Aromatic Cyclolinear Phosphazene Polyimides Based on a Novel Bis-Spiro-Substituted Cyclotriphosphazene Diamine

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ABSTRACT: A new class of aromatic cyclolinear phosphazene polyimides has been synthesized from a novel bisspiro(arylenedioxy)cyclotriphosphazenediamine. The geminal diamine, 2,2-bis(4′-aminophenoxy)-4,4,6,6-bis[spiro(2′,2″-dioxy-1′,1″-biphenylyl)]cyclotriphosphazene (**5**) was polymerized by two-stage condensation polymerization with 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (BTDA, **7**) and 4,4′-hexafluoroisopropylidenediphthalic anhydride (6FDA, **8**), respectively. The obtained poly(amic acid)s **9** and **10** were spread on soda-lime glass plates with a doctor blade and left in a low-humidity chamber. The tack-free film of poly(amic acid) **9** was cyclodehydrated to a light-yellow polyimide (**11**) film by heating 1 h each at 100, 200, and 300 °C in a nitrogen atmosphere. The poly(amic acid) **10** on thermal cyclodehydration at 160 °C for 0.5 h, 235 °C for 1.5 h, and 280 °C for 0.5 h gave almost a colorless polyimide (**12**) film. The polyimide films showed good thermal stability and are noteworthy for their high char yield in air, viz., 58–50% at 800 °C. A simple and useful procedure was developed for the synthesis of polymer-grade monomer diamine (**5**). This involved substitution of 2,2-dichloro-4,4,6,6-bis[spiro(2′,2″-dioxy-1′,1″-biphenylyl)]cyclotriphosphazene (**3**) with a potassium salt of 4-nitrophenol followed by catalytic reduction of the formed 2,2-bis(4′-nitrophenoxy)-4,4,6,6-bis[spiro(2′,2″-dioxy-1′,1″-biphenylyl)]cyclotriphosphazene (**4**). The acetylation of diamine (**5**) gave 2,2-bis(4′-acetamidophenoxy)-4,4,6,6-bis[spiro(2′,2″-dioxy-1′,1″-biphenylyl)]cyclotriphosphazene (**6**) in 95% yield. The structures of these cyclic phosphazene precursors and monomer diamine were confirmed by FT IR, ^{1}H-NMR, ^{31}P-NMR and differential scanning calorimetry (DSC).

Introduction

Aromatic polyimides have found wide usage as films, coatings, adhesives, and matrix resins due to their excellent electrical and mechanical properties, high thermal and chemical stability, good solvent resistance, and dimensional stability. For this reason they have been used in the aerospace, electronics industries,[1,2a,b] and membrane technologies[2c] for a wide variety of applications. The common strategies to obtain such materials involve incorporation of flexibilizing and/or bulky groups into the polymer backbone. Cyclomatrix phosphazene polymers containing cyclotriphosphazene rings are known[3] for their excellent fire resistance. These polymers are different from the well-known linear poly(phosphazenes).[4]

In recent years, our group and others have developed exciting alternative methodologies for incorporating cyclotriphosphazenes into the structure of polymers. This approach is based on exploiting the reactivity of organofunctional cyclophosphazenes. We have successfully developed cyclotriphosphazene-containing poly(bismaleimides),[3,5–7] polyimides,[8] poly(ether imides),[9] epoxy,[10] and ethynyl type[11] matrix resins. 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 polymers were developed from suitably end-capped hexakis(4-aminophenoxy)cyclotriphosphazene, tetrakis(4-aminophenoxy)diphenoxycyclotriphosphazene, and tris(4-aminophenoxy)triphenoxycyclotriphosphazenes.

It has been recognized that polyimide films such as Kapton-H degrade rapidly in low Earth orbit environment by atomic oxygen[12] and on exposure to oxygen plasma in a plasma reactor. It has been shown that a thin film coating of about 1000 Å of SiO_x (where $1.9 \leq x \leq 2.0$) ion beam sputter deposited on Kapton-H can provide an adequate oxidation barrier. Such coatings, however, need special handling, and the coated polymeric material on exposure to atomic oxygen can be drastically eroded by an undercutting process at the defect sites. Hence, there is a definite need to develop intrinsically stable improved polyimide films. For these and other reasons we have designed and synthesized a new cyclotriphosphazene-containing diamine (**5**) to develop polyimide films with inherent fire- and heat-resistance characteristics and stability toward oxygen atoms and oxygen plasmas.

The 2,2′-dioxybiphenylyl substitution was selected as it is possible[13] to synthesize mono- and bis-spiro-substituted cyclotriphosphazenes. Also, unlike several alkylenedioxy- and arylenedioxy-substituted spirocyclotriphosphazenes,[14] tris(2,2′-dioxybiphenylyl)cyclotriphosphazene[15] forms no inclusion adducts when recrystallized or brought into contact with organic solvents; furthermore, it is stable at least up to 350 °C and does not polymerize by ring-opening thermal polymerization. The structure of the selected bis-spiro substitution was expected to provide an opportunity of improved thermal stability and reduced flexibility of the dioxybiphenylyl spiro seven-membered ring. The diamine **5** was specially designed for this work and has several advantages: (1) The polymer-grade diamine can be conveniently synthesized in pure form and in high yield. (2) The selection of bis-spiro substitution on a cyclotriphosphazene ring was designed to exclude regioisomers, otherwise possible, and to synthesize a difunctional product with geminal orientation.

In this paper, we describe the synthesis and characterization of novel hitherto unreported bis(arylenediox-

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y)spiro-substituted cyclophosphazene-based diamine and polyimides therefrom.

Experimental Section

Materials. Hexachlorocyclotriphosphazene (**1**) obtained from Nippon Soda Co., Ltd., Tokyo, Japan, was purified by sublimation at 80–82 °C (0.1 mm), followed by recrystallization from *n*-heptane. Differential scanning calorimetery (DSC) of purified trimer showed, as expected, a single sharp endotherm at 112.8 °C, while the mass spectrum indicated the appropriate mass (*m/z* = 348). 4-Nitrophenol (Aldrich) was purified by recrystallization from ethanol and dried in a vacuum oven; mp 113–115 °C. Potassium 4-nitrophenoxide was prepared by adding a solution of 4-nitrophenol in absolute ethanol into a solution of potassium hydroxide in absolute ethanol. The orange solid of potassium 4-nitrophenoxide was dried in a vacuum oven; mp > 300 °C. Platinum oxide (Alpha Product, 40 mesh) was used as received. *N,N*-Dimethylacetamide (DMAC; Aldrich) was distilled over calcium hydride. Tetrabutylammonium bromide (TBAB) was used as received from Aldrich. Chlorobenzene (Aldrich) was distilled over anhydrous calcium chloride and stored on molecular sieves. 2,2′-Dihydroxy-1,1′-biphenyl (Aldrich; **2**) was used as received, mp 108–110 °C. Xylene was refluxed over sodium and distilled, bp 137–144 °C. Aniline was refluxed over zinc dust and distilled, bp 184–185 °C. Acetic anhydride was refluxed over fused sodium acetate and distilled; bp 138–140 °C. Pyridine was refluxed over potassium hydroxide pellets and distilled, bp 114–115 °C. Aromatic dianhydrides were purified by vacuum sublimation and tested before use on a differential thermal analyzer (DTA). 3,3′,4,4′-Benzophenonetetracarboxylic dianhydride (BTDA; **7**) and 4,4′-hexafluoroisopropylidenediphthalic anhydride (6FDA; **8**) showed a single endotherm at 223 and 239–240 °C, respectively.

Measurements. All NMR spectra were recorded on a Bruker WM-250 spectrometer with an Aspect 3000 computer. The operating frequencies were 250.1 (^{1}H) and 101.2 MHz (^{31}P). Tetramethylsilane (Me_4Si) was used as an internal reference for ^{1}H NMR measurements. For ^{31}P NMR measurements 85% H_3PO_4 was used as an external standard. Chemical shifts downfield of the reference were assigned a positive sign. ^{31}P NMR spectra were recorded under conditions of broad-band decoupling. Infrared spectra were recorded on a FT-Nicolet spectrophotometer on a KBr disk. Thermal analysis was performed on a Perkin-Elmer thermal analysis data station interfaced with a TGS-2 thermogravimetric system.

Synthesis. 2,2-Dichloro-4,4,6,6-bis[spiro(2′,2″-dioxy-1′,1″-biphenylyl)]cyclotriphosphazene (3). To a three-necked, round-bottom flask equipped with a condenser and a guard tube, a nitrogen inlet, and a magnetic stirring bar, were added chlorobenzene (50 mL), water (100 mL), hexachlorocyclotriphosphazene (**1**; 6 g, 0.0172 mol), 2,2′-dihydroxy-1,1′-biphenyl (**2**; 7 g, 0.038 mol), sodium hydroxide (2.2 g, 0.076 mol), and TBAB (0.56 g, 0.0018 mol). The reaction was rapidly stirred at room temperature for 3 h and then allowed to heat at 70 °C for another 3 h. The contents of the reaction mixture was quenched with concentrated hydrochloric acid (14 mL). A white solid was obtained on flash evaporation of the reaction mixture. It was washed with a 5% aqueous potassium hydroxide solution and then with water. The product was recrystallized from acetone to give a shining crystalline solid of **3** (7.9 g, 80% yield); mp 328–330 °C (lit.[13] mp 325.7 °C). Mass spectrum, found *m/z* 573, calcd *m/z* 573. ^{1}H-NMR ($CDCl_3$): δ 7.26–7.56 (m, 16H, aromatic protons of two dioxybiphenyl groups).

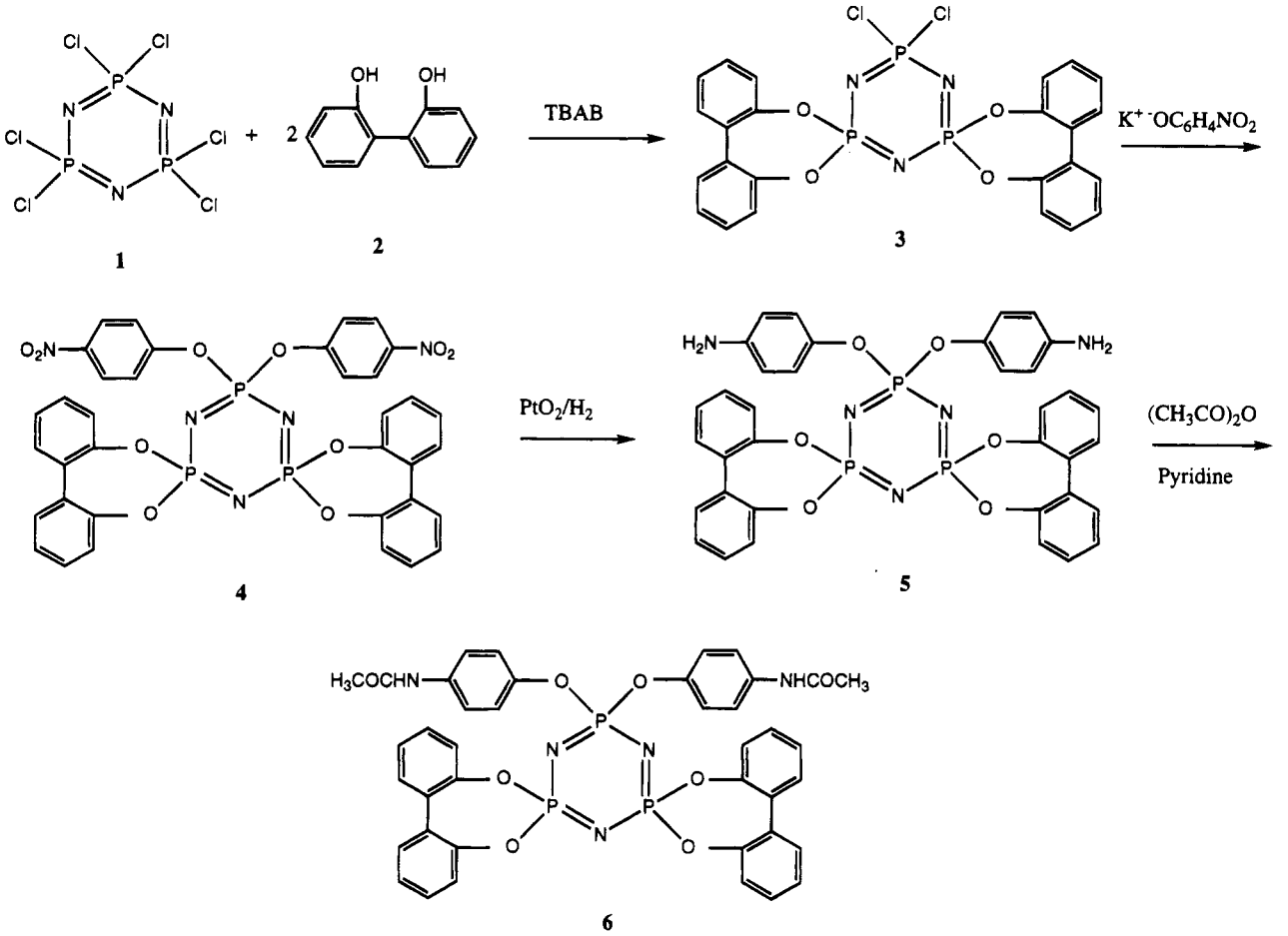
2,2-Bis(4′-nitrophenoxy)-4,4,6,6-bis[spiro(2′,2″-dioxy-1′,1″-biphenylyl)]cyclotriphosphazene (4). To a three-necked, round-bottom flask equipped with a nitrogen inlet and a Dean–Stark condenser with a guard tube was added 2,2-dichloro-4,4,6,6-bis[spiro-(2′,2″-dioxy-1′,1″-biphenylyl)]cyclotriphosphazene (**3**) (30 g, 0.0523 mol) to dissolve in xylene (700 mL). To this stirring solution were added potassium 4-nitrophenoxide (19.1 g, 0.1078 mol) and TBAB (2 g). The reaction mixture was refluxed at ~130 °C with vigorous stirring and a continuous purge of nitrogen until no more water was collected in a Dean–Stark trap. The product obtained after removal of xylene was poured over crushed ice. The solid obtained was filtered, suspended in a 10% aqueous solution of potassium hydroxide, and washed successively with water. Drying in air and a vacuum desiccator provided a white solid (37 g, 90% yield). It was recrystallized from hot xylene to give shining crystals of **4**, mp 263–264 °C. DSC: sharp endotherm at 266 °C. Anal. Calcd for $C_{36}H_{24}N_5P_3O_{10}$: C, 55.4; H, 3.1; N, 9.0; P, 11.9%. Found: C, 55.6; H, 3.1; N, 9.1; P, 11.9. IR (KBr pellet, cm^{-1}): ν 1519, 1339 (asymmetrical and symmetrical stretching of the nitro group); 1613, 1582, 1482 (aromatic); 1200, 1179, 1115 (P–N–P asymmetrical stretching of cyclotriphosphazene); 786 (P–N–P symmetrical stretching of cyclotriphosphazene); 950 (P–N stretching of cyclotriphosphazene); 1272 (ether). ^{1}H-NMR (DMSO-d_6): δ 7.27–7.29 (d, 4H aromatic, *meta* to nitro groups {≡P(–O–C_6H_4–NO_2)$_2$}, J = 7.4 Hz), 8.44–8.47 (d, 4H aromatic, *ortho* to nitro groups {≡P(–O–C_6H_4–NO_2)$_2$}, J = 7.4 Hz), 7.43–7.55 (m, 8H, aromatic protons of dioxybiphenyl groups), 7.60–7.61 and 7.64–7.65 (dd, 4H, aromatic protons of dioxybiphenyl groups, J = 7.4 and 1.5 Hz), 7.66–7.67 and 7.69–7.70 (dd, 4H, aromatic protons of dioxybiphenyl groups, J = 7.4 and 1.5 Hz).

2,2-Bis(4′-aminophenoxy)-4,4,6,6-bis[spiro(2′,2″-dioxy-1′,1″-biphenylyl)]cyclotriphosphazene (5). A 250-mL, heater-equipped, autoclave pressure bottle was charged with a solution of 2,2-bis(4′-nitrophenoxy)-4,4,6,6-bis[spiro(2′,2″-dioxy-1′,1″-biphenylyl)]cyclotriphosphazene (**4**; 12 g) in aniline (90 mL). To this solution was added platinum oxide (0.04 g). The mixture was agitated at 40–50 °C and 40 psi of hydrogen for ~2 h until no pressure drop was observed. Filtering off the catalyst provided a clear solution, which was concentrated on a rotatory evaporator under reduced pressure. The residue was treated with hexane. The product was filtered and dried to give a white solid (8 g, 75% yield). It was recrystallized from chlorobenzene and hexane to give a crystalline solid of **5**; mp 304–306 °C. DSC: sharp endotherm at 306.9 °C. Anal. Calcd for $C_{36}H_{28}N_5P_3O_6$: C, 60.1; H, 3.9; N, 9.7; P, 12.9. Found: C, 60.2; H, 4.0; N, 9.2; P, 13.0. IR (KBr pellet, cm^{-1}): ν 3470 and 3365 (N–H stretching of the amino group); 1619 and 1592 (N–H bending, amino); 1508 and 1470 (aromatic); 1198, 1171 (P–N–P asymmetrical stretching of cyclotriphosphazene); 780 (P–N–P symmetrical stretching of cyclotriphosphazene); 941 (P–N stretching of cyclotriphosphazene); 1258 (ether). ^{1}H-NMR (DMSO-d_6): δ 5.10 (s, 4H, ≡P(–O–C_6H_4–NH_2)$_2$, exchangeable to D_2O), 6.64–6.67 (d, 4H$_A$ aromatic, *meta* to amino groups {≡P(–O–C_6H_4–NH_2)$_2$}, J = 9 Hz), 6.97–7.0 (dd, 4H$_C$ aromatic, *ortho* to ether of dioxybiphenyl groups, J = 8 and 1.5 Hz), 7.17–7.2 (d, 4H$_D$ aromatic, *meta* to ether of dioxybiphenyl groups, J = 8 Hz), 7.43–7.55 (m, 4H$_E$ and 4H$_F$ aromatic, *para* and *meta* to ether of dioxybiphenyl groups), and 7.68–7.71 (d, 4H$_B$ aromatic, *ortho* to amino groups {≡P(–O–C_6H_4–NH_2)$_2$}, J = 9 Hz).

2,2-Bis(4′-acetamidophenoxy)-4,4,6,6-bis[spiro(2′,2″-dioxy-1′,1″-biphenylyl)]cyclotriphosphazene (6). To a round-bottom flask equipped with a guard tube and a magnetic stirring bar was added 2,2-bis(4′-aminophenoxy)-4,4,6,6-bis-[spiro(2′,2″-dioxy-1′,1″-biphenylyl)]cyclotriphosphazene (**5**; 0.5 g) in acetic anhydride (5 mL). To this stirring mixture was added dry pyridine (0.1 mL). The clear solution was allowed to stir overnight. The solution of the flask was poured over crushed ice to give a solid which was filtered and washed with water. The obtained solid on drying gave a white compound (**6**) in 95% yield. Anal. Calcd for $C_{40}H_{32}N_5P_3O_8$: C, 59.8; H, 4.0; N, 8.7; P, 11.6. Found: C, 60.0; H, 4.0; N, 8.8; P, 11.7. IR (KBr pellet, cm^{-1}): ν 1668 (carbonyl of CH_3–CO–NH–C_6H_4O–); 1499 (aromatic); 1199, 1168 (P–N–P asymmetrical stretching of cyclotriphosphazene); 780 (P–N–P symmetrical stretching of cyclotriphosphazene); 935 (P–N stretching of cyclotriphosphazene); 1258 (ether).

Polyimides Derived from BTDA, 6FDA, and Diamine 5 Containing Geminal Bis-Spiro-Substituted Cyclotriphosphazene. The diamine, 2,2-bis(4′-aminophenoxy)-4,4,6,6-bis[spiro(2′,2″-dioxy-1′,1″-biphenylyl)]cyclotriphosphazene (**5**; 3.59 g, 0.005 mol) was dissolved in DMAC (29.52 g, ~17% solution w/w) in a dry flask equipped with a magnetic

Scheme 1



stirring bar. To this continuously stirred solution was added in one lot[16] granular 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (BTDA, **7**; 1.62 g, 0.005 mol), and the polymerization was performed at room temperature in a closed flask to give a viscous poly(amic acid) **9**. A similar polymerization was carried out in *m*-cresol. The inherent viscosity of the poly(amic acid) **9** in DMAC was 0.48 dL/g at a concentration of 0.5 g/dL at 30 °C.

A *N,N*-dimethylacetamide (DMAC) solution (15–20% solids) of the poly(amic acid) **9** was spread on a clean, dry soda-lime glass plate with a doctor blade and dried to a tack-free film in a low-humidity chamber. The poly(amic acid) **9** film on thermal cyclodehydration 1 h each at 100, 200, and 300 °C in a forced oven in a nitrogen environment resulted in a light-yellow polyimide **11** film.

The polyimide **12** was similarly synthesized by the condensation polymerization of the diamine **5** and 4,4′-hexafluoroisopropylidenediphthalic anhydride (6FDA; **8**) in an equimolar quantity in DMAC, followed by thermal cyclodehydration of the resulting poly(amic acid) **10** at 160 °C for 0.5 h, 235 °C for 1.5 h, and 280 °C for 0.5 h. An almost colorless polyimide **12** film was obtained. The inherent viscosity of the poly(amic acid) **10** in DMAC was 0.50 dL/g at a concentration of 0.5 g/dL at 30 °C.

Results and Discussion

The specific reaction sequences used for the synthesis of cyclotriphosphazene-containing linear polyimides are given in Schemes 1 and 2. The diamine 2,2-bis(4′-aminophenoxy)-4,4,6,6-bis[spiro(2′,2″-dioxy-1′,1″-biphenylyl)]cyclotriphosphazene (**5**) has been synthesized for the first time. The cyclic trimer hexachlorocyclotriphosphazene (**1**) was conveniently reacted with 2,2′-dihydroxy-1,1′-biphenyl (**2**) by a typical interfacial condensation reaction in the presence of a phase-transfer catalyst (TBAB) using sodium hydroxide in water as an aqueous phase and chlorobenzene as an organic phase. A high-melting, soluble, white crystalline compound 2,2-dichloro-4,4,6,6-bis[spiro(2′,2″-dioxy-1′,1″-biphenylyl)]-cyclotriphosphazene (**3**) was obtained in pure form in high yield (~80%). No monosubstituted spiro product such as 2,2,4,4-tetrachloro-6,6-spiro(2′,2″-dioxy-1′,1″-biphenylyl)cyclotriphosphazene was isolated. This reaction provided a clean pathway to synthesize difunctional polymer-grade monomers required for the development of linear polymers. The dichloro compound **3** was characterized by ^{1}H-NMR, mass, and differential scanning calorimetry. The mass spectra showed M^+ at *m/z* 573 consistent with its structure and indicated substitution at two phosphorus atoms by bis-spiro groups. The IR spectra showed bands assigned to the P–N stretching mode and biphenyl stretching mode.

To examine the conformations assumed by the dioxybiphenyl unit, the X-ray crystal structure of 2,2,4,4-tetrachloro-6,6-spiro(2′,2″-dioxy-1′,1″-biphenylyl)cyclotriphosphazene was obtained.[17] The data demonstrated that the O–P–O bond angle was about 102.6°, similar to the reported[18] Cl–P–Cl bond angle of 101.8–102° in hexachlorocyclotriphosphazene, indicating that the presence of a bulky seven-membered ring at phosphorus virtually has no effect in widening the O-P-O bond angle due to the marked twisting of the seven-membered ring. The principal axis of the biphenyl group is twisted from the mean PN phosphazene ring plane. Furthermore, the average 41° twist between phenyl units within the biphenyl group further increases the molecular volume occupied by the substituents imparting thermal and chemical stability.

Scheme 2

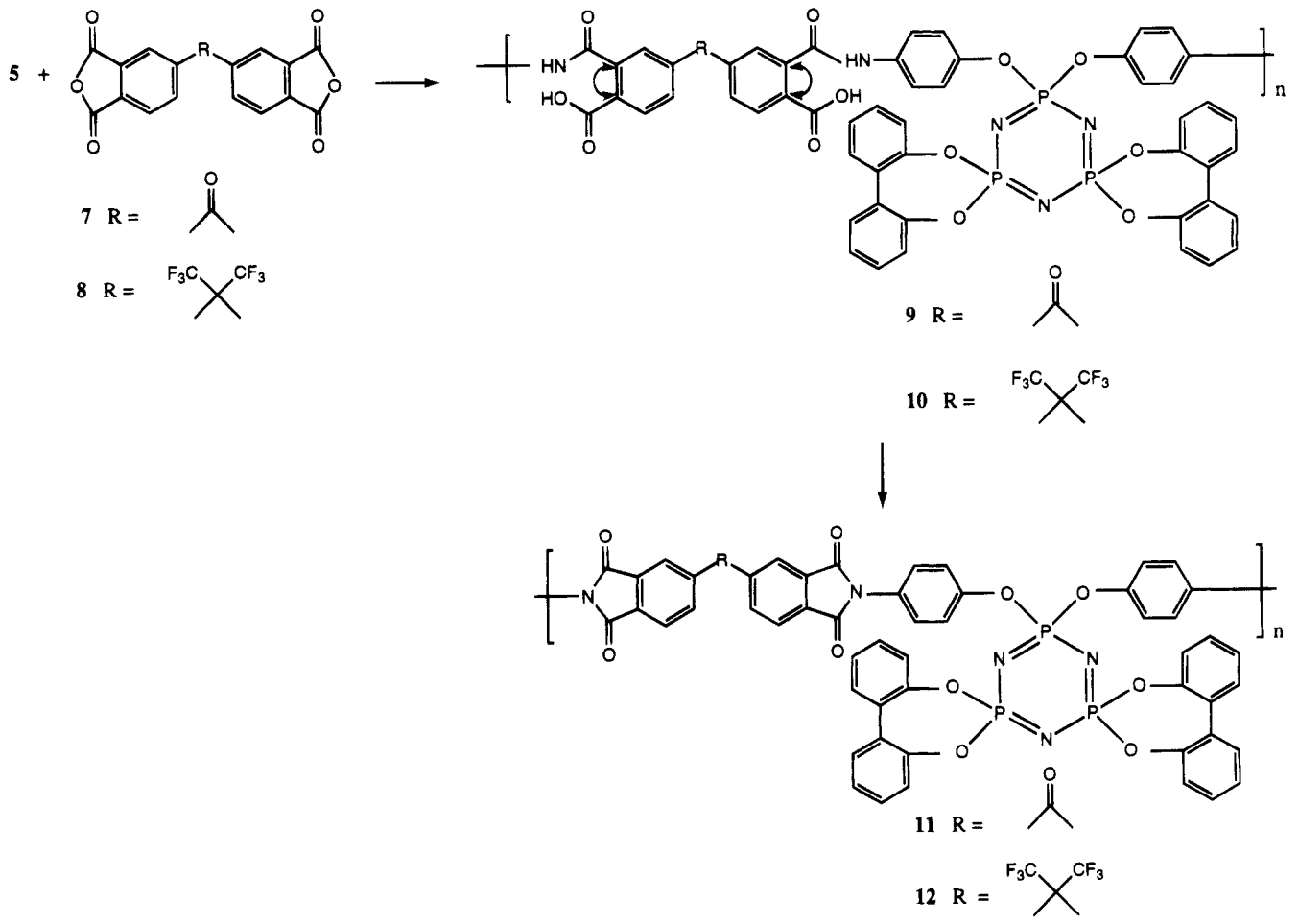
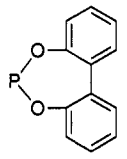
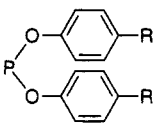


Table 1. ^{31}P NMR Spectral Data for Spiro(dioxybiphenyl)cyclotriphosphazenes[a]

	δp_2 and δp_3			δp_1		
compound	ppm	J_{pp}, Hz	R	ppm	J_{pp}, Hz	P1:P2:P3
4	30.54, 30.51	29.61, 29.58, 91.59	NO_2	15.59, 14.69, 14.63, 13.73	91.59	1:1:1
5	31.68, 31.65	30.80, 30.77, 88.20	NH_2	17.33, 16.46, 16.43, 15.57	88.20	1:1:1
6	31.40, 31.38	30.47, 30.44, 89.00	$NHCOCH_3$	16.92, 16.04, 16.00, 15.12	89.00	1:1:1

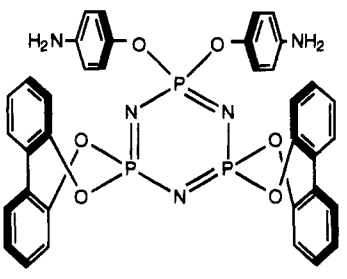
[a] Structures given in Scheme 1.

The reaction of 2,2-dichloro-4,4,6,6-bis[spiro(2′,2″-dioxy-1′,1″-biphenylyl)]cyclotriphosphazene (**3**) with potassium 4-nitrophenoxide in refluxing xylene provided the complete substitution. The water was removed as an azeotrope in the presence of a phase-transfer catalyst (TBAB). A white crystalline solid (**4**) in 90% yield was obtained. The differential scanning calorimetry of nitro compound **4** showed a sharp endotherm at 266 °C. The proton NMR of nitro compound **4** showed characteristic *ortho*-coupled doublets at 7.27–7.29 and 8.44–8.47 ppm, respectively, for eight aromatic protons of the two 4-nitrophenoxy groups. The downfield shift of the *ortho* protons to 8.44–8.77 ppm was characteristic[19] of the 4nitrophenoxy group. The dioxybiphenyl aromatic protons were seen intact. The integration of the 4-nitrophenoxy aromatic protons to dioxybiphenyl aromatic protons was seen in a ratio of 1:2, confirming complete sub-stitution of the intermediate dichlorocyclotriphosphazene derivative with 4-nitrophenoxy groups. The IR spectra showed characteristic bands for the presence of nitro groups, phosphazene, and bisspiro dioxybiphenyl ring.

One of the most interesting features of compound **4** is connected with the overall conformations of the dioxybiphenyl side groups. The phosphorus-31 NMR spectra surprisingly did not show the expected AB_2 pattern. Further splitting was observed (Table 1). This indicated that the two phosphorus atoms attached to the dioxybiphenyl ring are not magnetically equivalent, and the molecule is not symmetrical. This nonequivalence of the two phosphorus atoms could be due to the difference in the angle of twist of the two phenyl groups of the biphenyl moieties and their twist in a different direction. The reason for this reversal twist/distortion

could be due the advantageous thermodynamically-stable seven-membered dioxybiphenyl ring conformation by imparting reduced 6,6′ hydrogen−hydrogen contacts without broadening the O−P−O angle. The observation of a splitted doublet (Table 1) due to the two phosphorus atoms attached to the dioxybiphenyl groups indicates that such a conformation possibly exists in the solution. This may be due to the fact that in solution either averaging of the conformational possibilities is not complete or the twisted biphenyls of the dioxybiphenyl seven-membered spiro rings attend kinetically-stable conformations due to the intrinsic nature of the substitution groups.

The nitro groups of **4** were catalytically reduced with molecular hydrogen in the presence of PtO_2 to yield 2,2-bis(4′-aminophenoxy)-4,4,6,6-bis[spiro(2′,2″-dioxy-1′,1″-biphenylyl)]cyclotriphosphazene (**5**) in good yield. The differential scanning calorimetery examination of the obtained diamine **5** showed a sharp endotherm at 306.9 °C. The crystalline, high-melting diamine **5** was soluble in THF, chlorobenzene, and aprotic solvents. An IR spectrum of **5** showed the absence of nitro stretching which indicates the completion of reduction. Also, the presence of amino, cyclotriphosphazene, and dioxybiphenyl groups was observed. Its proton NMR in deuterated DMSO showed the presence of two D_2O exchangeable amino groups (four protons) along with eight *ortho*-coupled aromatic protons of the two 4-aminophenoxy groups and 16 aromatic protons of the two dioxybiphenyl groups; the 2:4:8 ratio of the respective protons confirmed the structure of diamine **5**. The phosphorus-31 NMR demonstrated two types of phosphorus atoms in the cyclotriphosphazene ring due to aminophenoxy and spiro substituents (Table 1); however, the spiro-substituted phosphorus atoms were seen magnetically nonequivalent as found in nitro compound **4**. On the basis of the observed phosphorus-31 NMR magnetic nonequivalance of the spiro-substituted phosphorus atoms of the diamine **5** and the X-ray crystal structure of 2,2,4,4-tetrachloro-6,6-spiro(2′,2″-dioxy-1′,1″-biphenylyl)cyclotriphosphazene,[17] tris[spiro(2′,2″-dioxy-1′,1″-biphenylyl)]cyclotriphosphazene,[15] and 2,4-bis(4-aminophenoxy)-2,4-diphenoxy-6,6-diphenylcyclotriphosphazene,[20] it is believed the structure of diamine **5** may have twisted seven-membered spiro rings and the side group conformations are arranged with phenyl groups twisted in the opposite direction from the plane of the cyclotriphosphazene ring. A perspective structure of diamine **5** can be shown as



To further confirm the structure of diamine **5**, its acetylation was performed at room temperature with acetic anhydride and pyridine. The obtained 2,2-bis(4′-acetamidophenoxy)-4,4,6,6-bis[spiro(2′,2″-dioxy-1′,1″-biphenylyl)]cyclotriphosphazene (**6**) was characterized by FT IR and ^{31}P-NMR spectroscopy. The FT IR spectrum showed a band at 1668 cm^{-1} due to the carbonyl of the acetamido group, indicating acetylation

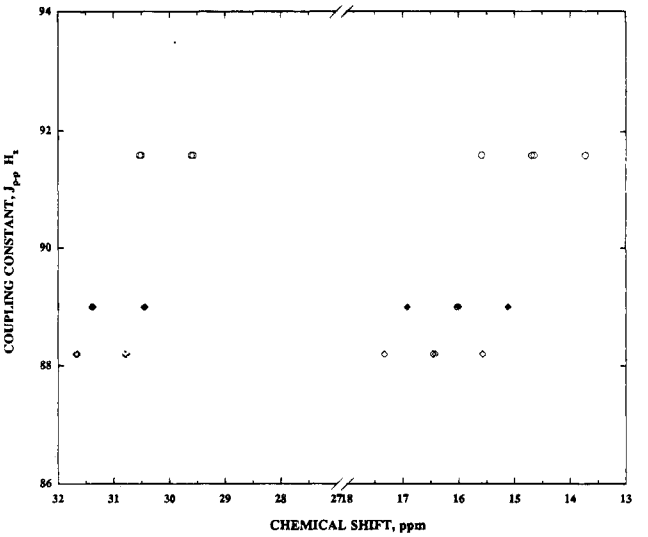


Figure 1. Plot of ^{31}P NMR chemical shift (δ_p) and coupling constant (J_{pp}) values of bis(4-nitrophenoxy)bis[spiro(2′,2″-dioxy-1′,1″- biphenylyl]cyclotriphosphazene (**4**) (○), bis(4-acetamidophenoxy)bis[spiro(2′,2″-dioxy-1′,1″-biphenylyl)]cyclotriphosphazene (**6**) (◆), and bis(4-nitrophenoxy)bis[spiro(2′,2″-dioxy-1′,1″- biphenylyl)]cyclotriphosphazene (**5**) (◇).

of the amino groups. The presence of phosphazene and dioxybiphenyl was seen intact. ^{31}P-NMR spectra recorded in DMSO-d_6 showed a splitted AB_2 type of pattern with a coupling constant of 89.0 Hz, indicating the presence of two types of phosphorus in the cyclotriphosphazene ring due to acetamidophenoxy and spiro substituents (Table 1); however, the spiro-substituted phosphorus atoms were seen magnetically nonequivalent, similar to that observed in nitro compound **4** and amino compound **5**.

The proton-decoupled ^{31}P NMR spectral data obtained for dioxybiphenyl-substituted spirocyclophosphazenes **4**−**6** are given in Table 1 and plotted in Figure 1. It was observed that the chemical shift positions of all three phosphorus atoms and their coupling constants are influenced by the presence of the nature of the substitution [4-NO_2 (**4**), 4-NH_2 (**5**), or 4-$NHCOCH_3$ (**6**)] on the phenoxy group attached to one of the phosphorus atoms (P_1) of the cyclophosphazene ring. The net effect of the respective substitution groups was such that the P_1 phosphorus resonance signals were observed most downfield for 4-aminophenoxy group substituted phosphorus and least for 4-nitrophenoxy group substituted phosphorus, and the order was 4-aminophenoxy > 4-acetamidophenoxy > 4-nitrophenoxy. A similar trend was observed for the chemical shift of the dioxybiphenyl-substituted phosphorus atoms (P_2 and P_3). However, a similar, but opposite, trend was observed for the coupling constants (J_{pp}, Hz). That is, the coupling constant was found lowest in the case of the 4-aminophenoxy group (88.2 Hz) and highest in the case of the 4-nitrophenoxy group (91.59 Hz), and the order was 4-nitrophenoxy > 4-acetamidophenoxy > 4-aminophenoxy. Also, a linear corelationship was found when the chemical shift values of the phosphorus atoms were plotted against the coupling constant values (Figure 1). It demonstrated that as the coupling constant increases the chemical shift correspondingly decreases.

Condensation polymerization of the diamine **5** with an equimolar amount of 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (BTDA; **7**) was performed at room temperature to give the corresponding poly(amic acid) **9**. The polymerization was carried out by the two-

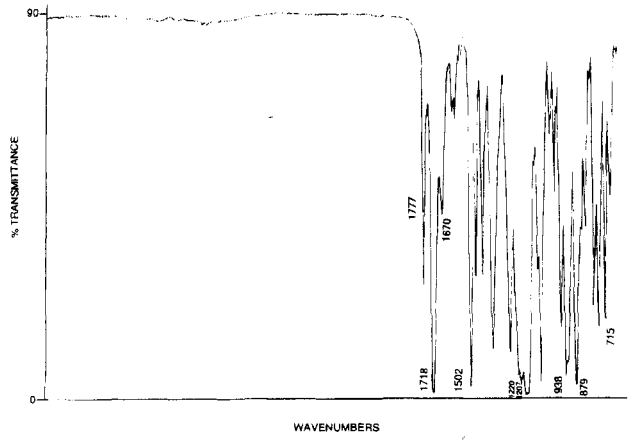


Figure 2. Infrared spectrum of polyimide **11** on a KBr disk.

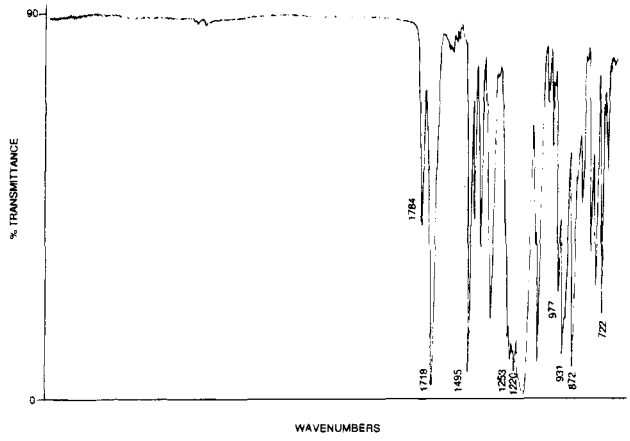


Figure 3. Infrared spectrum of polyimide **12** on a KBr disk.

stage polycondensation reaction. The first step of the condensation polymerization was performed in an aprotic solvent such as *N,N*-dimethylacetamide or in a phenolic solvent such as *m*-cresol. The addition of a solid dianhydride was performed[16] in one lot to avoid any premature hydrolysis of the dianhydride. The viscous solutions of the poly(amic acid)s obtained can be stored for several days. Cyclodehydration, the second stage of imidization, of the tack-free film was carried out thermally 1 h each at 100, 200, and 300 °C in a forced oven in a nitrogen environment. The IR spectrum (Figure 2) of the obtained light-yellow polyimide **11** showed characteristic bands due to imide (1777 and 1718 cm^{-1}), cyclophosphazene ring (1207, 1199, and 1167 cm^{-1}), and aromatic groups. The band at 1670 cm^{-1} was characteristic of the carbonyl of the benzophenone moiety. A colorless polyimide **12** film was similarly obtained by condensation polymerization of diamine **5** with 4,4′-hexafluoroisopropylidenediphthalic anhydride (6FDA; **8**) followed by cyclodehydration of the resulting poly(amic acid) **10** at 160 °C for 0.5 h, 235 °C for 1.5 h, and 280 °C for 0.5 h. The infrared spectra (Figure 3) of this film showed characteristic imide (1784 and 1718 cm^{-1}) bands. A cluster of bands due to CF_3–C–CF_3 spread over 1253 cm^{-1} from the 6FDA moiety were seen along with the phosphazene bands at 1198 and 1161 cm^{-1}.

The thermal stability of cyclotriphosphazene-containing aromatic polyimides **11** and **12** was investigated by dynamic thermogravimetry in air (Figure 4). The polyimides **11** and **12** showed thermooxidative decomposition starting at ~410 °C and a char yield in the range of 58–50% at 800 °C in an air atmosphere. It

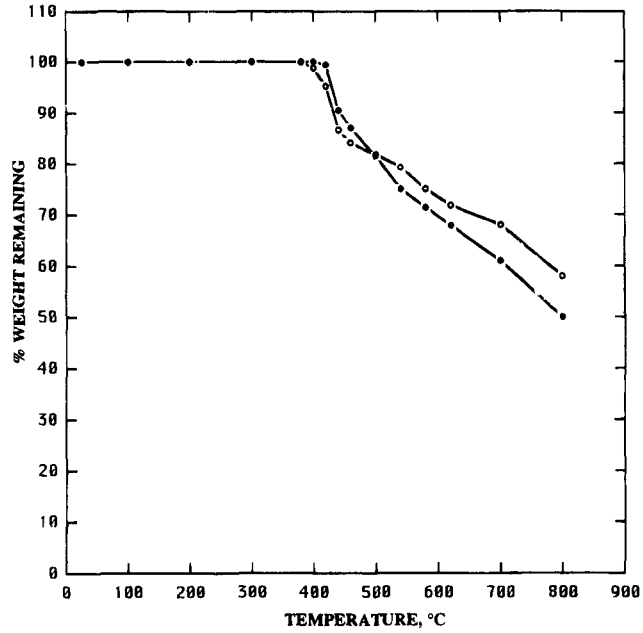


Figure 4. Thermogravimetric analysis of polyimides **11** and **12** in air. Conditions: gas flow rate, 100 mL/min; heating rate, 20 °C/min.

should be noted that such a high char yield is characteristic of these cyclotriphosphazene-containing polyimides. Most of the available commercial linear polyimides degrade almost catastrophically in an air atmosphere beyond 600 °C without leaving any residue. In comparison to other phosphorus-containing linear polyimides,[21] the developed cyclotriphosphazene-containing polyimide films exhibit higher char yield at 800 °C in air. The observation of high char yield may be explained due to the presence of a higher percentage of phosphorus (in the form of a cyclotriphosphazene ring) per repeat unit of the polyimide chain in comparison to phosphorus-containing polyimides.

Conclusion. We have developed a new class of cyclolinear polyimides containing bis(arylenedioxy)spirocyclotriphosphazene as an integral part of the polymer chain and reported them here for the first time. In comparison to other polyimides that are now commercially available, these polyimides offer advantages of thermooxidative stability and high char yield in air. The possibility of regioisomeric mixture and contamination with tris- and terakisfunctional cyclophosphazenes has been conveniently removed in the diamine **5** by molecular design (selection of bis-spiro substituents) and proper synthetic procedures and pathway. The observation of high char yield in an air atmosphere, colorless to light-yellow color films, and bulky bis-spiro-substituted pendants makes cyclotriphosphazene-containing polyimides potential candidates for a variety of applications in space, aerospace, microelectronics, and membrane technologies.

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