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Pendant Cyclodicarbaphosphazatriene-Containing Monomers and Polymers: Synthesis, Crystal Structures and Polymerization Behavior of $[NC(NMe_2)]_2[NP(O\text{-}C_6H_4\text{-}p\text{-}C_6H_4\text{-}p\text{-}CH{=}CH_2)(X)]$, X = Cl, OCH_2CF_3, OC_6H_5, $OC_6H_4\text{-}m\text{-}CH_3$, $OC_6H_4\text{-}p\text{-}Br$[†]

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The reaction of the dicarbaphosphazene, $[NC(NMe_2)]_2[NPCl_2]$ (**2**), with the sodium salt of 4-hydroxy-4′-vinylbiphenyl afforded the vinyl group containing monomer $[NC(NMe_2)]_2[NP(Cl)(O\text{-}C_6H_4\text{-}p\text{-}C_6H_4\text{-}p\text{-}CH{=}CH_2)]$ (**3**). Replacement of the lone chlorine atom of **3** by oxygen nucleophiles gave $[NC(NMe_2)]_2[NP(OR)(O\text{-}C_6H_4\text{-}p\text{-}C_6H_4\text{-}p\text{-}CH{=}CH_2)]$ [R = CH_2CF_3 (**4**); C_6H_5 (**5**); $C_6H_4\text{-}m\text{-}CH_3$ (**6**); $C_6H_4\text{-}p\text{-}Br$(**7**)]. The X-ray crystal structures of **3**–**7** reveal that all the cyclodicarbaphosphazenes have a planar N_3PC_2 ring; the ring carbons are completely planar, while the geometry around phosphorus is pseudotetrahedral. The presence of weak intermolecular hydrogen bonding {C–H---X(Cl or Br), C–H---N, or C–H---π} interactions in **3**–**7** leads to the formation of polymeric architectures in the solid-state. The monomers **4**–**7** can be polymerized by a free-radical initiator to afford the corresponding air-stable homopolymers **8**–**11**. These have moderate molecular weights with polydispersity indices ranging from 1.33 to 1.58. All of these polymers have high glass transition temperatures and have excellent thermal stability.

Introduction

Polyphosphazenes, $[N{=}PR_2]_n$, are the largest family of inorganic polymers with over 800 different examples.[1] Another class of related polymers contains an *intact* cyclophosphazene ring as a pendant group attached at regular intervals to the backbone of an organic polymer.[2] These polymers are obtained by polymerizing a cyclotriphosphazene monomer $N_3P_3R_5X$ (X = a vinyl-containing substituent; R = other type of substituent). While the initial studies were curiosity driven and were aimed to establish the proof of principle in terms of the concepts of monomer design and their polymerization behavior,[3] later studies in this area have embarked on the utility of such polymers in diverse applications such as ion-conducting materials,[4] polymeric ligands for preparing new catalyst systems,[5] and thermally stable materials.[6] In contrast to the successful

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[†] Dedicated to Prof. Christopher W. Allen on the occasion of his sixtieth birthday.

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strategies that exist for the incorporation of cyclophosphazenes as pendants on organic polymers, relatively few other inorganic rings have been similarly incorporated on polymer backbones. There have been a few reports on polymers containing silsesquioxanes,[7] boron−nitrogen rings and carboranes,[8] or cyclothiaphosphazenes[9] as pendants. Surprisingly there have been no attempts to prepare carbacyclophosphazene based monomers and to study their polymerization behavior. Apart from academic curiosity, such an exercise is also of interest from the point of view of generating novel polymers. The considerable difference in properties between polyphosphazenes and polycarbaphosphazenes is already documented.[10] With these objectives in mind we have embarked on the design of appropriate polymerizable dicarbaphosphazene synthons. Previously, Inoue and we have shown that $N_3P_3Cl_5(O\text{-}C_6H_4\text{-}p\text{-}C_6H_4\text{-}p\text{-}CH{=}CH_2)$ and related monomers can be utilized successfully to prepare homo- and copolymers containing cyclophosphazene as the pendant group.[3d,2f] In view of this we have decided to incorporate the $(O\text{-}C_6H_4\text{-}p\text{-}C_6H_4\text{-}p\text{-}CH{=}CH_2)$ group in a cyclodicarbaphosphazene skeleton. Accordingly we report in the following the synthesis, crystal and molecular structures, and polymerization studies of the novel dicarbaphosphazenes $[NC(NMe_2)]_2[NP(Cl)(O\text{-}C_6H_4\text{-}p\text{-}C_6H_4\text{-}p\text{-}CH{=}CH_2)]$ (**3**), $[NC(NMe_2)]_2[NP(OCH_2CF_3)(O\text{-}C_6H_4\text{-}p\text{-}C_6H_4\text{-}p\text{-}CH{=}CH_2)]$ (**4**), $[NC(NMe_2)]_2[NP(OC_6H_5)(O\text{-}C_6H_4\text{-}p\text{-}C_6H_4\text{-}p\text{-}CH{=}CH_2)]$ (**5**), $[NC(NMe_2)]_2[NP(OC_6H_4\text{-}m\text{-}CH_3)(O\text{-}C_6H_4\text{-}p\text{-}C_6H_4\text{-}p\text{-}CH{=}CH_2)]$ (**6**), $[NC(NMe_2)]_2[NP(OC_6H_4\text{-}p\text{-}Br)(O\text{-}C_6H_4\text{-}p\text{-}C_6H_4\text{-}p\text{-}CH{=}CH_2)]$ (**7**). We also report the thermal properties of the polymers derived from these dicarbaphosphazene monomers. To the best of our knowledge these represent the first examples of dicarbaphosphazene pendant containing monomers and polymers.

Experimental Section

General. Solvents and other general reagents used in this work were purified according to standard procedures.[11] AIBN was freshly recrystallized from methanol before use. 4-Hydroxy-4′-vinylbiphenyl,[12] $[NCCl]_2[NPCl_2]$[13] (**1**), *N*,*N*,*N*′,*N*′-tetramethylmethylenediamine,[14] and $[NC(NMe_2)]_2[NPCl_2]$[15] (**2**) were prepared according to literature procedures.

Instrumentation. ^1H, ^{31}P, ^{19}F, and ^{13}C NMR spectra were recorded in $CDCl_3$ solution on a JEOL spectrometer operating at 400.0, 135.0, 376.0, and 100.4 MHz, respectively. Chemical shifts are reported with respect to internal tetramethylsilane (^1H and ^{13}C), external 85% H_3PO_4 (^{31}P), and external $CFCl_3$ (^{19}F). Mass spectra were recorded on a JEOL SX 102/DA 6000 mass spectrometer using xenon (6kV, 10mA) as the FAB gas. IR spectra were recorded as KBr pellets on a Bruker Vector 22 FT IR spectrophotometer operating from 400 to 4000 cm^{-1}. TGA was recorded on a Perkin-Elmer Pyris 6 thermo gravimetric analyzer in nitrogen or an oxygen atmosphere at a heating rate of 20 °C/min. Differential scanning calorimetric studies were carried out on a Perkin-Elmer Pyris 6 DSC machine at the rate of 10 °C/min in a nitrogen atmosphere. Gel permeation chromatography was carried out on Maxima 800 instrument with THF as the solvent and polystyrene as the standard.

X-ray Crystallography. Colorless crystals of **3, 4, 5, 6,** and **7** were grown from a solution of dichloromethane by allowing *n*-hexane to diffuse slowly at room temperature. X-ray diffraction data for **3** were collected on an Enraf Nonius FR590 CAD-4 diffractometer. The structure of **3** was solved by using WINGX version 1.63, a crystallographic collective package (L. J. Farrugia, WINGX ver 1.63, an integrated system of Windows programs for the solution, refinement, and analysis of single-crystal X-ray diffraction data, Department of Chemistry, University of Glasgow). The structure was solved initially with SIR97 and was refined with the SHELX-97[16] package incorporated in WINGX. X-ray data for the crystals **4** and **5** were collected on a Siemens P4S diffractometer, and for **6** and **7** the data were collected on a SMART APEX CCD (Bruker-AXS) diffractometer. The crystal structures of **4**, **5**, **6,** and **7** were solved and refined with the SHELXTL program.[17] All the structures were refined against F^2 with full-matrix least-squares algorithm. Hydrogen atoms were fixed at calculated positions and their positions were refined by a riding model. Non-hydrogen atoms were refined with anisotropic displacement parameters.

Disordered carbon atoms of phenyl and vinyl groups in **3** were found with occupancies of 60% for C15, C16, C28, C23, C31, and C34, 40% for C29, C11a, C22, C27, C25, and C24a, and 50% each for C18, C19, C32 and C33, C26, C39. In the case of **4** there are two independent molecules **4A** and **4B** in the asymmetric unit cell. In **4B** disordered fluorine atoms of the trifluoroethoxy group were found with occupancies of 52% for F1b, F2b, and F3b and 48% for F1bb, F2bb, and F3bb. In both **4A** and **4B** one of the carbon atoms in the vinyl group is disordered with occupancies of 70% for C22a and C22b and 30% for C22c and C22d, respectively.

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Preparation of $[NC(NMe_2)]_2[NP(Cl)(O\text{-}C_6H_4\text{-}p\text{-}C_6H_4\text{-}p\text{-}CH{=}CH_2)]$ (3). A solution of the sodium salt of 4-hydroxy-4′-vinylbiphenyl prepared by the reaction of NaH (0.29 g, 12.0 mmol) and 4-hydroxy-4′-vinylbiphenyl (2.40 g, 12.0 mmol) was taken in tetrahydrofuran (50 mL) and added dropwise to a solution of $[NC(NMe_2)]_2[NPCl_2]$ **(2)** (3.14 g, 12.0 mmol) in tetrahydrofuran (50 mL) at room temperature. The reaction mixture was subsequently heated under reflux for 24 h, allowed to cool, and filtered through a G3 frit containing Celite. Removal of solvent from the filtrate in vacuo afforded a pale yellow precipitate. This was subjected to flash column chromatography on a neutral alumina column using ethyl acetate/*n*-hexane (5:95) as the eluant to obtain pure **3**. Yield: 3.3 g, 65%. Mp 130−131 °C. IR (KBr) cm^{-1}: 3033 (m), 2932 (s), 2866 (s), 2350 (w), 1471 (s), 1373 (s), 1268 (s), 1191 (s), 1078 (s), 957 (s), 918 (s), 868 (s), 824 (s), 761 (s), 652 (m), 594 (s), 538 (s). MS(FAB): $416(M^+)$. Anal. Calcd for $C_{20}H_{23}N_5OPCl$ (415.86): C, 57.76; H, 5.57; N, 16.84. Found: C, 57.21; H, 5.26; N, 16.53. ^1H NMR: δ 7.19−7.50 (m, 8 H, aromatic), 6.68 (dd, 1 H, $J = 17.6$ and 11.0 Hz, $-CH{=}CH_2$), 5.72 (d, 1 H, $J = 17.6$ Hz, $-CH{=}CH_2$ (trans)), 5.21 (d, 1 H, $J = 11.0$ Hz, $-CH{=}CH_2$ (cis)), 3.04 (s, 12 H, NMe_2). $^{31}P\{^1H\}$ NMR: δ 49.1(s). ^{13}C NMR: δ 165.1 (ring carbon, d, $^2J(^{31}P-N-^{13}C) = 10.0$ Hz), 150.0 (ipso carbon of the biphenylyloxy group, d, $^2J(^{13}C-N-^{31}P) = 9.9$ Hz), 139.4, 137.9, 136.5, 136.2, 127.9, 127.0, 126.6, 121.6, 113.9, 36.4, 36.2.

Preparation of $[NC(NMe_2)]_2[NP(OCH_2CF_3)(O\text{-}C_6H_4\text{-}p\text{-}C_6H_4\text{-}p\text{-}CH{=}CH_2)]$ (4). A solution of sodium trifluoroethoxide, prepared by the addition of sodium (0.06 g, 2.4 mmol) to trifluoroethanol (0.24 g, 2.4 mmol) in 30 mL of tetrahydrofuran, was added to a stirred solution of **3** (1.00 g, 2.4 mmol) in 30 mL of tetrahydrofuran. The mixture was stirred at room temperature for 48 h and filtered and the solvent was removed from the filtrate in vacuo to yield a solid. This was purified on a silica gel column by using ethyl acetate:*n*-hexane (7:93) as the eluant. Yield: 1.04 g, 90%. Mp 115−116 °C. IR (KBr) cm^{-1}: 3031 (w), 2933 (s), 2868 (m), 2359 (w), 1482 (s), 1399 (s), 1285 (s), 1217 (s), 1170 (s), 1089 (s), 987 (s), 956 (s), 894 (s), 833 (s), 765 (m), 657 (w), 609 (w), 544 (w). Anal. Calcd for $C_{22}H_{25}F_3N_5O_2P$ (479.44): C, 55.11; H, 5.26; N, 14.61. Found: C, 54.81; H, 5.13; N, 14.19. MS (FAB): $480(M^+)$. ^1H NMR: δ 7.20−7.52 (m, 8 H, ar), 6.74 (dd, 1 H, $J = 17.7$ and 11.0 Hz, $-CH{=}CH_2$), 5.78 (d, 1 H, $J = 17.6$ Hz, $-CH{=}CH_2$ (trans)), 5.27 (d, 1 H, $J = 11.0$ Hz, $-CH{=}CH_2$ (cis)), 4.24 (q, 2 H, $J = 7.6$ Hz, CH_2), 3.07 (s, 12 H, NMe_2). $^{31}P\{^1H\}$ NMR: δ 34.9 (s). ^{19}F NMR ($CDCl_3$): δ −74.8 (t, $^3J(^1H-^{19}F) = 7.14$ Hz).^{13}C NMR: δ 166.4 (ring carbon, d, $^2J(^{13}C-N-^{31}P) = 11.5$ Hz), 150.0 (d, ipso carbon of the biphenylyloxy group, $^2J(^{13}C-N-^{31}P) = 6.6$ Hz), 139.6, 137.3, 136.6, 136.3, 127.9, 127.0, 126.6, 121.7, 113.9, 62.2 (CF_3, q, $^1J(^{13}C-^{19}F) = 39.7$ Hz), 36.4, 36.2.

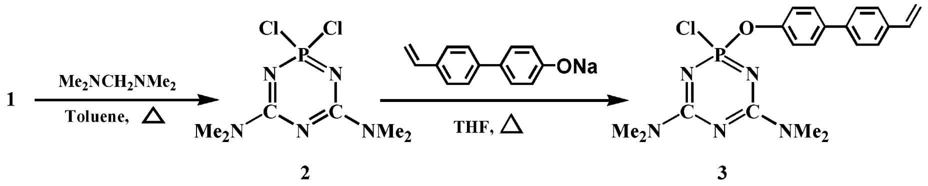
Preparation of $[NC(NMe_2)]_2[NP(OPh)(O\text{-}C_6H_4\text{-}p\text{-}C_6H_4\text{-}p\text{-}CH{=}CH_2)]$ (5). The preparation of **5** was carried out in an analogous manner as that given above except that the reaction was carried out by heating under reflux for a period of 20 h. The reagents involved are sodium phenoxide prepared in situ by the addition of sodium (0.06 g, 2.4 mmol) to phenol (0.23 g, 2.4 mmol) and **3** (1.0 g. 2.4 mmol). The crude product was purified on a silica gel column using ethyl actetate:*n*-hexane (6:94) as the eluant. Yield: 0.51 g, 45%. Mp 125−126 °C. IR (KBr) cm^{-1}: 3033 (w), 2930 (m), 2864 (w), 2358 (w), 1483 (s), 1375 (s), 1239 (m), 1198 (s), 1084 (s), 1017 (w), 969 (s), 934 (s), 828 (m), 764 (m), 690 (w), 655 (w), 603 (w), 563 (w), 518 (w), 479 (w). Anal. Calcd for $C_{26}H_{28}N_5O_2P$ (473.51): C, 65.95; H, 5.96; N, 14.79. Found: C, 65.31; H, 5.33; N, 14.58. MS (FAB): $473(M^+)$. ^1H NMR: δ 7.11−7.53 (m, 13 H, ar), 6.74 (dd, 1 H, $J = 17.6$ and 11.0 Hz, $-CH{=}CH_2$), 5.78 (d, 1 H, $J = 17.6$ Hz, $-CH{=}CH_2$ (trans)), 5.26 (d, 1 H, $J = 11.0$ Hz, $-CH{=}CH_2$ (cis)), 3.06 (s, 12 H, NMe_2). $^{31}P\{^1H\}$ NMR: δ 30.5 (s). ^{13}C NMR: δ 166.3 (ring carbon, d, $^2J(^{13}C-N-^{31}P) = 11.6$ Hz), 150.8 (d, ipso carbon of the phenoxy group, $^2J(^{13}C-N-^{31}P) = 6.6$ Hz), 150.4 (d, ipso carbon of the biphenylyloxy group, $^2J(^{13}C-N-^{31}P) = 6.6$ Hz), 139.7, 137.1, 136.4, 136.3, 129.3, 127.8, 127.0, 126.6, 124.9, 121.1, 120.9, 113.8, 36.2.

Preparation of $[NC(NMe_2)]_2[NP(OC_6H_4\text{-}m\text{-}CH_3)(O\text{-}C_6H_4\text{-}p\text{-}C_6H_4\text{-}p\text{-}CH{=}CH_2)]$ (6). This was prepared in a similar manner as that of **5** except that the reaction time was 36 h. The reagents used are sodium (0.03 g, 1.2 mmol), 3-methylphenol (0.13 g, 1.2 mmol), and **3** (0.5 g. 1.2 mmol). **6** was purified on a silica gel column using ethyl acetate:*n*-hexane as the eluant (7:93). Yield: 0.51 g (89.5%). Mp 97−98 °C. IR (KBr) cm^{-1}: 3031 (w), 2931 (m), 2866 (w), 2361 (w), 1485 (s), 1372 (s), 1245 (s), 1145 (s), 1084 (s), 1010 (m), 972 (s), 940 (s), 831 (s), 780 (s), 718 (m), 690 (w), 656 (w), 599 (w), 576 (w), 547 (w), 516 (w). Anal. Calcd for $C_{27}H_{30}N_5O_2P$ (487.53): C, 66.52; H, 6.20; N, 14.36. Found: C, 66.21; H, 6.03; N, 14.68. MS (FAB): 488 (M^+). ^1H NMR ($CDCl_3$): δ 6.85−7.45 (m, 12 H, ar), 6.67 (dd, 1 H, $J = 17.6$ and 10.8 Hz, $-CH{=}CH_2$), 5.71 (d, 1 H, $J = 17.6$ Hz, $-CH{=}CH_2$ *(trans)), 5.19 (d, 1 H,* $J = 10.8$ Hz, $-CH{=}CH_2$ (cis)), 2.99 (s, 12 H, NMe_2), 2.24 (s, 3 H, $m\text{-}CH_3$). $^{31}P\{^1H\}$ NMR: δ 30.4 (s). ^{13}C NMR ($CDCl_3$): δ 166.4 (ring carbon, d, $^2J(^{13}C-N-^{31}P) = 11.6$ Hz), 150.7 (ipso carbon of the phenoxy group, d, $^2J(^{13}C-N-^{31}P) = 6.6$ Hz), 150.5 (ipso carbon of the biphenylyloxy group d, $^2J(^{13}C-N-^{31}P) = 6.6$ Hz), 139.8, 139.4, 137.0, 136.4, 136.3, 129.0, 127.8, 127.0, 126.6, 125.4, 121.7, 121.2, 117.0, 113.8, 36.3, 21.3.

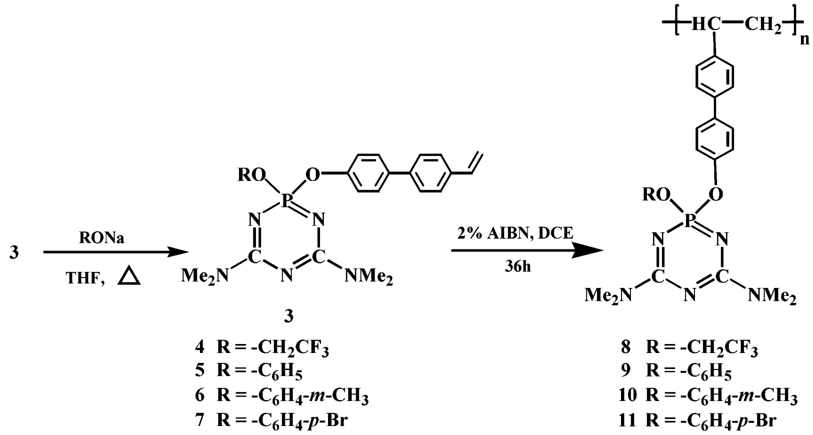
Preparation of $[NC(NMe_2)]_2[NP(OC_6H_4\text{-}p\text{-}Br)(O\text{-}C_6H_4\text{-}p\text{-}C_6H_4\text{-}p\text{-}CH{=}CH_2)]$ (7). This compound was prepared by using a similar procedure as that employed for **5** except that the reaction time was 36 h. The reagents used are sodium (0.02 g, 1.06 mmol), 4-bromophenol (0.18 g, 1.1 mmol), and **3** (0.44 g. 1.1 mmol). The compound **7** was purified on a silica gel column using ethyl acetate: *n*-hexane (8:92) as the eluant. Yield: 0.45 g (77.6%). Mp 118−119 °C. IR (KBr) cm^{-1}: 3033 (w), 2931 (m), 2865 (w), 2361 (w), 1478 (s), 1375 (s), 1203 (s), 1084 (s), 1011 (s), 968 (s), 930 (s), 829 (s), 761 (m), 660 (w), 602 (w), 561 (w), 527 (w), 422 (w). Anal. Calcd for $C_{26}H_{27}N_5O_2PBr$ (552.4): C, 56.53; H, 4.93; N, 12.68. Found: C, 56.41; H, 4.73; N, 12.32. MS (FAB): 552 (M^+). ^1H NMR: δ 7.02−7.45 (m, 12 H, ar), 6.67 (dd, 1 H, $J = 17.6$ and 11.0 Hz, $-CH{=}CH_2$), 5.71 (d, 1 H, $J = 17.6$ Hz, $-CH{=}CH_2$ (trans)), 5.20 (d, 1 H, $J = 11.0$ Hz, $-CH{=}CH_2$ (cis)), 2.98 (s, 12 H, NMe_2). $^{31}P\{^1H\}$ NMR: δ 30.8 (s). ^{13}C NMR ($CDCl_3$): δ 166.2 (ring carbon, d, $^2J(^{13}C-N-^{31}P) = 11.6$ Hz), 150.8 (ipso carbon of the phenoxy group, d, $^2J(^{13}C-N-^{31}P) = 6.6$ Hz), 150.4 (ipso carbon of the biphenylyloxy group, d, $^2J(^{31}P-O-^{13}C) = 6.6$ Hz), 139.7, 136.5, 136.3, 132.3, 127.9, 127.0, 126.6, 122.8, 121.1, 113.9, 36.3.

General Procedure of Polymerization. The general procedure for the polymerization of the dicarbaphosphazene derivatives (**3**−**7**) is as follows. The monomer (0.5 g) was taken in a thick walled glass ampule along with the initiator AIBN (2 wt %) in dichloroethane (5 mL) and the mixture was subjected to three freeze−thaw cycles. Subsequently the reaction vessel was sealed under vacuum and heated in an oil bath at 80 °C for 36 h. At the end of the polymerization the reaction vessel was carefully opened (by breaking the glass) and the contents were poured in *n*-hexane (400 mL). A white powder identified as the homopolymer was isolated in each case. The purification protocol for the polymers was slightly different and is as follows. Polymer **8** was purified by reprecipitation using dichloromethane as the solvent and hot methanol as the nonsolvent. Polymers **9**, **10** and **11** were purified by reprecipitation

Scheme 1. Preparation of **3**



Scheme 2. Preparation of Dicarbaphosphazene Derivatives (**4**−**7**) and Their Polymers (**8**−**11**)



using dichloromethane as the solvent and hot diethyl ether as the nonsolvent. The purified polymers were thoroughly dried at 50 °C and 10^{-1} Torr for several hours. The isolated yields and the spectroscopic data for these polymers are given below.

Polymer 8. Yield: 64%. IR (KBr) cm^{-1}: 3026 (w), 2929 (m), 2867 (w), 1490 (s), 1381 (s), 1286 (m), 1210 (s), 1170 (s), 1092 (s), 958 (s), 895 (w), 825 (m), 767 (m), 659 (w), 603 (w), 541 (w). ^1H NMR ($CDCl_3$): δ 7.19−6.41 (m, 8 H, ar), 4.15 (s, 2 H, C*H*$_2$), 2.93 (s, 12 H, N*Me*$_2$), 1.58−1.18 (m, 3 H, aliphatic). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 34.9 (s). ^{19}F NMR ($CDCl_3$): δ −77.6 (s).

Polymer 9. Yield: 45%. IR (KBr) cm^{-1}: 3026 (w), 2925 (m), 2861 (w), 1487 (s), 1377 (s), 1278 (m), 1199 (s), 1085 (s), 1025 (s), 931 (s), 823 (m), 768 (m), 685 (w), 603 (w), 541 (w), 528 (w). ^1H NMR ($CDCl_3$): δ 7.26−6.52 (m, 13 H, ar), 3.00 (s, 12 H, N*Me*$_2$), 1.64−1.43 (m, 3 H, aliphatic). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 34.52 (s).

Polymer 10. Yield: 36%. IR (KBr) cm^{-1}: 3026 (w), 2924 (m), 2861 (w), 1490 (s), 1378 (s), 1212 (m), 1146 (m), 1086 (m), 947 (s), 827 (w), 776 (w), 720 (w), 686 (w), 605 (w), 537 (w). ^1H NMR ($CDCl_3$): δ 7.17−6.43 (m, 12 H, ar), 2.91 (s, 12 H, N*Me*$_2$), 2.18 (s, 3 H, C*H*$_3$), 1.72−1.18 (m, 3 H, aliphatic). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 34.5 (s).

Polymer 11. Yield: 72%. IR (KBr) cm^{-1}: 3026 (w), 2925 (m), 2861 (w), 1551 (s), 1484 (s), 1379 (s), 1203 (s), 1086 (m), 930 (s), 825 (m), 767 (w), 610 (w), 531 (w). ^1H NMR ($CDCl_3$): δ 7.29−6.46 (m, 12 H, ar), 2.94 (s, 12 H, N*Me*$_2$), 1.77−1.18 (m, 3 H, aliphatic). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 34.8 (s).

Results and Discussion

Synthesis of the Dicarbaphosphazenes 3−7. The tetrachlorodicarbaphosphazene $[NCCl]_2[NPCl_2]$ (**1**) has four reactive chlorine atoms. To avoid complexity in terms of the formation of regio isomers in the process of incorporating the vinyl-containing substituent on the inorganic heterocyclic ring, we decided to *block* the reactive C−Cl groups. This is accomplished by a dealkylation reaction involving a tertiary amine as reported recently.[15a] Accordingly the reaction of **1** with $Me_2NCH_2NMe_2$ proceeds with cleavage of the N−CH_2 bond and substitution occurs specifically on the carbon centers in the inorganic heterocyclic ring to afford $[NC(NMe_2)]_2[NPCl_2]$ (**2**). Reaction of **2** with the sodium salt of 4-hydroxy-4′-vinylbiphenyl afforded the compound $[NC(NMe_2)]_2[NP(Cl)(O\text{-}C_6H_4\text{-}p\text{-}C_6H_4\text{-}p\text{-}CH{=}CH_2)]$ (**3**) (Scheme 1). The polymerizable vinyl group in **3** is well separated from the inorganic heterocyclic ring by means of the biphenyl spacer group.

We have substituted the lone chlorine in **3** by four different oxygen based nucleophiles without disturbing the polymerizable functional group and have assembled the compounds **4**−**7** (Scheme 1).

While compound **3** is sensitive to moisture, compounds **4**−**7** are quite stable and are insensitive to either air or moisture. Further, all the cyclodicarbaphosphazenes **(3**−**7)** are quite lipophilic and are soluble in a wide variety of organic solvents. Infrared spectra of **3**−**7** are characterized by strong absorption in the region of 1471−1485 cm^{-1} (C═N stretching) and 1372−1399 cm^{-1} (P═N stretching). The latter values are higher than those observed in cyclotriphosphazenes.[18] The FAB mass spectra of all the monomers gave the molecular ion peak as the base peak. ^{31}P NMR spectra show that while **3** gives a singlet at +49.1 ppm, substitution of chlorine from the P−Cl bond with oxygen-based nucleophiles results in upfield chemical shifts for the compounds **4**−**7**. These trends are comparable to those observed in cyclophosphazenes.[19] The ^1H NMR spectra of **3**−**7** reveals the presence of an AMX multiplet between 6.67 and 5.19 ppm typical of the vinyl group, R−CH═CH_2. The ^{13}C NMR spectrum of compound **3** shows that the vinyl

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(18) Chandrasekhar, V.; Thomas, K. R. J. *Struct. Bonding (Berlin)* **1993**, *81*, 41.

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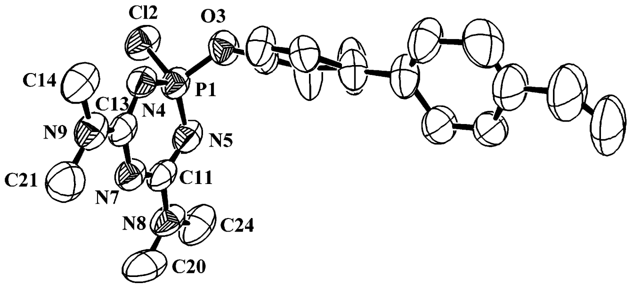

Figure 1. ORTEP diagram of **3**. Hydrogen atoms have been omitted for clarity.

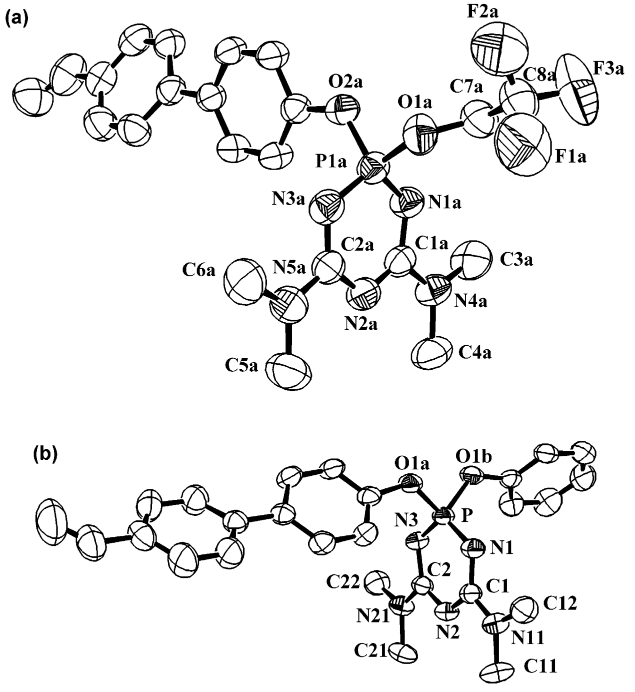

Figure 2. ORTEP diagrams of **4**(a) and **5**(b). Hydrogen atoms have been omitted for clarity.

carbons resonate at 113.9 (CH$_2$) and 138.0 (CH) ppm. The similarity of these chemical shifts with that observed for 4-hydroxy-4′-vinylbiphenyl (114.3 and 136.0 ppm) suggests that there is no electronic effect of the cyclodicarbaphosphazene ring on the vinyl group.

X-ray Crystallography. The molecular structures of **3**, **4**, **5**, **6**, and **7** were confirmed by a single-crystal X-ray diffraction study. The X-ray data pertaining to data collection, crystal systems, and structure solution for compounds **3**, **4**, **5**, **6**, and **7** are given in the supporting information. In the case of **4** two independent molecules **4A** and **4B** are present in the asymmetric unit. The ORTEP diagrams of these compounds are given in Figures 1, 2, and 3.The X-ray analysis of compounds **3**−**7** reveals that all of them contain a nearly planar N_3PC_2 core. Selected metric parameters for these compounds have been summarized (see the supporting information). Minor deviations from planarity are found in **3** (P(1) and N(1) deviate from the mean plane by 0.14 and 0.21 Å, respectively) and **4A**,**B**) (N(1A) and N(1B) deviate from the plane by −0.15 and −0.11 Å, respectively) (supporting information).

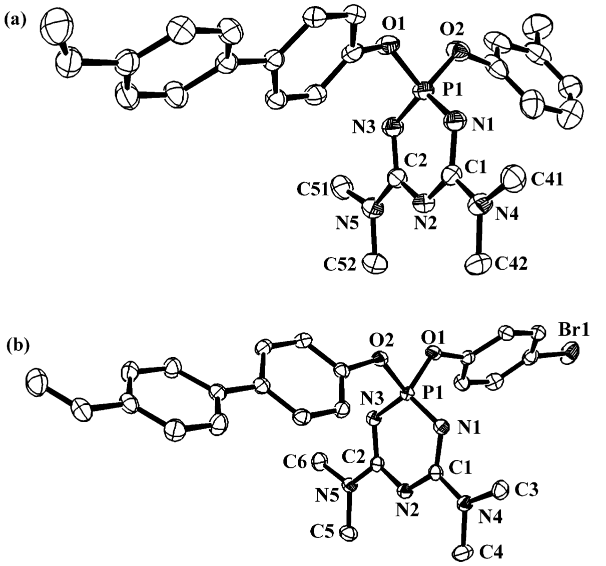

Figure 3. ORTEP diagrams of **6**(a) and **7**(b). Hydrogen atoms have been omitted for clarity.

The two endocyclic P−N bond distances are nearly similar in magnitude in each compound. This distance is shortest in **3** (av 1.567 Å) and the longest in **7** (av 1.589 Å). These values are comparable to those found in cyclotriphosphazenes.[18] Two types of endocyclic C−N bond distances are found. The distances corresponding to the C−N−C segment are shorter in comparison to distances found for the C−N−P segment. For example in **3** the C13−N4 and C11−N5 distances are 1.363(5) and 1.360(5) Å, respectively. In contrast the C11−N7 and the C13−N7 distances are 1.342(5) and 1.328(4) Å, respectively. Two types of exocyclic C−N distances are also seen in **3**−**7**. Thus the C11−N8 distance is 1.340(5), while the N8−C20 distance is 1.444(8) Å. These metric parameters are indicative of the partial multiple bond character of *all* the C−N bonds around the ring carbon. These trends are comparable to analogous compounds studied earlier.[15] The bond angles within the ring suggest an approximately tetrahedral arrangement around phosphorus and a completely planar arrangement around carbon. The smallest angles around the ring nitrogen are those found in the C−N−P segment: thus in **3** the P1−N4−C13 and the P1−N5−C11 angles are 115.0(2)° and 114.7(3)° while the C11−N7−C13 angle is 119.1(3)°. The angles around the exocyclic nitrogen atoms add to 360°. Thus, the effect of the variation of the substituent in **3**−**7** either on the basic structure or on the metric parameters observed is quite minimal.

A closer inspection of the molecular structures of **3**−**7** reveals that these molecules are engaged in secondary interactions in the form of weak hydrogen bonds leading to the formation of interesting supramolecular arrays (Figures4−6). The metric parameters observed in these hydrogen bonds are consistent with literature precedents.[20]

In **3** a *chainlike* structure is formed by an intermolecular C−H---Cl hydrogen bond (Figure 4(i)).

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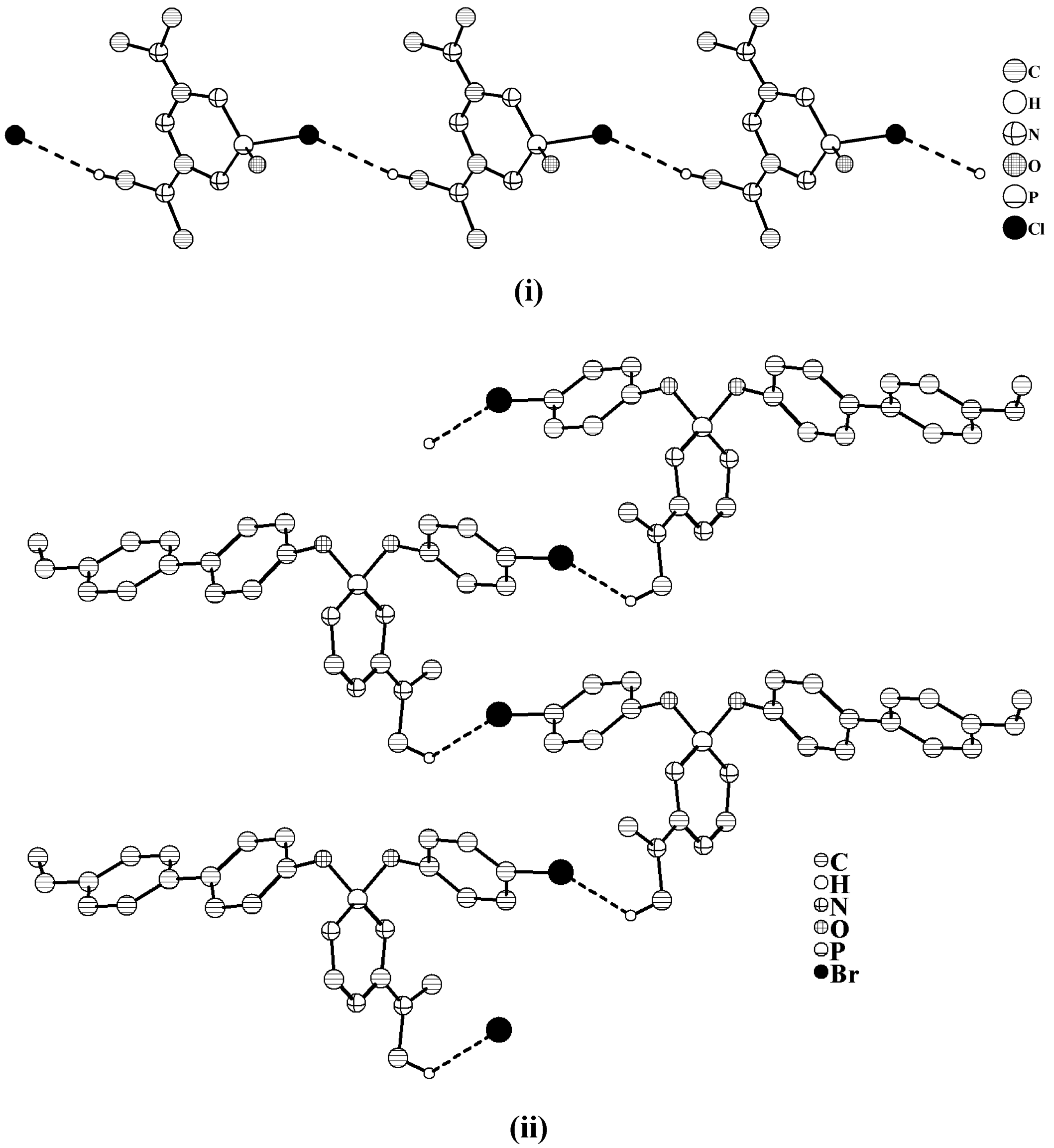
(20) (a) Desiraju, G. R. *Acc. Chem. Res.* **2002**, *35*, 565. (b) Thallapally, P. K.; Nangia, A. *Cryst. Eng. Commun.* **2001**, 2.



(i)

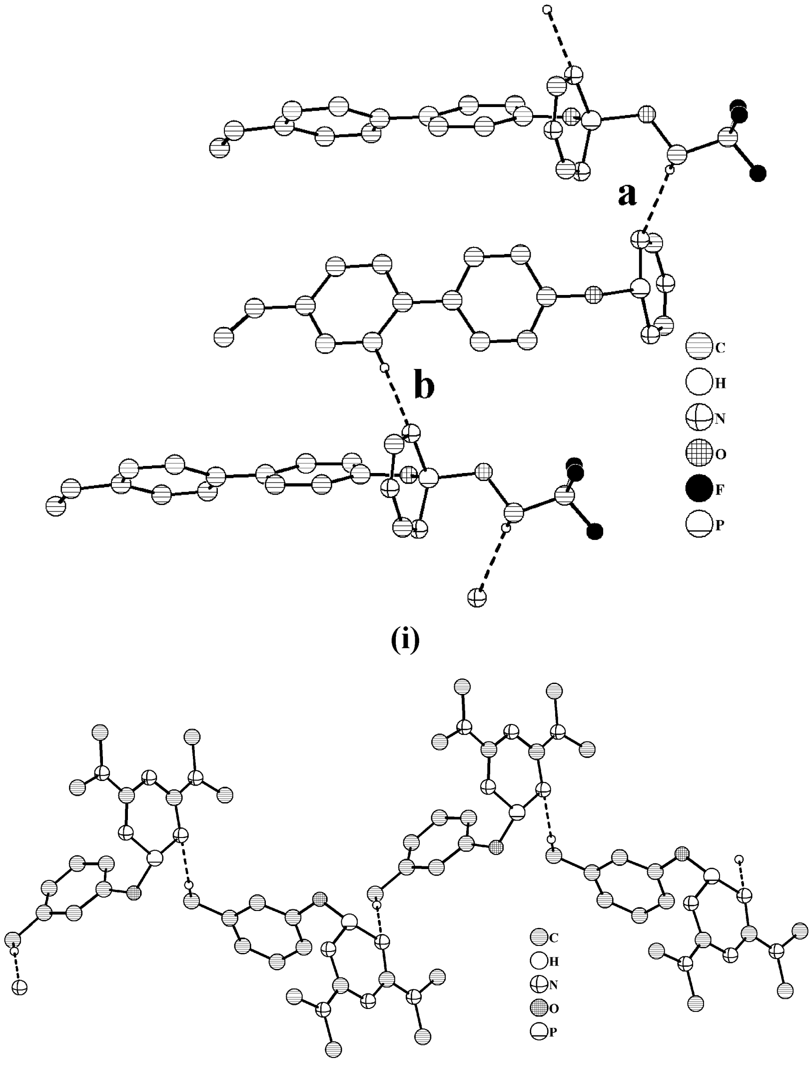
(ii)

Figure 4. DIAMOND view of hydrogen bonding present in **3** (i) and **7** (ii). All the hydrogen atoms except those involved in hydrogen bonding have been omitted for clarity. In **3** the 4′-vinylbiphenylyloxy group and in **7** one of the dimethylamino groups have also been omitted for clarity. The important bond lengths (Å) and bond angles (deg) for **3** are C(20)−H(20A)---Cl(2), C−H 1.000(82), H---Cl 2.867(83), C−Cl 3.811(11), and C−H---Cl 157.92(566) and the symmetry is x, $-1 + y$, z. The important bond lengths (Å) and bond angles (deg) in **7** are C(5)−H(5B)---Br(1), C−H 0.959(2), H---Br 2.998(1), C−Br 3.512(3), and C−H---Br 114.98(12) and the symmetry is $2 - x$, $-0.5 + y$, $2.5 - z$.

Thus the chlorine atom Cl(2) is involved in hydrogen bonding to one of the hydrogen atoms H(20A) of the dimethylamino group from a neighboring molecule, leading to the formation a linear one-dimensional chain. In **7** a similar interaction is also present. The difference is that the interaction is between the hydrogen atom H(5B) of the dimethylamino group and the bromine atom Br(1) of the *p*-bromophenoxy substituent of the neighboring molecule. Such a C−H---Br hydrogen bonding leads to a zigzag type of a polymeric chain (Figure 4(ii)).

Compounds **4** and **6** show intermolecular C−H----N secondary interactions arising from the ring nitrogen atom. Thus, the two independent molecules present in the asymmetric unit of **4** are hydrogen bonded to each other. The nitrogen atom N(1B) of one of the molecules (**4B**) is hydrogen bonded to the hydrogen atom H(7AA) (of the methylene group of OCH_2CF_3) of **4A**. At the same time the hydrogen H(20B) (of the biphenylyloxy group) of **4B** is hydrogen bonded to N(3A) of **4A**. Thus each molecule is involved in a proton donor and proton acceptor interaction with its neighbors. This leads to the formation of a polymeric array in the solid state (Figure 5(i)). In the compound **6** the ring nitrogen atom N(1) is hydrogen bonded to one of the hydrogen atoms H(23B) of the *m*-methyl group of the phenyl ring from the neighboring molecule, leading to the formation of a zigzag one-dimensional polymer (Figure 5(ii)).

In contrast to the above, in **5** there are two types of intermolecular C−H---π interactions present in the structure. Thus H(5BA) of the phenoxy substituent is involved in a C−H---π interaction with the phenyl ring of the phenoxy substituent of the neighboring molecule [C(1B), C(2B), C(3B), C(4B), C(5B), C(6B)]. At the same time the hydrogen H(11D) of the dimethylamino group is involved in a similar C−H---π interaction with one of the phenyl rings of the



(i)

(ii)

Figure 5. DIAMOND view of hydrogen bonding present in **4** (i) and **6** (ii). All the hydrogen atoms which are not involved in the hydrogen bonding have been omitted for clarity. In compound **4**, two types of H---N interactions (a) and (b) are present. In **4** dimethylamino groups in the cyclodicarbaphosphazene ring and in **6** the 4′-vinyl-4-biphenylyloxy group have also been omitted for clarity. The important bond lengths (Å) and bond angles (deg) in **4** are (a) C(7A)−H(7AA)---N(1B); C−H 0.970(4), H---N 2.625(11), C−N 3.528(11), and C−H---N 154.98(17), and the symmetry is *x*, *y*, *z* and (b) C(20B)−H(20B)---N(3A), C−H 0.931(5), H---N 2.638(9), C−N 3.556(13), and C−H---N 169.08(20) and the symmetry is $-1 + x$, $1 + y$, z. The important bond lengths (Å) and bond angles (deg) in **6** are C(23)−H(23B)---N(1), C−H 0.959(6), H---N 2.689(9), C−N 3.646(14), and C−H---N 175.35(26) and the symmetry is x, $0.5 - y$, $-0.5 + z$.

biphenylyloxy substituent [C(1A), C(2A), C(3A), C(4A), C(5A), C(6A)]. The cumulative effect of these interactions is the formation of a two-dimensional ladder-like polymeric structure (Figure 6).

Polymerization of 3−7. Homopolymerization of **3**−**7** is readily accomplished by standard free-radical polymerization protocol. Moderate to good yields of polymers were obtained under the reaction conditions employed in this study. The polymer obtained from **3** was very sensitive to moisture and rapidly degraded in ambient conditions. In contrast, polymers obtained from the monomers **4**−**7** were stable free-flowing white powders and were amenable to complete characterization. The ^{1}H NMR spectra of these polymers **8**−**11** revealed the absence of the characteristic vinyl AMX multiplet observed in the corresponding monomers. The ^{31}P NMR of **8**−**11** consists of a single resonance whose peak position is nearly invariant in comparison to the corresponding monomers (vide supra, Experimental Section). ^{19}F NMR of the polymer **8** showed a singlet at −77.6 ppm. Similarly, P═N and C═N stretching frequencies of the monomers and the polymers are nearly the same. These above results suggest the retention of the cyclodicarbaphosphazene ring in the polymers.

The molecular weights of these polymers were obtained by Gel Permeation Chromatography (GPC) using polystyrene as the standard and the data are summarized in Table 1. The M_n values obtained are in the range of 12 000−28 000 Da with polydispersity indices between 1.33 and 1.54. These molecular weights are lower than those observed by Inoue and co-workers for the homopolymer obtained from N_3P_3-

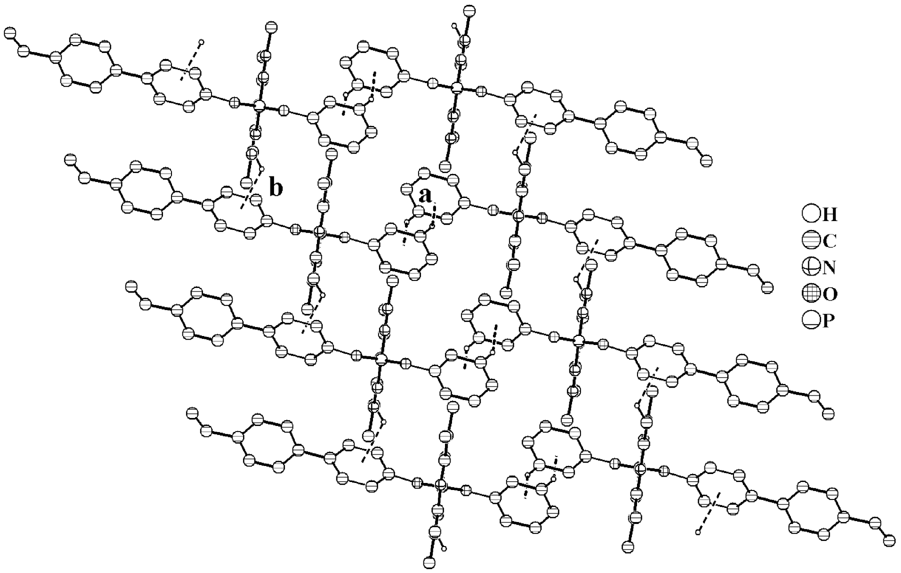


Figure 6. DIAMOND view of the two types of C−H---π interactions (a) and (b) present in **7**. All the hydrogens except those are involved in the C−H---π interaction have been omitted for clarity. The important bond lengths (Å) and bond angles (deg) are (a) C(5B)−H(5BA)---π[C(1B), C(2B), C(3B), C(4B), C(5B), C(6B)], C−H 0.929(1), H---π 3.221(4), C---π 4.015(6), and C−H---π 144.72(1) and the symmetry is $3 - x$, $-0.5 + y$, $3.5 - z$. (b) C(1)−H(11D)---π[C(1A), C(2A), C(3A), C(4A), C(5A), C(6A)], C−H 0.960(4), H---π 2.833(11), C---π 3.511(15), and C−H---π 128.42(20) and symmetry is x, $-0.5 - y$, $0.5 + z$.

Table 1. Molecular Weight and Thermal Data for Polymers **8**−**12**

				in nitrogen			in oxygen				residue,[b] %	
					char yields, %			char yields, %				
polymer	M_w, Da	M_n, Da	M_w/M_n	PDT,[c] °C	800 °C	900 °C	PDT, °C	600 °C	700 °C	T_g, °C	in nitrogen	in oxygen
8	37 166	28 045	1.33	376	31.6	29.0	285	32.7	21.4	126.0	92.3	35.6
9	18 605	12 396	1.50	366	45.0	41.0	260	32.9	20.1	125.2	98.3	57.8
10	21 357	13 905	1.54	376	39.7	36.8	290	22.9	13.5	115.6	63.4	54.0
11	16 295	11 832	1.38	381	35.4	31.7	285	31.3	10.1	120.2	93.9	90.1
12[d]	180 000	56 000	3.2	300	65.0	62.5	280[e]	64.0[e]	76.0[e]	76	60	55[e]

[a] Data from thermo gravimetric analysis. [b] Data from isothermal gravimetric analysis. Residue percent obtained by heating the polymer at 600 °C for 3 h. [c] Polymer decomposition temperature. [d] Data from ref 3d,e. [e] Analysis carried out in air.

$Cl_5(O-C_6H_4$-p$-C_6H_4$-p-$CH=CH_2)$.[3d] Although in both instances 1,2-dichloroethane has been used as the solvent for polymerization, it appears that chain-transfer to the solvent is more significant in the present instance leading to lower molecular weights.

Thermal Behavior. A qualitative flame test revealed that the polymers **8**−**11** are self-extinguishing, similar to many cyclophosphazene pendant containing homo- and copolymers.[6a]

The polymers **8**−**11** show high T_g values (Table 1). These are higher than the value of 76 °C reported for the homopolymer **12** obtained from $N_3P_3Cl_5(O$-C_6H_4-p-C_6H_4-p-$CH=CH_2)$.[3e] The thermal stability and degradation behavior of the polymers **8**−**11** was investigated both in nitrogen and oxygen atmospheres by thermogravimetric analysis (TGA). These studies in the nitrogen atmosphere reveal that the polymer decomposition temperatures (PDT) of polymers **8**−**11** are observed at 376, 366, 376, and 381 °C, respectively.

These values are higher than those observed for the homopolymer **12**[3e] containing cyclotriphosphazene pendant groups (table). In contrast, the final char yields obtained for polymers **8**−**11** at 800 °C are lower than those observed for **12**. In the polymers **8**−**11** the highest char yield at 800 °C (45%) is observed for polymer **9** where the phosphorus contains the phenoxy substituent (Figure 7).

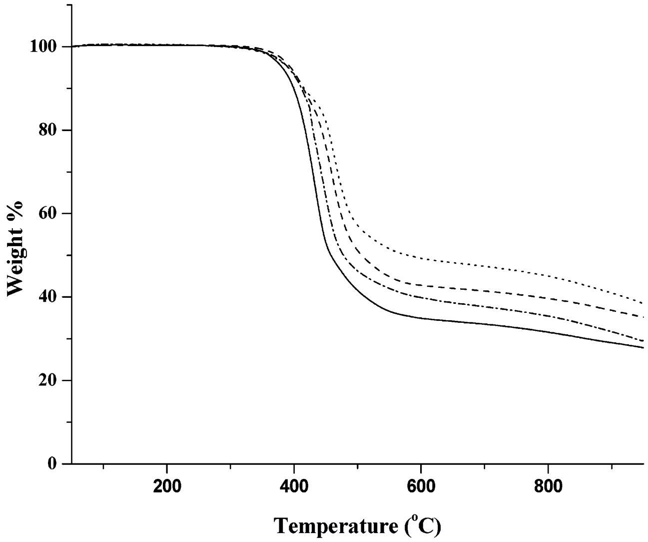


Figure 7. Thermogravimetric analysis of the polymers (—) **8**, (•••) **9**, (---) **10,** and (-•-)s **11** under nitrogen atmosphere.

As anticipated the PDT and final char yield values for all the polymers are considerably less in the oxygen atmosphere. In fact the polymers completely decompose by 800 °C.

To assess the thermal behavior of the polymers under nitrogen and oxygen atmospheres further, isothermal gravimetric analyses of the polymers were carried out at 600 °C for 3 h. Under nitrogen atmosphere all the polymers are stable and show less than 10% weight loss except **10** (37% weight loss). In contrast in oxygen atmosphere the weight loss is much higher. In comparison, polymer **12** shows greater decomposition at 600 °C (Table 1).

Conclusion

We have assembled the first examples of cyclodicarbaphosphazenes containing a remote polymerizable vinyl functional group. These have been characterized by multinuclear NMR as well as by X-ray crystal structure studies. The X-ray crystal structure studies apart from confirming the molecular structures also reveal interesting supramolecular formation as a result of intermolecular C−H---X (Cl or Br) or C−H---N interactions. All the monomers can be readily homopolymerized by the standard free-radical initiator, AIBN, to afford moderate molecular weight polymers. Moisture- and air-stable polymers are readily obtained by the substitution of the P−Cl bond from the monomer **3** by an alkoxy or aryloxy group. All the polymers are self-extinguishing as revealed in a qualitative flame test. They have high glass transition temperatures. They are also thermally quite stable as shown by low decomposition in isothermal studies at 600 °C. In this regard they appear to be better than the homopolymer prepared from $N_3P_3Cl_5(O\text{-}C_6H_4\text{-}p\text{-}C_6H_4\text{-}p\text{-}CH{=}CH_2)$. In addition, the polymers reported in the present study also show reasonable char yields even at 800 °C. In conclusion, we have successfully demonstrated the design and assembly of new cyclodicarbaphosphazenes that can be readily homopolymerized leading to a new family of interesting hybrid inorganic−organic polymers. We are currently exploring the possibility of utilizing this approach to prepare new multisite coordinating polymeric ligands.

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Supporting Information Available: Tables (S1−S7) and additional figures (S1−S4). This material is available free of charge via the Internet at htpp://pubs.acs.org.

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