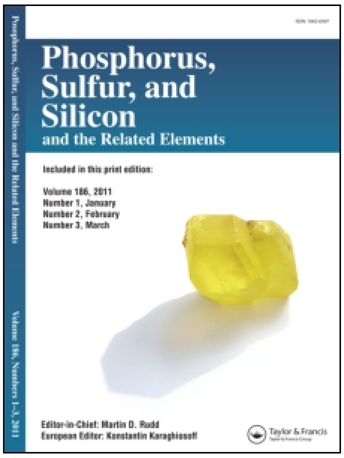

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A NEW CYCLOLINEAR PHOSPHAZENE POLYURETHANE: SYNTHESIS FROM A DIISOCYANATE AND A BIS-SPIRO-SUBSTITUTED CYCLOTRIPHOSPHAZENE DIOL

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A NEW CYCLOLINEAR PHOSPHAZENE POLYURETHANE: SYNTHESIS FROM A DIISOCYANATE AND A BIS-SPIRO-SUBSTITUTED CYCLOTRIPHOSPHAZENE DIOL

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New cyclolinear polymers from bifunctional organic molecules and cyclotriphosphazenes containing two reactive groups have been synthesized. The reaction between 2,2-bis(4-hydroxyphenoxy)-bis[spiro(2',2"- dioxy-1',1"-biphenylyl)]cyclotriphosphazene **3**, obtained by the reaction of 2,2-bis(4-methoxyphenoxy)- bis[spiro(2',2"- dioxy-1',1"- biphenylyl)] cyclotriphosphazene **2** with BBr_3 /H_2O, and hexamethylene diisocyanate (HDI) led to the new cyclotriphosphazene containing polyurethane **4**. The structures of **4** and also of compounds involved in its synthesis were investigated by ^{31}P, ^{13}C and ^{1}H NMR, infrared spectroscopy, mass spectrometry and elemental analysis. The molecular weight was determined by SEC analysis. The thermogravimetric behaviour of **4** was compared with that of a similar polyurethane containing a cyclotriphosphazene as a pendant group. The results show that the incorporation of phosphorus atoms into the backbone improves the thermal properties of the polymers.

Keywords: Cyclotriphosphazenes; Polyurethanes; Synthesis; NMR; IR; TGA

INTRODUCTION

Conventional hydrocarbon polymers sometimes suffer from some limitations in applications where mechanical properties, thermal stability, light-heat or fire resistance are required. Therefore the research of new polymer structures is aimed to built up new hybrid organic-inorganic materials in order to avoid these deficiencies. For example, phosphorus and nitrogen give a higher thermal stability and a better fire resistance when incorporated into the polymer.[1–3]

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*Corresponding author.

More precisely, in recent years, many studies dealt whith the introduction in conventional organic polymers of the phosphazene rings $(N = PX_2)_n$ (n = 3, 4...; X = OR, OAr, NHR, NHAr...) as inorganic moiety. This modification can be obtained by exploiting the reactivity of functionalized cyclotriphosphazenes. Depending on the nature and the number of reactive groups introduced into the phosphazene ring, the new materials are divided in three classes:

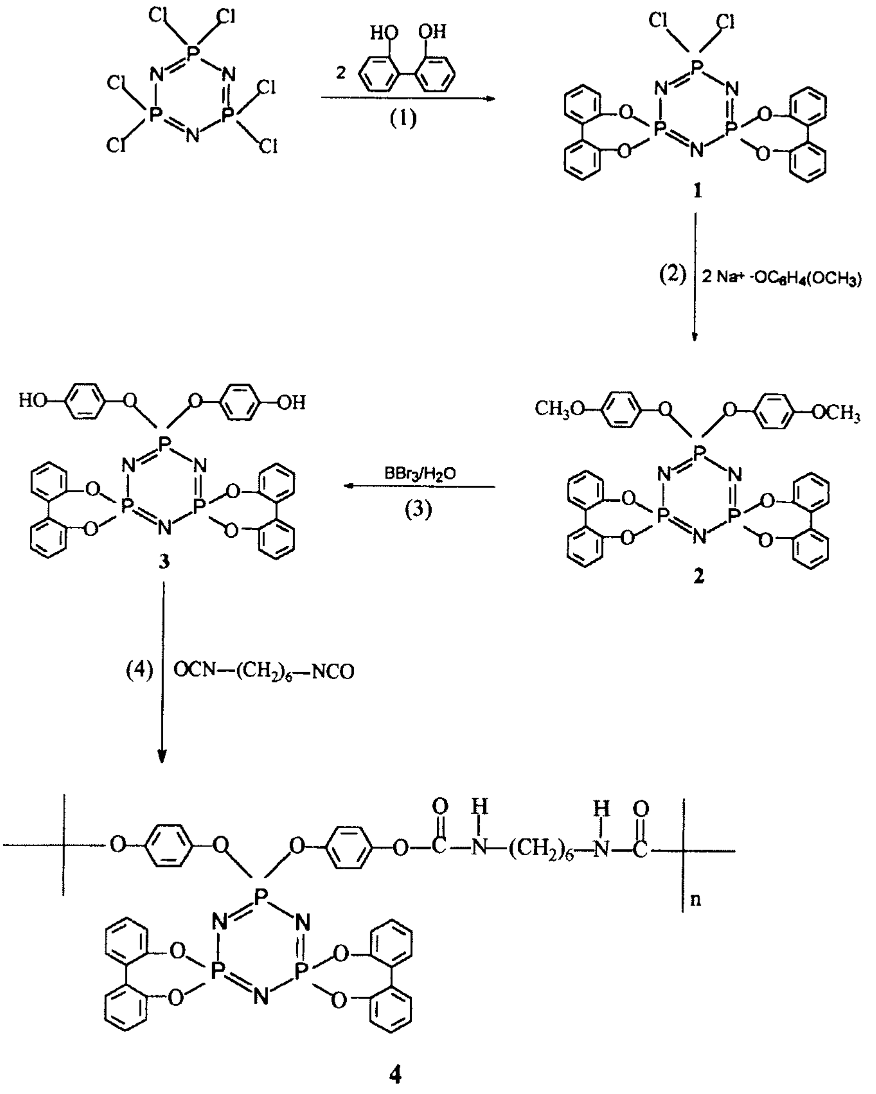
- The cyclolinear materials, synthesized from the reaction between a two functional sites containing cyclotriphosphazene and a difunctional organic molecule. For example, Kumar and Gupta[4] reported the synthesis of cyclolinear phosphazene polyimides starting from a bis-spiro-substituted cyclotriphosphazene diamine, and Kajiwara,[5] the one of new polyurethanes from diaminotetraalkoxy-or aryloxy-cyclotriphosphazenes and tolylenediisocyanate.
- The cyclomatrix polymers which involves cyclotriphosphazenes with more than two reactive sites, causing a three dimensional network. It is not possible here to review these synthesis in detail. However an example is given with the polymerisation of cyclotriphosphazenes containing insaturated sites synthesized by the reaction of hexachlorocyclotriphosphazene with an allyl alcohol[6–12] or an allyl amine.[12–14] This polymerization can be obtained by heating them in the presence of radical initiators,[10,13] or by direct UV irradiation in the presence of suitable photoinitiators.[11,15]
- The organic polymers containing cyclotriphosphazene side groups chemically bonded to the organic chain. It is the case with polymers obtained from cyclophosphazene containing olefinic functions by radical homopolymerization, or radical copolymerization with organic olefins.[16–19]

We describe here the synthesis of a new cyclolinear organic-inorganic polymer, starting from hexamethylene diisocyanate (HDI) and a cyclotriphosphazene containing two hydroxyl groups, the 2,2-bis(4-hydroxyphenoxy)-bis[spiro(2′,2″-dioxy-1′, 1″-biphenylyl)] cyclotriphosphazene (**3**).

The synthesis of the hydroxylated cyclotriphosphazene, the characterization of the intermediate compounds involved in this process, the preparation, characterization and thermal behaviour of the polymer will be detailed.

RESULTS AND DISCUSSION

The reaction sequences used for the preparation of hydroxyl groups containing cyclotriphosphazenes and cyclotriphosphazene containing polyurethanes are given in the Scheme 1

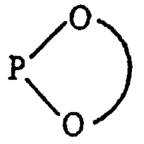


The 2,2-dichloro-4,4,6,6-bis [spiro (2′,2″-dioxy-1′,1″-biphenylyl)] cyclotriphosphazene **1** was obtained as previously described by reaction of hexachlorocyclotriphosphazene with 2,2′-dihydroxy-1,1′-biphenyl in the heterogeneous system water-chlorobenzene in the presence of sodium hydroxyde as an HCl acceptor and tetrabutylammonium bromide as the phase transfer catalyst according to the procedure described by Kumar and Gupta.[4] Equation (1). This method is selective and no monospiro derivative was detected by ^{31}P NMR.

The hydroxyphenoxy derivative **3** was thereafter synthesized by reaction of **1** with sodium methoxyphenolate giving **2** which was then treated with boron tribromide BBr_3, and finally hydrolyzed according to the procedure previously described for the preparation of (3,5-dihydroxyphenoxy) (pentaphenoxy)cyclotriphosphazene.[20] Equations (2) and (3).

The intermediate compounds **1** and **2**, and the final hydroxylated cyclotriphosphazene **3** were all characterized by infrared spectroscopy, ^1H, ^{31}P, ^{13}C NMR and mass spectrometry. The corresponding data are given in Table I. ^{31}P NMR spectra of **1**, **2**, **3** show an A_2X pattern corresponding to the two types of phosphorus atoms in the phosphazene rings.

They include a triplet (PCl_2 or $P(OC_6H_4X)_2$; ($X = OCH_3, OH$)) and a doublet



They are plotted in Figure 1.

The formation of **2** from **1** is characterized by the upfield shift of the triplet from $\delta = 29.4$ ppm (**1**) to $\delta = 10.8$ ppm (**2**), and the downfield shift of the doublet from $\delta = 19.7$ ppm (**1**) to $\delta = 25.9$ ppm (**2**), indicating a complete substitution of chlorine atoms in **1**. This is confirmed in ^1H NMR by the integration of the 4-methoxyphenoxy methyl protons ($\delta = 3.9$ ppm) to all aromatic protons ($\delta = 6.8$–7.4 ppm) seen in the ratio 1:4 (Figure 2).

The conversion of **2** to **3** is distinguished in ^1H and ^{13}C NMR by the complete disappearance of the signals corresponding to the methoxy groups ($\delta = 3.9$ ppm, ^1H NMR; $\delta = 55.5$ ppm, ^{13}C NMR). The ^1H NMR spectrum of **3** in deuterated acetone shows the signal representative of the OH protons at $\delta = 8.3$ ppm. The experimental intensity ratio 1:4:8 of the hydroxyl, 4-hydroxyphenoxy, and dioxybiphenyl aromatic protons at $\delta = 8.3$ ppm; $\delta = 6.8$ and 7.6 ppm; $\delta = 6.9$–7.3 ppm respectively, confirm the structure of **3** (Figure 2). The presence in **3** of the hydroxyl functions is finally characterized in the FTIR spectrum by a broad band near $v = 3350\ cm^{-1}$ due to the O-H stretching vibration (Figure 3).

The polymerization reaction of the dihydroxylated compound **3** with an equimolar amount of hexamethylene diisocyanate was performed in DMF at 80°C, to give the corresponding polyurethane **4** according to the procedure described by Lee *et al.*[21] for polyurethanes synthesized from tolylene diisocyanates and bis (hydroxyalkoxy)benzenes. **4** is a brown solid soluble in dimethylformamide, dimethylsulfoxide and tetrahydrofuran. A summary of its spectroscopic data is presented in Table I.

TABLE I Spectroscopic data for compounds **1–3** and polymer **4**.

compound	*δ ppm*			*IR* *frequency (cm^{-1})*	*m/e*
	^{31}P NMR	*^{1}H NMR*	*^{13}C NMR*		
1	29.4 (t)	7.3–7.55 (m,16H,aromatic)	147.3 (m, aromatic)	3065.7 (υ C-H, Ar)	Calcd: 574
	19.7 (d)		129.9 (m, aromatic)	1606.6 (υ =C-C=C, Ar)	found: 575 (MH^+)
	J = 86.1 Hz		129.7 (m, aromatic)	1501.5 (υ =C-C=C, Ar)	
			128.5 (m, aromatic)	1476.4 (υ =C-C=C, Ar)	
			126.5 (m, aromatic)	1226.7 (υP=N)	
			121.8 (m, aromatic)	967.2 (υ P-O-Ar)	
				1171.7 (υ P-O-Ar)	
2	25.9 (d)	3.9 (s, 6H, CH_3)	55.5 (s, CH_3)	3066.6 (υ C-H, Ar)	calcd: 749
	10.8 (t)	6.8 (d, 4H, aromatic)	114.4 (m, aromatic)	1606.6 (υ =C-C=C, Ar)	found: 750 (MH^+)
	J = 93.3Hz	7.4 (d, 4H, aromatic)	122.2 (m, aromatic)	1503.4 (υ =C-C=C, Ar)	
		6.9–7.3 (m, 16H, aromatic)	122.6 (m, aromatic)	1476.4 (υ =C-C=C, Ar)	
			125.9 (m, aromatic)	1231.5 (υP=N)	
			128 (m, aromatic)	948 (υ P-O-Ar)	
			129.5 (m, aromatic)	1172.7 υ(P-O-Ar)	
			129.6 (m, aromatic)	2836.2 (υ C-H, OCH_3)	
			146 (m, aromatic)		
			147 (m, aromatic)		
			155.5 (m, aromatic)		
3	27.4 (d)	6.8 (d, 4H, aromatic)	116.8 (m, aromatic)	3067.8 (υ C-H, Ar)	calcd: 721
	12.66 (t)	7.6 (d, 4H, aromatic)	122.7 (m, aromatic)	1603.7 (υ =C-C=C, Ar)	found: 722 (MH^+)
	J = 90.4Hz	6.9–7.3 (m, 16H, aromatic)	122.8 (m, aromatic)	1505.4 (υ =C-C=C, Ar)	
		8.3 (s, 2H, OH)	122.9 (m, aromatic)	1476.4 (υ =C-C=C, Ar)	
			127.1 (m, aromatic)	1231.5 (υP=N)	
			129.4 (m, aromatic)	950.9 (υ P-O-Ar)	

TABLE I *continued*

compound	*δ ppm*			*IR frequency (cm^{-1})*	*m/e*
	^{31}P NMR	*^{1}H NMR*	*^{13}C NMR*		
			130.7 (m, aromatic) 143 (m, aromatic) 148.9 (m, aromatic) 155.2 (m, aromatic)	1174.6 (υ P-O-Ar) 3357.9 (υ O-H)	
4	26.2 (d) 11.4 (t) J = 89.8 Hz	1.31 (CH_2) 1.46 (CH_2) 3.05 (CH_2) 7.11–7.62 (m, aromatic) 9.53 (s, NH)		3065.7 (υ C-H, Ar) 1603.7 (υ =C-C=C, Ar) 1495.7 (υ =C-C=C, Ar) 1230.5 (υP=N) 946 (υ P-O-Ar) 1170.7 (υ P-O-Ar) 1745.5 (υ C=O) 3330–3425 (υ N-H)	

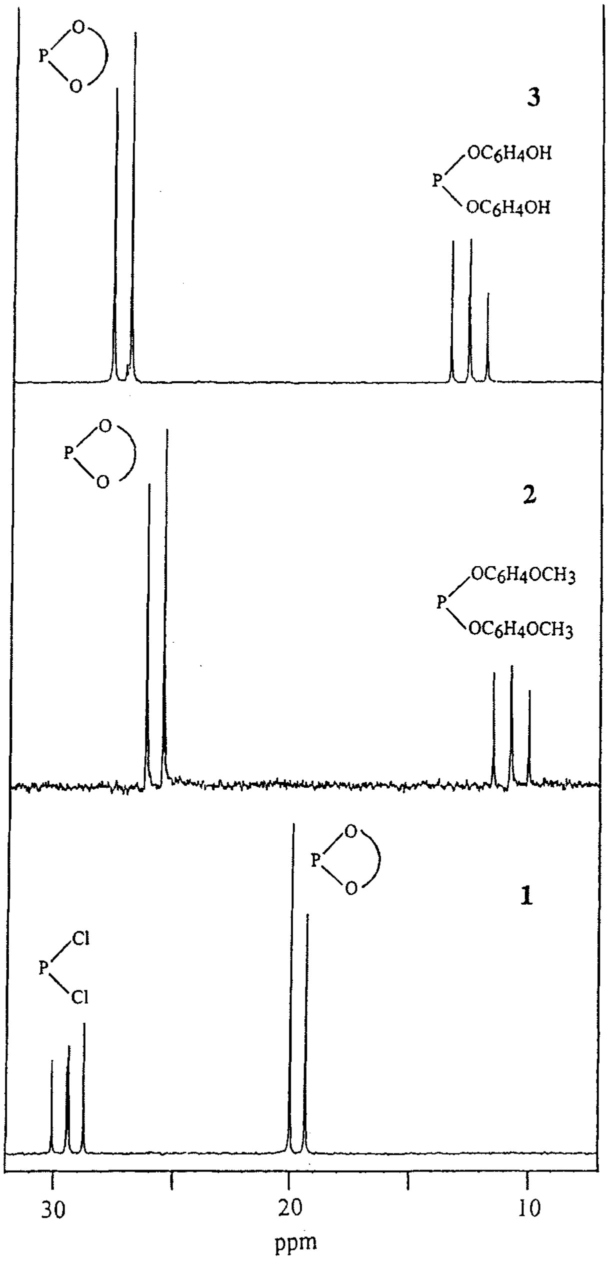


FIGURE 1 conversion **1** → **2** → **3**: evolution of ^{31}P NMR spectra.

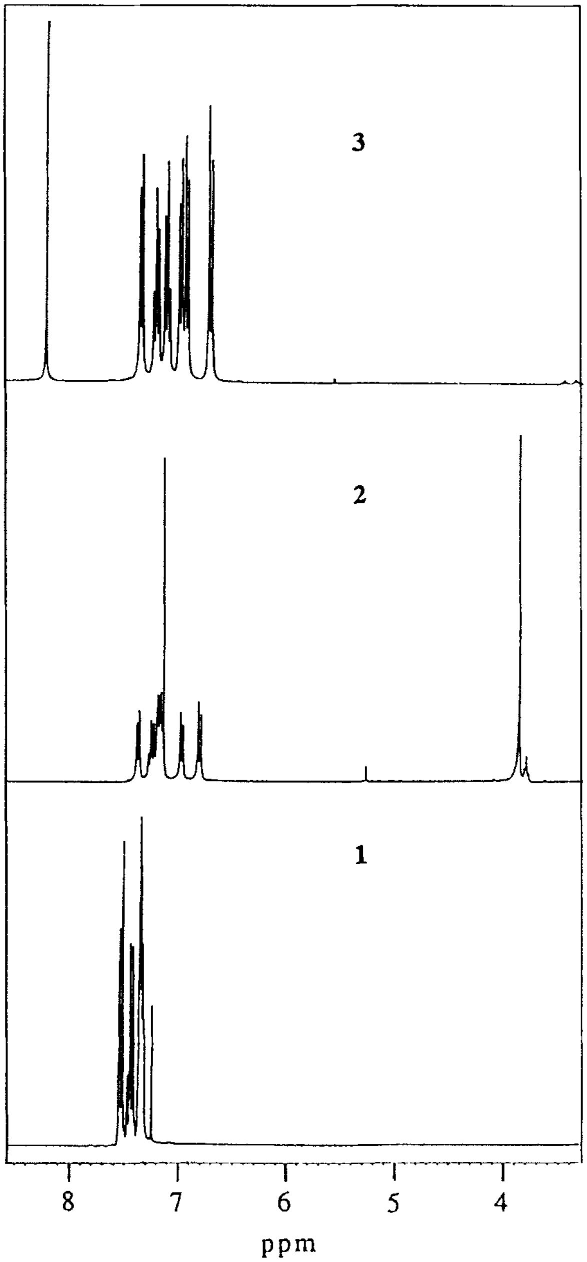


FIGURE 2 conversion **1** → **2** → **3**: evolution of ^1H NMR spectra.

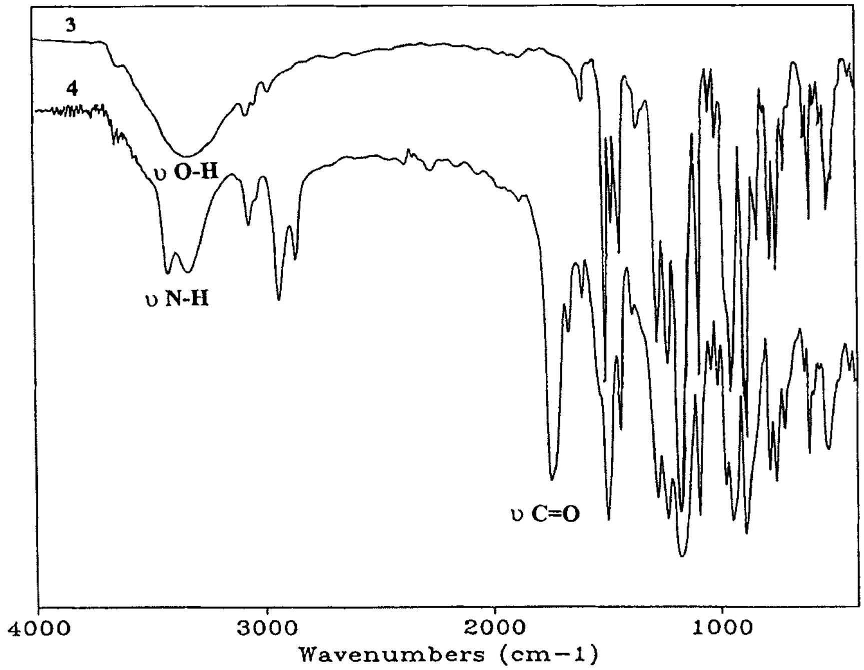


FIGURE 3 Infrared spectra of **3** and of polymer **4**.

The ^{31}P NMR spectrum in deuterated DMSO is similar to the one of **3** (triplet at $\delta = 11.4$ ppm and doublet at $\delta = 26.2$ ppm, $J = 89.8$ Hz). The ^{1}H NMR and IR spectra confirm the polyurethane structure. Indeed the formation of **4** is characterized in ^{1}H NMR by the appearance of four signals at $\delta = 1.3$, 1.5, 3.0 and 9.5 ppm representative of the methylene-(CH_2)-($\delta = 1.3$, 1.5 ppm), -$NHCH_2$- and -C(O)-N*H*- protons respectively (Table I). The IR spectra of **3** and **4** are given in Figure 3. They show all characteristic bands due to the cyclotriphosphazene ring and aromatic groups mainly around $v = 1230$, 1170 and 950 cm^{-1} attributed respectively to P=N, (P)-C-O and P-O-(C) stretching vibrations.[20,22,23] The presence of the urethane groups in **4** is characterized by two absorption bands in the region of 3330–3425 cm^{-1} and one at $v = 1745$ cm^{-1} which are assigned to the NH and carbonyl stretching vibrations respectively (the bands at $v = 3424$ cm^{-1} and $v = 3335$ cm^{-1} can be assigned to the free and hydrogen bonded NH stretching vibrations repectively).

The molecular weight of **4** determined by steric exclusion chromatography is Mw = 17000 with a molecular weight distribution Mw/Mn = 1.7. The thermal stability of the cyclolinear polyurethane **4** was investigated by thermogravimetric analysis in air. The corresponding thermogram is represented in Figure 4. The

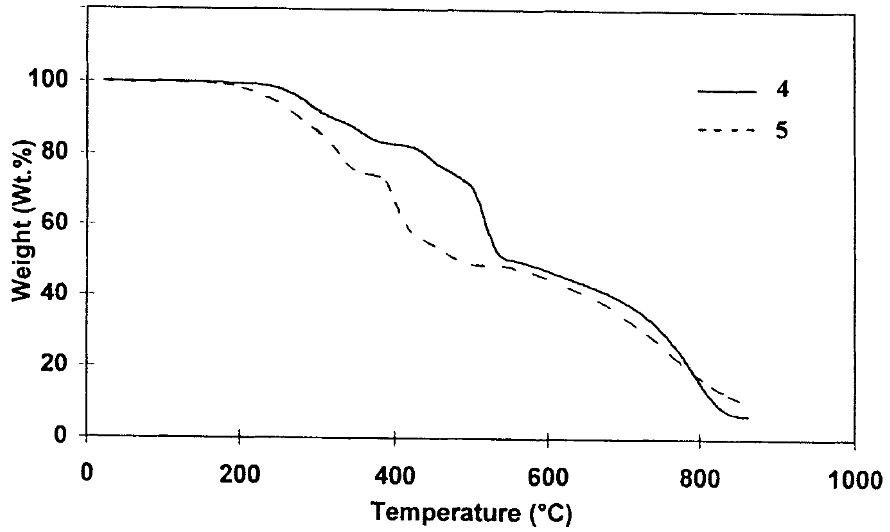


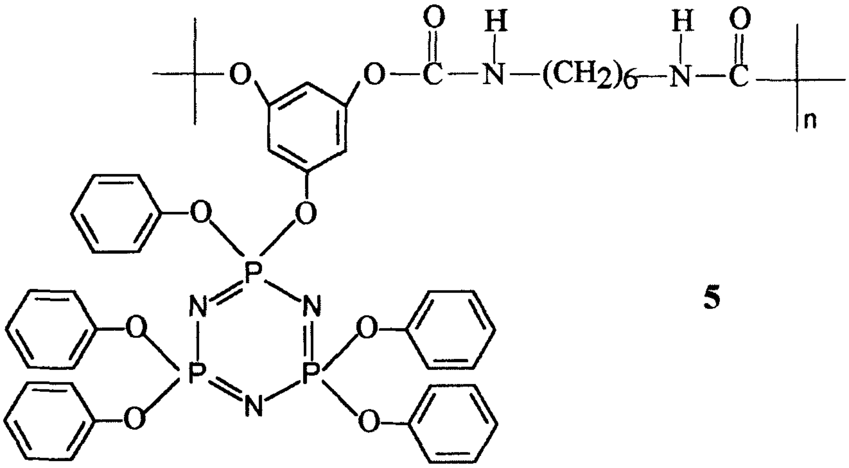
FIGURE 4 Thermogravimetry of **4** and **5** conducted at a heating rate of 8°C/min in an air atmosphere.

temperature corresponding to 10% weight loss (T_{10}) is 320°C, and 50% of the original weight is retained at 600°C. This high char yield which reflects the property of flame retardancy is characteristic of cyclotriphosphazenes containing polymers.[4,24] In fact for a polyurethane synthesized from the 1,3-bis(hydroxy)benzene/HDI reaction, the T_{10} is 209°C and the decomposition is achieved at 600°C.[1]

The influence of the cyclotriphosphazene on the thermal degradation of **4** is confirmed by the infrared spectrum of the residue obtained after the first degradation at 350°C. In fact the disappearence of the C = O stretching vibration at $\upsilon = 1750\ \mathrm{cm}^{-1}$ indicating the complete breaking down of the urethane linkages occurs at first, whereas the bands at $\upsilon = 1247, 1170, 960\ \mathrm{cm}^{-1}$ already observed for **3–4** and attributed to the substituted cyclotriphosphazene are kept at this stage. These bands are not identified in the spectrum of the polyurethane obtained from the 1,3-bis(hydroxy)benzene.

Figure 4 gives the thermogram of a polyurethane with pendant cyclotriphosphazene **5**. This polymer was synthesized from (3,5-dihydroxyphenoxy)penta(phenoxy)cyclotriphosphazene and HDI.[1]

The comparison between the two thermal degradation curves shows that the introduction of phosphorus atoms in the backbone, lightly improves the thermal properties of the polymer, the temperature required for 10% weight loss being only 287°C for **5**. The char yield at 600°C is the same in both cases(50%).



5

EXPERIMENTAL

Equipment

^{31}P, ^{1}H, and ^{13}C NMR spectra were recorded in $CDCl_3$ for compounds **1** and **2**, in acetone-d_6 for **3**, and in DMSO-d_6 for polymer **4** using a Bruker WP 300 NMR spectrometer. Chemical shifts (ppm) are positive in the low-field direction and are relative to external 85% H_3PO_4 (^{31}P) or external TMS (^{1}H, ^{13}C). Infrared spectra were recorded with a Bomem MB-100 spectrometer. The samples were dispersed in KBr. Molecular weights were obtained by means of steric exclusion chromatography on a Waters Millipore apparatus equipped with Shodex columns using THF as eluant. The calibration curve was established using standards polystyrene. Mass spectra were recorded with a Nermag R10–10B (fast atom bombardment) spectrometer. Thermogravimetry measurements were performed in air on a Setaram NTB10–8 instrument at a heating rate of 8°C/min. Elemental analysis were carried out at the Service Central d'Analyse CNRS, France.

Materials

Tetrahydrofuran (THF), Chlorobenzene, dichloromethane, and dimethylformamide (DMF) were obtained from SDS (Solvants Documentation Synthesis, France). THF and CH_2Cl_2 were purified by distillation. The other solvents were dried over molecular sieves. Sodium hydride (80%), bisphenol, sodium hydroxide, 4-methoxyphenol, boron tribromide and 1,6-hexamethylene diisocyanate (HDI) were Aldrich products and used as received. Hexachlorocyclotriphosphazene $N_3P_3Cl_6$ (Nippon Soda) was purified by vacuum sublimation. All reactions and manipulations were carried out under inert atmosphere.

Synthesis of 2, 2-Dichloro-4,4,6,6- bis[spiro(2',2"- dioxy-1',1"-biphenylyl)]cyclotriphosphazene (1)

Compound **1** was synthesized according to a procedure reported elsewhere.[25] To a three-necked round-bottom flask were added chlorobenzene (50ml), water (100ml), $N_3P_3Cl_6$ (5g, 14.3mmol), 2,2'-dihydroxy-1,1'-biphenyl (5.35g, 28.7 mmol), sodium hydroxide (2.29g, 57.4 mmol) and TBA (0.46g, 1.43mmol). The reaction was rapidly stirred at room temperature for 3h and heated at 70°C for another 3h. The solvents were removed under reduced pressure giving a brown residue which was washed with chlorobenzene and acetone and dried. A white solid was obtained (6.5g, yield: 79%). *Anal.* Calcd for $C_{24}H_{16}N_3O_4P_3Cl_2$ (**1**): C, 50.17; H, 2.79; N, 7.32; O, 11.15; P, 16.20; Cl, 12.37. Found: C, 50.98; H, 2.94; N, 7.15; O, 10.94; P, 16.11; Cl, 12.36. Spectroscopic data are given in Table I.

Synthesis of 2,2-bis(4-methoxyphenoxy)- bis[spiro(2',2"- dioxy-1',1"-biphenylyl)]cyclotriphosphazene (2)

A solution of 4-methoxyphenol (2.349g, 18.9 mmol) in THF was added dropwise to a solution of **1** (5.437 g, 9.46 mmol) with an excess of NaH (0.48 g, 20 mmol) in THF. The mixture was heated to 70°C for 24h, then cooled at room temperature and ultracentrifuged (3000 rpm) to separate the solid from the liquid. The THF was removed under reduced pressure. The residue was dissolved in dichloromethane, extracted twice with 10% aqueous NaOH, washed with water (three times), and dried over anhydrous sodium sulfate. After removal of the solvent under reduced pressure, we obtained 6 g of **2** (yield: 85%). *Anal.* Calcd for $C_{38}H_{30}N_3O_8P_3$ (**2**): C, 60.9; H, 4.0; N, 5.6; O, 17.1; P, 12.4. Found: C, 60.4; H, 4.1; N, 5.4; O, 16.8; P, 12.2. Spectroscopic data are given in Table I.

Synthesis of 2,2-bis(4-hydroxyphenoxy)- bis[spiro(2',2"- dioxy-1',1"-biphenylyl)]cyclotriphosphazene (3)

A solution of 3.35 g (13.4 mmol) of boron tribromide in anhydrous CH_2Cl_2 (30 ml) was added dropwise to a solution of **2** (5 g, 6.7 mmol) in anhydrous CH_2Cl_2 (50 ml). The reaction mixture was stirred at room temperature for 3 h and then poured into water (50ml). The obtained residue dissolved in CH_2Cl_2 was washed with water (three times) and dried over molecular sieves (4 Å). The solvent was finally removed under reduced pressure and we obtained 3.3 g of **3** (yield: 68%). *Anal.* Calcd for $C_{36}H_{24}N_3O_8P_3$ (**3**): C, 59.9; H, 3.6; N, 5.8; O, 17.7; P, 12.9. Found: C, 59.7; H, 3.8; N, 5.6; O, 16.9; P, 12.7. Spectroscopic data are given in Table I.

Synthesis of polyurethane (4)

A solution of 0.77 g (4.57 mmol) of 1,6-hexamethylene diisocyanate in dry DMF (10 ml) was added dropwise to a solution of **3** (4.57 mmol, 3.3 g) in the same solvent (10 ml) placed in a three-necked round-bottom flask. The reaction mixture was stirred at 80°C for 48h. The latter was then poured into cold methanol to precipitate the polymer, which was washed with methanol and finally dried under vaccum at 100°C for 12 h. We obtained 2.3 g of **4** (yield: 57%). *Anal.* Calcd for $C_{44}H_{36}N_5O_{10}P_3$ (**4**): C, 59.4; H, 4.3; N, 7.9; O, 18.0; P, 10.5. Found: C, 58.6; H, 4.5; N, 8.2; O, 18.1; P, 10.6. Spectroscopic data are given in Table I.

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