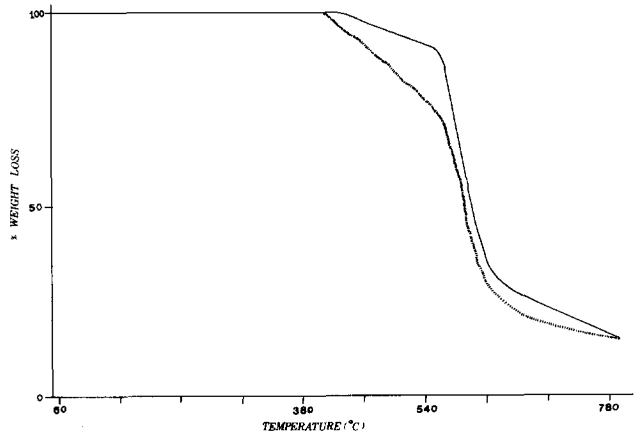


Figure 4 The dynamic thermogravimetric analysis of polymers VI (———) and VII (·····) in air

CONCLUSION

This research constitutes the first report of synthesis of cyclotriphosphazene-containing poly(ether imide)s and has demonstrated the utilization of cyclotriphosphazene-containing 3- and 4-nitrophthalimidophenoxycyclotriphosphazene polymer precursors by the nucleophilic nitro displacement method. The observed characteristics of the polymer **VI**, namely good thermal stability, solubility in practical solvents, moderate glass transition temperature and ease of preparation, make this polymer a suitable candidate for the development of fibre-reinforced composite systems and advanced materials. Further developments of poly(ether imide)s using disubstituted 3- and 4-nitrophthalimidocyclotriphosphazene polymer precursors is continuing and will be part of a forthcoming publication.

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