

Phosphazene Cyclomatrix Network Polymers: Some Aspects of the Synthesis, Characterization, and Flame-Retardant Mechanisms of Polymer

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ABSTRACT: Novel phosphazene cyclomatrix network polymers were synthesized via nucleophilic displacement of activated nitro groups of tri(4-nitrophenoxy)tri(phenoxy)cyclotriphosphazene and hexa(*p*-nitrophenoxy)cyclotriphosphazene with the hydroxyls of bisphenol A. Both the monomers and polymers were characterized by Fourier transform infrared (FTIR) and ¹H-NMR spectroscopy, and their structures were identified. The thermal and flame-retardant properties of the polymers were investigated with thermogravimetric analysis in air, pyrolysis, and combustion experiments. Both solid and gaseous degradation products were collected in a pyrolysis process and analyzed with FTIR

spectroscopy, gas chromatography/mass spectrometry, and scanning electron microscopy. The results demonstrated that the cyclomatrix phosphazene polymer would have excellent thermal stability and flame-retardant properties if it could form a crosslinked phosphorous oxynitride structure during pyrolysis or combustion. A flame-retardant mechanism of "intumescent" was proposed to elucidate the pyrolysis and combustion process. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 95: 880–889, 2005

Key words: polyphosphazenes; cyclomatrix; thermal properties; flame retardance

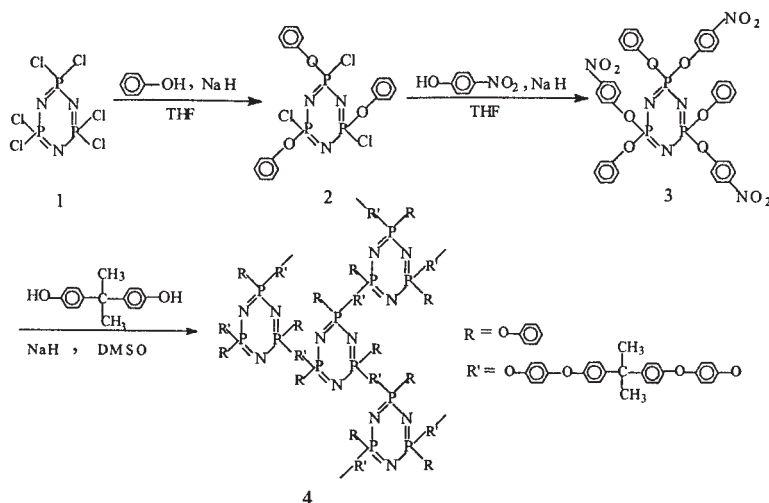
INTRODUCTION

In recent years, there has been considerable interest in the polyphosphazene family of materials because they not only have a wide range of thermal and chemical stabilities^{1,2} but can also provide improved thermal and flame-retardant properties to reinforced polymers and composites.^{3–6} The best known phosphazene materials are linear polymers with an alternating P—N backbone synthesized by the ring-opening polymerization of hexachlorocyclotriphosphazene (**1**), and these have been extensively studied for applications as solid polyelectrolytes, biomedical and metallorganic polymers, and flame-retardant materials.⁷ However, their main disadvantage, in further widening the application of linear polyphosphazenes, is their low yield and high cost. Other kinds of phosphazene materials, having long attracted attention, are cycloliner- and cyclomatrix-type polymers, in which phosphazene rings are linked via exocyclic groups to form linear chains or a crosslinked matrix. More research has been focused on the generation of cyclomatrix

materials because the complexities involved with the synthesis of cycloliner materials severely limit their desirability. In past decades, a series of phosphazene cyclomatrix polymers have been reported,⁷ and they are used in adhesives,^{8,9} flame-retardant polymeric additives,^{10,11} and thermoset resins^{3,4,12,13} for their high thermal stability. Most of these cyclomatrix polymers are synthesized in two or more complicated steps: a bifunctional compound, such as hydroquinone or amino-phenol, is attached to a phosphazene ring first, and subsequently, the obtained precursors are crosslinked with other bifunctional compounds, such as compounds with anhydride and carbonyl chloride groups. It is hard to prevent a chain extension reaction thoroughly in this process, and it is likely to result in defective structure formation in the final cyclomatrix products. Therefore, one active group of the bifunctional component must be protected first and then deprotected to form a distinct cyclic trimer, which complicates the reaction procedure and limits its applications.^{14,15} Recently, a particularly interesting cyclomatrix system aimed at flame-retardant application was derived from reactions of phosphazene-ring-containing maleamic acids, which resulted in highly crosslinked resins on heating and further thermal curing. The polymerization of the tris-*p*-aminophenoxy-tris-*p*-phenyl maleimide species gave a resin with 82% char at 800°C. Graphite cloth laminates of this resin exhibited a limited oxygen index of 100.³ This encour-

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Scheme 1

aging result revealed that cyclomatrix phosphazene polymers are powerful candidates as flame-retardant materials and may have wide applications if their manufacture can be ameliorated and simplified.

An active nitro displacement reaction was discovered earlier,^{16,17} and a review of the exploitation of the aromatic nucleophilic displacement of the activated nitrogen group was published by Beck.¹⁸ Thus, it is possible to synthesize the phosphazene cyclomatrix with a simple procedure and mild conditions if it is prepared by the coupling of 4-nitrophenol-substituted phosphazene rings with bisphenol A sodium salt.

However, the flame-retardant mechanism of phosphazene cyclomatrix polymers is still not very clear, although phosphazenes have considerable potential on the basis of their flame-retardant properties. There have been many proposals for the flame-retardant mechanisms of phosphazene cyclomatrix polymers, such as the gas phase mechanism,¹⁹ the condensed phase mechanism,¹¹ and the phosphorus–nitrogen synergism mechanism.²⁰ Further studies on the thermal decomposition and flame-retardant mechanisms of phosphazene cyclomatrix polymers are necessary to define them.

In this article, we report the synthesis and characterization of two new phosphazene cyclomatrix polymers prepared via a simple and easily controlled nitro group displacement reaction with alkoxy sodium; their ideal structures are presented in Schemes 1 and 2. Subsequently, we evaluated their thermal and flame-retardant properties and propose a flame-retardant mechanism for these two novel cyclomatrix phosphazene polymers.

EXPERIMENTAL

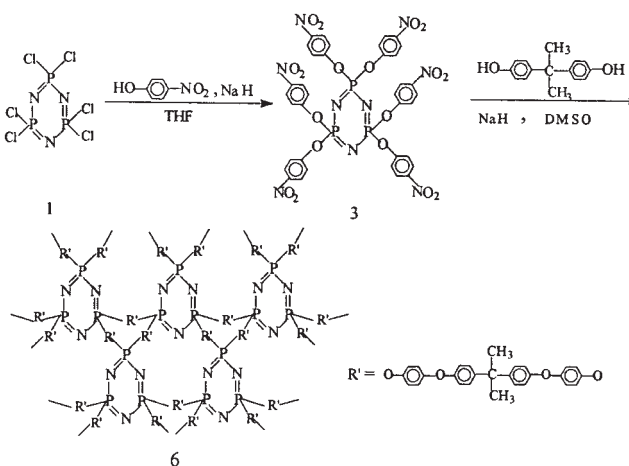
Materials

All of the chemicals and solvents were reagent grade. Compound 1 (synthesized as described in the litera-

ture^{21,22}) was recrystallized from heptane and sublimed (60°C, 0.05 mmHg) before use (mp = 112.5–113.0°C). 4-Nitrophenol was purified by recrystallization from alcohol. Sodium hydride, as a 60% dispersion in oil, was washed with dry heptane before use. *N,N'*-Dimethyl sulfoxide (DMSO) was distilled from CaH₂ and was distilled under dry nitrogen before use. Tetrahydrofuran (THF) and heptane were distilled over sodium.

Equipment

Calorimetric studies were carried out on a dynamic scanning calorimeter (PerkinElmer Pyris-1, U.S.) with nitrogen as the purge gas at a 10°C/min scanning rate from 50 to 400°C. Thermal stability studies were performed on a PCT-IA thermogravimetric system (Beijing Optical Instrument Factory, China) in air, and the heating rate was 10°C/min. Fourier transform infrared (FTIR) spectra were recorded on



Scheme 2

a Nicolet Nexus-670 IR (Thermotech, U.S.) spectrophotometer as a KBr disc. All $^1\text{H-NMR}$ spectra, in deuterated DMSO (DMSO-d_6), were measured on a Bruker AV-600 NMR spectrometer (Switzerland). The morphology of the solid residue was observed on a Cambridge S250MK3 scanning electron microscope (U.K.). The degradation products (gaseous products and solid residue) were collected by pyrolysis gas chromatography (PGC). Gases evolved on thermal decomposition were characterized by the direct-inlet procedure at 70 eV on an HP 5890-VG70SE gas chromatography mass spectrometer (U.K.), and the solid residue was confirmed on a Nicolet Nexus-670 IR spectrophotometer as a KBr disc. Elemental analysis was done with an Elementar Vario EL elemental analyzer (Germany).

Synthesis and characterization

Synthesis of tris(4-nitrophenoxy)tris(phenoxy)cyclotriphosphazene (3)

Compound **3** was synthesized according to the literature.²³ A solution of **1** (6.952 g, 0.02 mol) in 60 mL of THF was stirred. To this solution, another solution of sodium phenoxide, prepared from phenol (6.647 g, 0.06 mol) and sodium hydride (2.88 g, 0.12 mol) in THF (60 mL), was added dropwise at room temperature. Then, the stirred mixture was allowed to reflux under a nitrogen atmosphere. After 48 h, a slurry of sodium 4-nitrophenoxide, prepared from 4-nitrophenol (12.51 g, 0.09 mol) and sodium hydride (3.24 g, 0.135 mol) in THF (80 mL), was added dropwise. The orange reaction mixture was further refluxed for 3 days with stirring in a nitrogen atmosphere. The yellow reaction mixture was filtered, and the THF solution was concentrated, cooled, poured over crushed ice, and macerated for 24 h. The creamy viscous product obtained was washed with 10% aqueous potassium hydroxide, water, and methanol; then, the solid was recrystallized from acetonitrile–methanol and dried in a vacuum oven at 90°C to give 13 g of compound **3** as a white crystalline solid (mp = 106–107°C).

IR (KBr pellets, cm^{-1}): 1489 (aromatic); 1520 and 1346 (asymmetrical and symmetrical nitro group stretching); 1203, 1176, and 1158 (cyclotriphosphazene ring $\text{P}=\text{N}$).

$^1\text{H-NMR}$ (DMSO): 8.135–8.086 (dd, $J = 9.8$ and 2.4 Hz, 6H, aromatic ortho to nitro group), 7.318–7.145 (m, 15H, phenoxy), 6.967–6.954 (dd, $J = 9.8$ and 2.4 Hz, 6H, aromatic meta to nitro group).

$\text{C}_{36}\text{H}_{27}\text{N}_6\text{O}_{12}\text{P}_3$; ANAL. Calcd: C, 52.17%; H, 3.62%; N, 10.14%; P, 11.23%. Found: C, 52.09%; H, 3.31%; N, 10.27%; P, 11.02%.

Synthesis of hexakis(4-nitrophenoxy)cyclotriphosphazene (5)

Compound **5** was synthesized according to the literature.²⁴ A mixture consisting of 4-nitrophenol (25.02 g, 0.18 mol), potassium hydroxide (10.8 g, 0.27 mol), and xylene (150 mL) was slowly heated with stirring to 80°C. At this temperature, **1** (6.96 g, 0.02 mol) in xylene (150 mL) was added dropwise for 1 h. The mixture was then refluxed for 24 h. The yellow precipitate was separated and washed with warm 10% aqueous potassium hydroxide and water. Recrystallization of the dried solid from dimethylformamide gave 15.42 g of compound **5** as a yellow crystalline solid (mp = 262–263°C).

IR (KBr pellets, cm^{-1}): 1592 (aromatic); 1522 and 1346 (asymmetrical and symmetrical nitro group stretching); 1204, 1184, and 1163 (cyclotriphosphazene ring $\text{P}=\text{N}$).

$^1\text{H-NMR}$ (DMSO): 8.172–8.146 (d, $J = 9.0$ Hz, 12H, aromatic ortho to nitro group), 7.314–7.299 (d, $J = 9.6$ Hz, 12H, aromatic meta to nitro group).

$\text{C}_{36}\text{H}_{24}\text{N}_6\text{O}_{18}\text{P}_3$; ANAL. Calcd: C, 44.85%; H, 2.49%; N, 13.08%; P, 9.66%. Found: C, 44.68%; H, 2.61%; N, 13.11%; P, 9.58%.

Synthesis of the phosphazene cyclomatrix polymer 4

In a flame-dried, three-necked flask equipped with a stirrer, thermometer, nitrogen inlet, and condenser with a guard tube, sodium metal (0.69 g, 0.03 mol) was dissolved in absolute ethanol (40 mL). To this solution, bisphenol A (3.42 g, 0.015 mol) was added and stirred for 0.5 h. The ethanol was removed by distillation, and a Dean–Stark condenser was fitted to the flask. Subsequently, toluene (15 mL) was added to the reaction, and the temperature of the reaction was raised to 120°C so that the toluene could be collected by distillation. Toluene (15 mL) and DMSO (10 mL) were added, and the temperature of the reaction was increased to 140°C. The toluene was continuously collected to ensure the complete removal of water; then, the Dean–Stark condenser was removed. The reaction mixture was cooled to 40°C, and compound **3** (8.28 g, 0.01 mol) was added along with anhydrous DMSO (10 mL) and toluene (10 mL). The reaction mixture was allowed to stir at 80°C for 72 h. Then, the reaction mixture was poured into cool water to obtain a brown powder. The brown powder was washed with methanol and dried *in vacuo* to obtain polymer **4** (yield = 70%).

IR (KBr pellets, cm^{-1}): 1489 (aromatic); 1261 (ether); 1196, 1176, and 1164 (cyclotriphosphazene ring $\text{P}=\text{N}$).

$^1\text{H-NMR}$ (DMSO): 7.362–6.653 (Ar–H); 1.694–1.519 (methyl–H in bisphenol A).

Synthesis of phosphazene cyclomatrix polymer 6

Similarly, compound **6** was synthesized by the nucleophilic nitro displacement of compound **5** (3.177 g, 3.3×10^{-3} mol) by the disodium salt of bisphenol A (2.257 g, 9.9×10^{-3} mol) in DMSO at 75°C for 72 h. The brown polymer **6** was obtained at an 80% yield.

IR (KBr pellets, cm^{-1}): 1238 (ether); 1203 and 1161 (cyclotriphosphazene ring $\text{P}=\text{N}$); 1504 and 1346 (asymmetrical and symmetrical nitro group stretching); 3600–3300 (hydroxyl).

$^1\text{H-NMR}$ (DMSO): 7.327–6.680 (Ar–H); 1.696–1.515 (methyl–H in bisphenol A); 8.264–8.249 (Ar– NO_2 , H).

RESULTS AND DISCUSSION

Synthesis and characterization of the substituted trimers and phosphazene cyclomatrix polymers

Compounds **3** and **5** were synthesized, and their structures were confirmed by FTIR and $^1\text{H-NMR}$ spectroscopy and elemental analysis. The characterization data were identical to those published in the literature.^{23,24}

Polymerization was conveniently performed in anhydrous DMSO under a nitrogen atmosphere to give a brown polymer (**4**) with a good yield (70%). DMSO was chosen as the solvent for polymerization because this dipolar aprotic solvent has been reported as able to minimize the easy reduction of the nitro group in basic media and to facilitate nucleophilic substitution reactions.

A typical IR spectrum for polymer **4** is shown in Figure 1(b) in comparison with that of compound **3** [Fig. 1(a)]. As shown in Figure 1(a), two strong absorption bands at 1520 and 1346 cm^{-1} were observed, which were assigned to the presence of nitro groups in compound **3**, whereas the strength of these two bands was significantly decreased in compound **4** [Fig. 1(b)]. This demonstrated that most of the active nitro groups

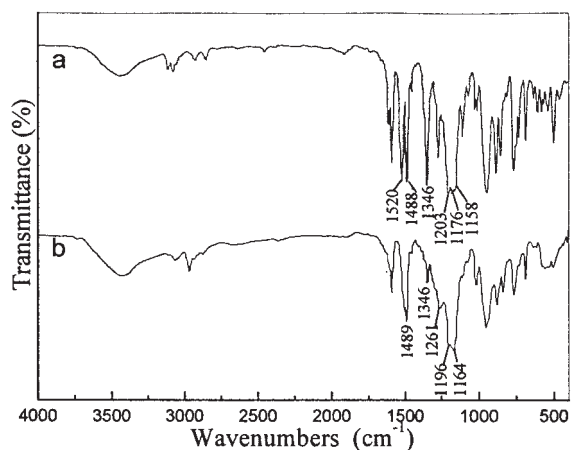


Figure 1 IR spectra of compounds (a) **3** and (b) **4**.

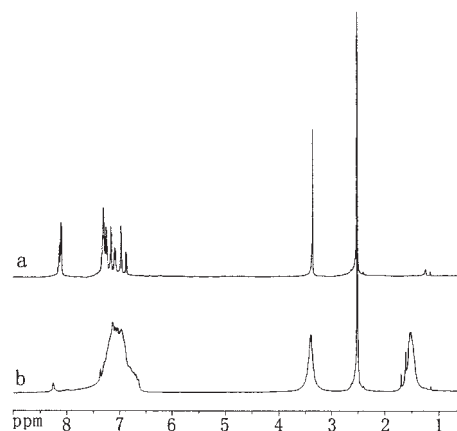


Figure 2 $^1\text{H-NMR}$ spectra of compounds (a) **3** and (b) **4**.

in compound **3** could be nucleophilically substituted by bisphenol A. However, absorptions of $-\text{P}=\text{N}-$ stretching and bending at 1196, 1176, and 1164 cm^{-1} of the aromatic group at 1489 cm^{-1} and the ether group at 1261 cm^{-1} were also detected in compound **4** [Fig. 1(b)], which indicated that the cyclotriphosphazene skeleton was incorporated with the formation of ether. In view of these results, we deduced that polymer **4** should have had a cyclomatrix structure.

However, the nitro groups in polymer **4** were not substituted completely, as illustrated by the presence of the faint absorptions bands at 1346 cm^{-1} , as shown in Figure 1(b). The probable reason for this phenomenon was that the molar ratios of nitro and hydroxyl groups were the same in the feed, which could have theoretically resulted in a cyclomatrix polyphosphazene material with an indefinitely large molecular weight, but in fact, it was difficult for the nitro groups to be completely substituted by the hydroxyl groups of bisphenol A because of steric hindrance.

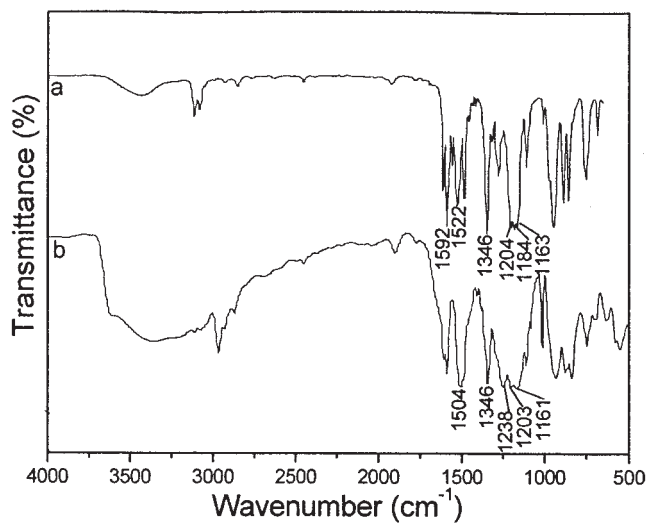


Figure 3 IR spectra of (a) compound **5** and (b) polymer **6**.

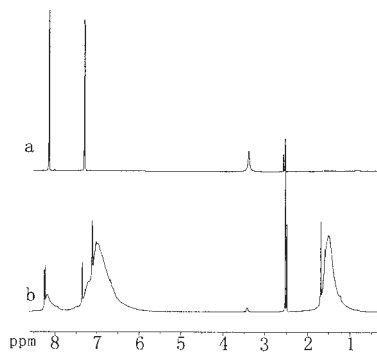


Figure 4 $^1\text{H-NMR}$ spectra of (a) compound **5** and (b) polymer **6**.

The formation of cyclomatrix polymer **4** derived from compound **3** and bisphenol A was further identified by the comparison of their $^1\text{H-NMR}$ spectra. As shown in Figure 2, the peaks at 8.135–8.086 ppm, corresponding to the ortho-aromatic protons to nitro groups, became weak and broad in the spectrum of polymer **4** and were much different from those in compound **3** [Fig. 2(a)], which were strong, sharp, and well split. This confirmed the nucleophilic substitution reaction of the nitro groups by hydroxyl groups; however, it also revealed incomplete substitution. The proton peaks of polymer **4** were somewhat broader than those of compound **3** because the chemical environment was varied because of the formation of the cyclomatrix structure in polymer **4**.

Moreover, polymer **4** was subjected to calorimetric studies. The measurements were carried out in the temperature range 50–400°C. However, no obvious glass transition was detected. This result suggests that polymer **4** should have had a cyclomatrix network and should have been free of cycloliner oligomers.

Similarly, polymer **6**, derived from **5** and bisphenol A, was synthesized and characterized by FTIR and $^1\text{H-NMR}$ analysis. Polymer **6** was confirmed as having a cyclomatrix structure, and the nucleophilic substitution of nitro groups by bisphenol A were proven by the significant changes in the absorption bands of the nitro groups (1504 and 1346 cm^{-1}) in its FTIR spectrum (Fig. 3) and the peaks corresponding to the or-

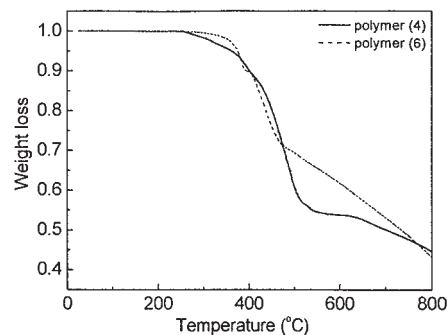


Figure 5 Dynamic TGA curves for polymers **4** and **6** in air.

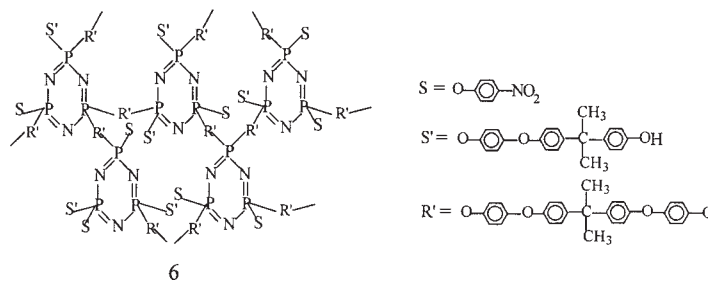
tho-aromatic protons to nitro groups (8.264–8.249 ppm) in its $^1\text{H-NMR}$ spectrum (Fig. 4). We envisioned polymer **6** to have a higher crosslinking density than polymer **4** because its intermediate (**5**) had six active nitro groups. Nevertheless, the substitution degree of nitro groups in polymer **6** was not as high as we expected. As shown in Figures 3 and 4, a considerable number of nitro groups did not participate in the reaction, as confirmed by the obvious corresponding signals present in the FTIR and $^1\text{H-NMR}$ spectra. It was also difficult to achieve a higher substitution degree, although many efforts were made. Therefore, because of the greater hindrance in compound **5** than in compound **3**, polymer **6** might have actually had more defects in its cyclomatrix network structure than polymer **4**, which would lead to different thermal stabilities and flame-retardant behaviors for each. As a result, polymer **6** should have had a structure as shown in Scheme 3.

Thermal characteristics

Thermal stability

The thermal stabilities of polymers **4** and **6** were determined with dynamic thermogravimetric analysis (TGA). The TGA curves were obtained in air.

As shown by the curves in Figure 5, both polymers began to decompose at 386°C. The char yields in air at 800°C for polymers **4** and **6** were 45.1 and 43.2%,



Scheme 3

TABLE I
Gaseous Pyrolysis Products of Polymers 4 and 6

Polymer	Gaseous Products
4	
6	

respectively. According to changes in the weight loss rate on heating, it seemed that polymer 6 had a slightly higher thermal stability than polymer 4, although we stated previously that polymer 6 might have had more defects in its cyclomatrix network structure than polymer 4.

Pyrolysis study

After polymers 4 and 6 were pyrolyzed at 600°C by PGC, the pyrolysis products (both gases and solid residue) were collected for characterization.

The gaseous specimens were analyzed by gas chromatography/mass spectrometry, and the results are shown in Table I. It was easy to deduce that these gaseous fragments mainly came from bisphenol A and derived substituted groups (phenoxy or 4-nitrophenoxy): no specimens containing phosphorous or nitrogen atoms were detected. This suggests that the weight loss in polymers 4 and 6 on heating (as illustrated in Fig. 5) resulted from the scission of bisphenol A bridges or the loss of substituents, whereas the cyclic phosphazenes should have remained in the solid residues.

The solid residues of pyrolyzed polymers 4 and 6 were characterized by FTIR spectroscopy, and the results are shown in Figures 6 and 7.

For polymer 4, the absorptions of P=N, at 1196, 1176, and 1164 cm^{-1} in the original polymer [Fig. 6(a)], merged into one peak and shifted to a higher wave number [1241 cm^{-1} ; Fig. 6(b)] after pyrolysis, which was apparently due to alterations in the chemical structures

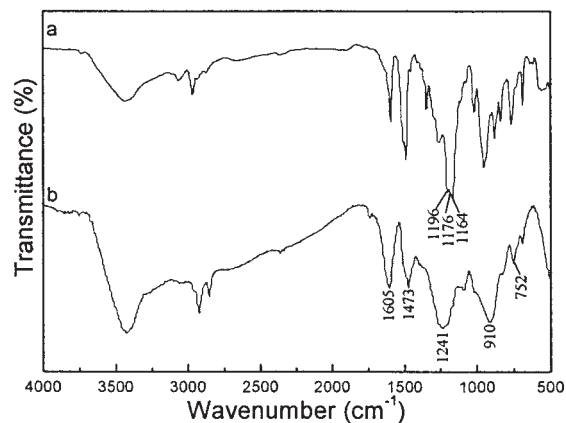


Figure 6 IR spectra of (a) polymer 4 and (b) its solid pyrolysis residue.

of the substituents.²⁵ Moreover, a new strong and broad band, attributed to P—O—P, appeared at 910 cm^{-1} .²⁶ These two broad absorptions at 1241 cm^{-1} (P=N) and 910 cm^{-1} (P—O—P) were typical for phosphorous oxynitrides.²⁷ However, the broad bands at 1605, 1473, and 752 cm^{-1} corresponded to aromatics and were characteristic bands for carbonized polymers.²⁸ In view of all this, the solid residue of pyrolyzed polymer 4 seemed to consist of crosslinked phosphorous oxynitride and carbonized aromatic networks. As shown in Figure 7, a similar solid residue of pyrolyzed polymer 6 was observed with an absorption at 1241 cm^{-1} (P=N) and absorptions at 1604, 1469, and 752 cm^{-1} from the mixed mode (aromatic), where para, meta, and ortho substituents contributed.²⁶ However, the absorption at 930–910 cm^{-1} due to P—O—P [Fig. 7(b)] was indistinct, which implied that the content of P—O—P was very low in the solid residue of pyrolyzed polymer 6. In other words, little crosslinked phosphorous oxynitride and few carbonized aromatic networks were formed in polymer 6 during pyrolysis.

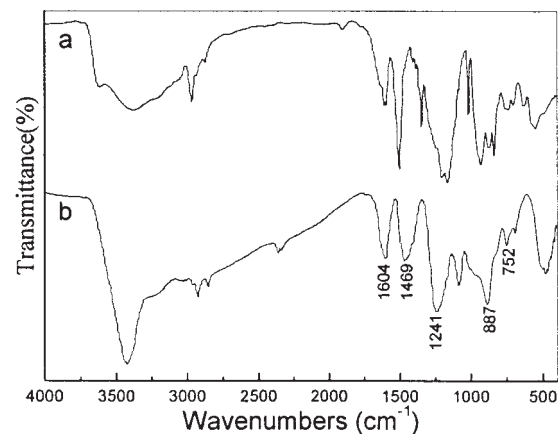
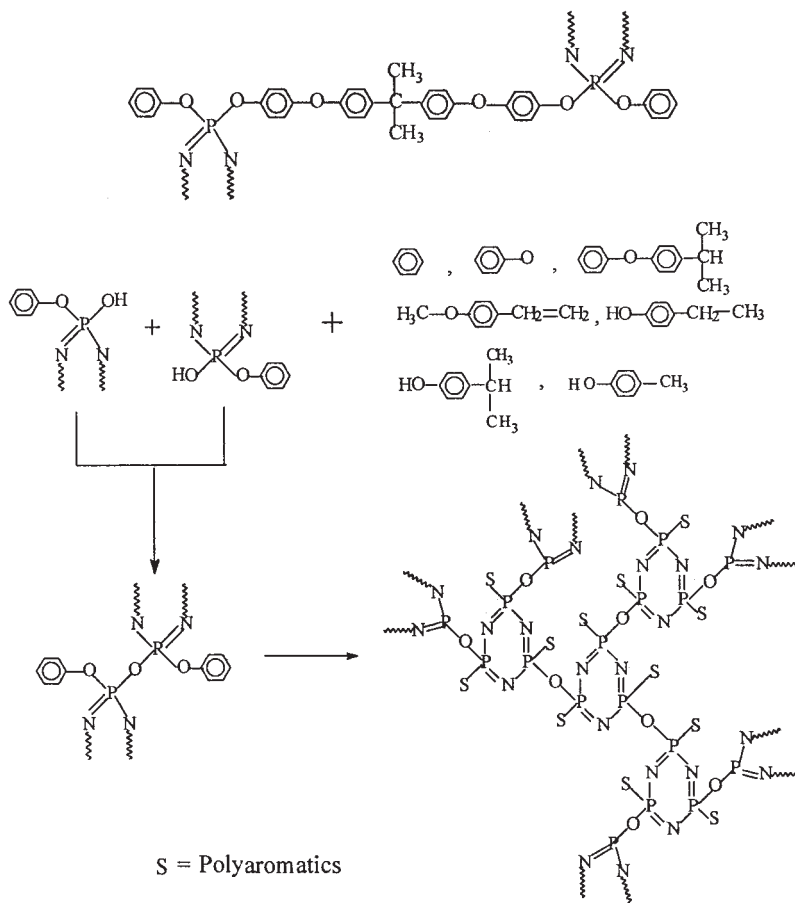


Figure 7 IR spectra of (a) polymer 6 and (b) its solid pyrolysis residue.



Scheme 4

Flame-retardant behavior

Different phenomena were observed for polymers **4** and **6** during their combustion. In the flame, the powder of polymer **4** began to melt and merged into one bulk at first and subsequently expanded. The color gradually changed from brown to dark, but the polymer did not burn, and no visible smoke was observed; the resulting residue was very hard and exhibited considerable strength. By contrast, polymer **6** was flammable and gave off heavy smoke. Moreover, no obvious fusion or swell behavior was observed, and the polymer combusted into a scattered strengthless powder.

Compared to those of polymer **6**, the excellent combustion properties of polymer **4** showed it to be a potential candidate for flame-retardant applications, such as additives in paints and composites.

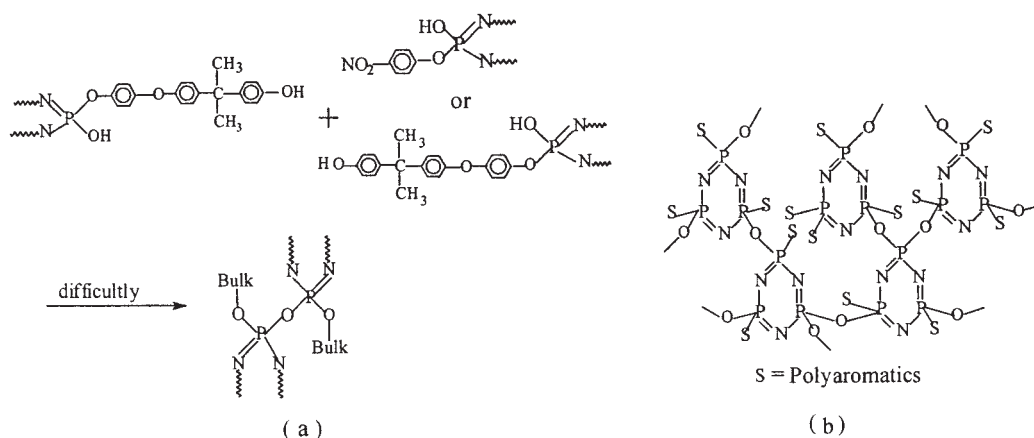
Pyrolysis and flame-retardant mechanisms

Pyrolysis pathway of the cyclomatrix phosphazene polymers

We stated earlier that cyclic phosphazenes remained in the solid residues after pyrolysis, whereas the bis-

phenol A bridges and substituents were lost as gaseous byproducts. In addition, the formation of P—O—P bridges was confirmed by the absorption appearing around 910–930 cm^{-1} in the FTIR spectra, in particular for pyrolyzed polymer **4**, which resulted from the reaction between —POH groups.²⁹ Moreover, the coexistence of P=N (proven by the absorption at 1241 cm^{-1} , shown in Figs. 6 and 7) and aromatic fragments (absorptions at 1605, 1473, and 752 cm^{-1} , shown in Fig. 6, and 1604, 1469, and 752 cm^{-1} , shown in Fig. 7) suggested that the pyrolyzed residues contained crosslinked phosphorus oxynitride and carbonized aromatic networks.

Compared to polymer **4**, however, it was more difficult for pyrolyzed polymer **6** to produce a perfect network for two possible reasons. One was inhibition of the formation of P—O—P bridges between P—OH groups because of steric hindrance of other bulk groups on the same phosphorus atom, such as an S' group or other bisphenol A bridges, as illustrated in Scheme 3. The other reason was that the defects existing in the original cyclomatrix networks of polymer **6** were disadvantageous for the formation of crosslinked phosphorus oxynitride and carbonized aromatic networks.



Scheme 5

In view of all this, thermal decomposition processes were deduced for cyclomatrix phosphazene polymers **4** and **6** and are shown in Schemes 4 and 5, respectively.

Although ring opening or ring extension can occur in hexagroup-substituted cyclotriphosphazenes at higher temperatures and longer times,³⁰ we thought it would be difficult for the cyclic phosphazenes in the network of pyrolyzed polymers **4** and **6** to be opened or extended because of steric hindrance.

Flame-retardant mechanisms

Cyclomatrix phosphazene polymer **4** demonstrated excellent flame-retardance, although polymer **6** did not. To obtain insight into the flame-retardant mech-

anism of these cyclomatrix phosphazene polymers, solid residues of pyrolyzed or combusted polymers **4** and **6** were collected for morphological observation with scanning electron microscopy. After pyrolysis, by step heating or combustion in a flame, polymer **4** changed from a powder into a bulk. As shown in Figure 8, the bulk had a continuous surface with many solidified molten drops on it but was porous inside.

Taking both the formation of crosslinked phosphorus oxynitride and carbonized aromatic networks and the generation of gaseous byproducts on heating into account, we propose an intumescent flame-retardant mechanism for the cyclomatrix phosphazene polymers because the materials could swell into a foam-like structure with a continuous surface when exposed

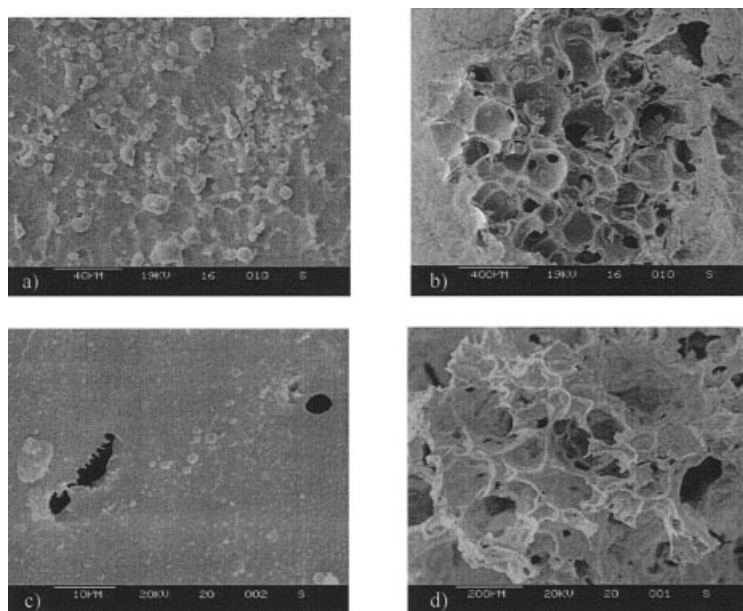


Figure 8 Morphology of the solid residues of polymer **4** after pyrolysis and combustion: (a) surface of the solid residue after pyrolysis, (b) inside morphology of the solid residue after pyrolysis, (c) surface of the solid residue after combustion, and (d) inside morphology of the solid residue after combustion.

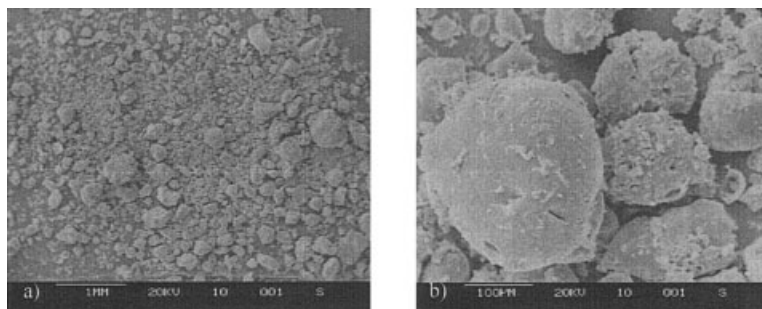


Figure 9 Morphology of the solid residue of polymer **6** after combustion.

to fire or heat. During pyrolysis or combustion, the powder of polymer **4** melted and merged into a bulk at first; then, crosslinked phosphorus oxynitride and carbonized aromatic networks were formed primarily at the bulk surface. Meanwhile, phosphorus could have also acted in the condensed phase to promote char formation at the surface.³¹ The dense surface slowed the elimination of the gaseous pyrolysis products, and the melt expanded to form a porous foamed mass, which in turn, acted as a barrier to further inhibit gaseous products from diffusing to the flame and to shield the inside polymer from heat and air. Thus, no ignition, flame spread, or visible smoke was visible because most of the flammable gases were entrapped. Cyclomatrix phosphazene polymer **4** actually acted in the condensed phase through a physical mechanism to interfere with the combustion process during heating, pyrolysis, ignition, or flame spread.

However, the residues of the pyrolyzed or combusted polymer **6** were fragile powders (Fig. 9), and no expansion was detected. This was thought to be due to the fact that perfect crosslinked networks were not formed in polymer **6**, as discussed previously. The released flammable gaseous pyrolysis products fueled the material's burning and heavy smoke. Polymer **6** did not show the good flame-retardant properties of polymer **4**. This phenomenon not only illustrated that the crosslinking structures of these materials affected the char formation on the surface and flame-retardant properties but was also further evidence that the intumescent mechanism played an important role in the case of the cyclomatrix phosphazene polymers acting as flame-retardant materials.

CONCLUSIONS

In this study, two new phosphazene cyclomatrix polymers were synthesized via nitro displacement polymerization. Polymer **4** had a better network structure than polymer **6** because of its lower steric hindrance in the nucleophilic displacement of active nitro groups when they were prepared via a coupling reaction of

4-nitrophenoxy-substituted cyclotriphosphazene with bisphenol A. We believe this research provides significant insight into the molecular design of phosphazene cyclomatrix network polymers.

Through the analysis of the thermally decomposed products of polymers **4** and **6**, we elucidated a chemical route for the formation of a thermally stable crosslinked phosphorus oxynitride structure during pyrolysis and combustion. A high crosslinking density and good network structure promoted char formation on the mass surface and affected the flame-retardant properties of the polymers significantly. Polymer **4** showed good flame-retardant properties, and we proposed an intumescent mechanism to interpret the phenomenon in which the pyrolyzed polymer **4** swelled to form a porous foamed mass when exposed to fire or heat, which in turn, acted as a barrier to inhibit gaseous products from diffusing to the flame and to shield the polymer from heat and air.

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