New hybrid inorganic-organic polymers containing cyclophosphazenes as pendant groups: Cyclophosphazene ligands containing hydrazone linkages and their conversion to polymers

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Abstract: The reaction of the cyclotriphosphazene $N_3P_3Cl_5[O\text{-}C_6H_4\text{-}p\text{-}C_6H_4\text{-}p\text{-}CH{=}CH_2]$ (**2**) with 10 equiv of *N*-methylhydrazine proceeds in a regio-specific manner to afford the multi-functional hydrazide $N_3P_3[N(Me)NH_2]_5[O\text{-}C_6H_4\text{-}p\text{-}C_6H_4\text{-}p\text{-}CH{=}CH_2]$ (**3**). Condensation of **3** with *o*-hydroxy benzaldehyde or pyridine-2-carboxaldehyde affords the corresponding hydrazones $N_3P_3[N(Me)N{=}CH\text{-}C_6H_4\text{-}o\text{-}OH]_5[O\text{-}C_6H_4\text{-}p\text{-}C_6H_4\text{-}p\text{-}CH{=}CH_2]$ (**4**) and $N_3P_3[N(Me)N{=}CH\text{-}C_6H_4N]_5[O\text{-}C_6H_4\text{-}p\text{-}C_6H_4\text{-}p\text{-}CH{=}CH_2]$ (**5**), respectively. These hydrazones can be homopolymerized to afford polymers **6** and **7** containing multi-site coordinating cyclophosphazenes as pendant groups.

Key words: cyclophosphazene, hydrazone, pendant polymers, hybrid polymers, polymeric ligands.

Résumé : La réaction du cyclotriphosphazène $N_3P_3Cl_5[O\text{-}C_6H_4\text{-}p\text{-}C_6H_4\text{-}p\text{-}CH{=}CH_2]$ (**2**) avec dix équivalents de *N*-méthylhydrazine se produit d'une façon régiospécifique et conduit à la formation de l'hydrazide multifonctionnel $N_3P_3[N(Me)NH_2]_5[O\text{-}C_6H_4\text{-}p\text{-}C_6H_4\text{-}p\text{-}CH{=}CH_2]$ (**3**). Les condensations du composé **3** avec l'*o*-hydroxybenzaldéhyde ou la pyridine-2-carboxaldéhyde fournissent respectivement les hydrazones correspondantes $N_3P_3[N(Me)N{=}CH\text{-}C_6H_4\text{-}o\text{-}OH]_5[O\text{-}C_6H_4\text{-}p\text{-}C_6H_4\text{-}p\text{-}CH{=}CH_2]$ (**4**) et $N_3P_3[N(Me)N{=}CH\text{-}C_6H_4N]_5[O\text{-}C_6H_4\text{-}p\text{-}C_6H_4\text{-}p\text{-}CH{=}CH_2]$ (**5**). Ces hydrazones peuvent être soumises à des homopolymérisations qui conduisent aux polymères **6** et **7** portant cyclophosphazènes à plusieurs sites de coordination comme groupes pendants.

Mots clés : cyclophosphazène, hydrazone, polymères pendants, polymères hybrides, ligands polymériques.

[Traduit par la Rédaction]

Introduction

Among the inorganic polymers, polyphosphazenes ($[N{=}PR_2]_n$) occupy a prominent place (1). These constitute the largest family of inorganic polymers with over 800 representative examples. A remarkable feature of polyphosphazenes is that the property and function of each polymer can be readily fine tuned by varying the nature of the "R" group on the phosphorus atom. Thus, polymers with diametrically opposite properties such as water solubility or hydrophobicity, or with varied applications such as bio-inert materials or polymer electrolytes, are readily assembled by choosing an appropriate substituent on the phosphorus atom (1). Another versatility of polyphosphazenes is that unlike organic polymers, the structural diversity can be introduced by a macromolecular nucleophilic substitution reaction involving the reactive P—Cl bonds of polydichlorophosphazene ($[N{=}PCl_2]_n$) (2, 3). The latter itself is prepared from a ring opening polymerization of $N_3P_3Cl_6$, or by a condensation reaction involving either $Cl_3P{=}NSiMe_3$ (4) or $Cl_3P{=}NP(O)Cl_2$ (5, 6).

Another class of closely related polymers is those that contain a cyclophosphazene unit as a pendant group (7–15). In contrast to polyphosphazenes, which contain an inorganic backbone and (mostly) organic substituents, the pendant polymers contain an organic backbone and *intact* cyclophosphazene groups as the substituents. Although these polymers have received much less attention than polyphosphazenes, in principle these systems also possess a similar potential in terms of easy tunability of polymer property and function. The pendant polymers are obtained by polymerizing cyclophosphazenes containing vinyl groups (Scheme 1).

Pioneering studies by Allen and co-workers (7–11) have revealed that the presence of an appropriate spacer group "Z" and (or) the presence of electron releasing substituents on the olefinic moiety facilitate the homopolymerization of the monomer by minimizing the σ-electron withdrawing effect of the cyclophosphazene group (11). The utility of this approach for the preparation of useful polymers has been demonstrated by Inoue and co-workers (13–15). They have found that polymers containing etheroxy-substituted cyclophosphazenes readily form complexes with lithium

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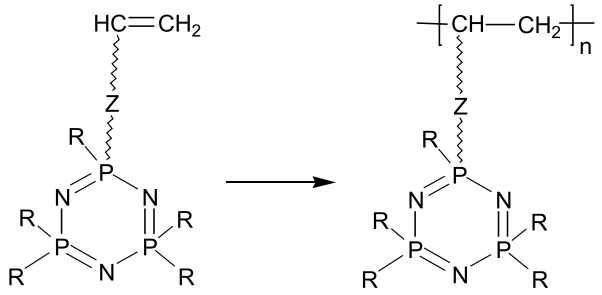
Scheme 1.



salts, which function as novel polymer electrolytes for lithium ion transport. We have been intrigued by the possibility of extending this approach to prepare new types of polymeric ligands that can bind to transition metal ions. Such ligands would also be of contemporary interest, in view of the importance of polymeric materials in organic synthesis, in the form of solid-phase inert supports or in the form of reagents and catalysts (16–21). Herein, we describe the synthesis and utility of a multi-functional cyclophosphazene monomer ($N_3P_3[N(Me)NH_2]_5[O\text{-}C_6H_4\text{-}p\text{-}C_6H_4\text{-}p\text{-}CH{=}CH_2]$) towards building new polymeric ligand systems.

Experimental section

General

Solvents and other general reagents used in this work were purified according to standard procedures. 4-Hydroxy-4′-vinylbiphenyl was prepared according to the reported procedure (13). 4-Hydroxy biphenyl (SD Fine Chemicals, India), *o*-hydroxybenzaldehyde (Fluka, Switzerland), and pyridine-2-carboxaldehyde (Fluka, Switzerland) were used as received. Hexachlorocyclotriphosphazene (Nippon Soda, Japan) was recrystallized from *n*-hexane before use. $N_3P_3Cl_5(O\text{-}C_6H_4\text{-}p\text{-}C_6H_4\text{-}p\text{-}CH{=}CH_2)$ was prepared according to the literature procedure (13, 22).

Instrumentation

^1H and ^{31}P NMR spectra were recorded on a JEOL-JNM LAMBDA 400 model spectrometer operating at 400.0 and 161.7 MHz, respectively. The chemical shifts are reported with respect to internal tetramethylsilane (^1H) and external 85% H_3PO_4 (^{31}P). FAB-MS were recorded on a JEOL SX 102/DA 6000 mass spectrometer using xenon (6 kV, 10 mA) as the FAB gas. TGA were recorded on a PerkinElmer Pyris 6 TGA model in a nitrogen atmosphere at a heating rate of 20°C min^{-1}. DSC were recorded on a PerkinElmer Pyris 6 DSC model in a nitrogen atmosphere at a heating rate of 10°C min^{-1}. Dilute solution viscosity studies were done on a Schott-Gerate viscometer using an Ubbelohde viscometer with a capillary pore size of 0.645 mm.

Preparation of $N_3P_3[N(Me)NH_2]_5[O\text{-}C_6H_4\text{-}p\text{-}C_6H_4\text{-}p\text{-}CH{=}CH_2]$ (3)

N-Methylhydrazine (2.03 g, 44.00 mmol) was dissolved in chloroform (40 mL) and to this was added a solution of **2** (2.03 g, 4.00 mmol) in chloroform. The reaction mixture was stirred at room temperature for 24 h. The *N*-methylhydrazine hydrochloride that formed was filtered and the solvent was evaporated in vacuo to afford **3**. It was purified, first by adding *n*-hexane to a solution of **3** in chloroform, and secondly by recrystallization from a mixture of chloroform and *n*-hexane (1:1). Yield: 1.82 g (81.9%); mp 62°C. ^1H NMR ($CDCl_3$) δ: 7.47–7.22 (m, 8H, aromatic), 6.75 (dd, 1H, J = 17.6 and 10.8 Hz, *H*RC=CH_2), 5.78 (d, 1H, J = 17.5 Hz, *trans*-HRC=C*H*H), 5.27 (d, 1H, J = 10.8 Hz, *cis*-HRC=CH*H*), 3.20 (broad, 10H, -NH_2), 3.06, 2.85, and 2.68 (d, 15H, J = 11.5, 11.0, and 10.8 Hz, -N(*Me*)). ^{31}P NMR ($CDCl_3$) δ: 29.4 (d, *P*(N(Me)NH_2)$_2$), 22.4 (t, $^2J_{P\text{-}N\text{-}P}$ = 40.4 Hz, *P*(OR)N(Me)NH_2). FAB-MS *m/z*: 555 ($[M]^+$). Anal. calcd. for $C_{19}H_{36}N_{13}OP_3$ (555.49): C 41.1, H 6.5, N 32.8; found: C 40.9, H 6.8, N 32.5.

Preparation of $N_3P_3[N(Me)N{=}CH\text{-}C_6H_4\text{-}o\text{-}OH]_5[O\text{-}C_6H_4\text{-}p\text{-}C_6H_4\text{-}p\text{-}CH{=}CH_2]$ (4)

To a solution of **3** (1.11 g, 2.00 mmol) in ethanol (50 mL) was added a solution of *o*-hydroxybenzaldehyde (1.46 g, 12.00 mmol) in ethanol (50 mL). The reaction mixture was heated under reflux for 17 h. It was then allowed to cool to room temperature and the solvent removed from it in vacuo to obtain **4**. Compound **4** was dissolved in acetonitrile (10 mL) and an excess of *n*-hexane was added to it, to allow re-precipitation. Yield: 1.39 g (64.5%); mp 117°C. ^1H NMR ($CDCl_3$) δ: 11.28, 11.09, and 11.03 (s, 5H, -O*H*), 7.64–7.51, 7.35–7.18, 7.13–6.99, and 6.82–6.75 (m, 28H, aromatic, N=CH), 6.72 (dd, 1H, J = 17.5 and 10.5 Hz, *H*RC=CH_2); 5.78 (d, 1H, J = 17.5 Hz, *trans*-HRC=C*H*H), 5.27 (d, 1H, J = 10.5 Hz, *cis*-HRC=CH*H*), 3.22, 3.14, and 2.99 (d, 15H, J = 8.8, 8.8, and 8.5 Hz, N(*Me*)). ^{31}P NMR ($CDCl_3$) δ: 16.4 (d, *P*(N(Me)N=CH-C_6H_4-*o*-OH)$_2$), 14.0 (t, $^2J_{P\text{-}N\text{-}P}$ = 58.2 Hz, *P*(OR)N(Me)N=CH-C_6H_4-*o*-OH). FAB-MS *m/z*: 1076 ($[M]^+$). Anal. calcd. for $C_{54}H_{56}N_{13}O_6P_3$ (1076.02): C 60.3, H 5.2, N 16.9; found: C 60.6, H 5.0, N 16.5.

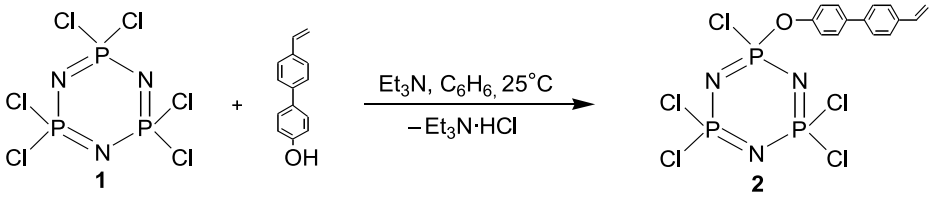
Preparation of $N_3P_3[N(Me)N{=}CH\text{-}C_6H_4N]_5[O\text{-}C_6H_4\text{-}p\text{-}C_6H_4\text{-}p\text{-}CH{=}CH_2]$ (5)

To a solution of **3** (1.11 g, 2.00 mmol) in ethanol (50 mL) was added a solution of pyridine-2-carboxaldehyde (1.28 g, 12.00 mmol) in ethanol (50 mL). The reaction mixture was heated under reflux for 17 h. After allowing the reaction mixture to cool to room temperature, solvent was removed from it under vacuum to obtain **5**. Compound **5** was re-precipitated using acetonitrile as the polar solvent and *n*-hexane as the non-polar solvent. Yield: 1.34 g (66.9%); mp. 99°C. ^1H NMR ($CDCl_3$) δ: 8.53–7.09 (m, 33H, aromatic and N=C*H*), 6.74 (dd, 1H, J = 17.7 and 11.0 Hz, *H*RC=CH_2), 5.78 (d, 1H, J = 17.8 Hz, *trans*-HRC=C*H*H), and 5.27 (d, 1H, J = 11.0 Hz, *cis*-HRC=C*H*H), 3.38, 3.28, and 3.14 (d, 15H, J = 8.3, 8.3, and 8.3 Hz, N(*Me*)). ^{31}P NMR ($CDCl_3$) δ: 18.1 (d, *P*(N(Me)N=CH-C_6H_4N)$_2$), 13.7 (t, $^2J_{P\text{-}N\text{-}P}$ = 56.6 Hz, *P*(OR)N(Me)N=CH-C_6H_4N). FAB-MS *m/z*: 1001 ($[M]^+$). Anal. calcd. for $C_{49}H_{51}N_{18}OP_3$ (1000.97): C 58.8, H 5.1, N 25.2; found: C 58.5, H 5.7, N 25.5.

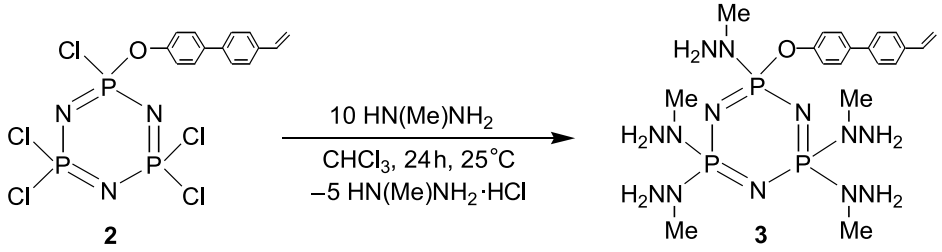
Preparation of (6)

Compound **4** (0.79 g, 7.4×10^{-1} mmol) was dissolved in 1,2-dichloroethane (10 mL) along with AIBN (2% by weight). The contents were purged with oxygen-free nitrogen for 30 min, and the reaction mixture was then

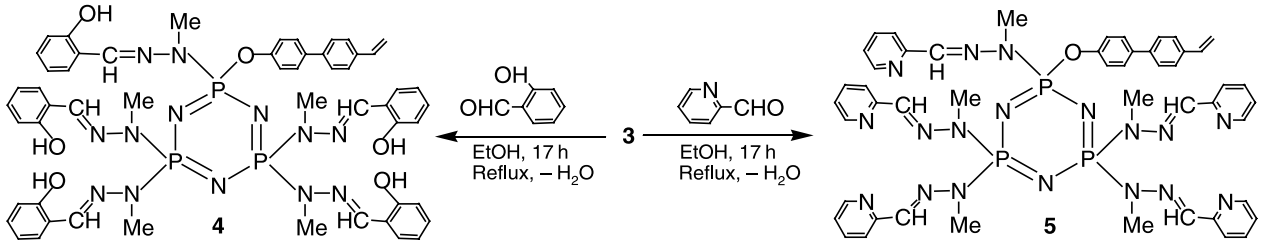
Scheme 2.



Scheme 3.



Scheme 4.



heated at 80°C for 24 h. It was then allowed to come to room temperature and poured into an excess of *n*-hexane to afford **6** as a powder. This was further purified by repeated re-precipitations (dichloromethane as the solvent and *n*-hexane as the non-solvent). Pure **6** was obtained as a white solid. It was dried in vacuum (10^{-3} torr (1 torr = 133.322 kPa)) at 40°C for 6 h. Yield: 0.48 g (60.7%). ^{1}H NMR ($CDCl_3$) δ: 11.27, 11.10, and 11.03 (s, 5H, O*H*), 7.10 (m(broad), 28H, aromatic and N=C*H*), 3.10 (m(broad), 15H, N(*Me*)), 1.25 (m, 3H, C*H*-CH_2). ^{31}P NMR ($CDCl_3$) δ: 16.4 (d, *P*(N(Me)N=CH-C_6H_4-*o*-OH)$_2$), 13.9 (t, $^2J_{P\text{-}N\text{-}P}$ = 58.3 Hz, *P*(OR)N(Me)N=CH-C_6H_4-*o*-OH). Intrinsic viscosity: 1.29 cm^3 g^{-1} (benzene), indicating a molecular weight of approximately 15 000 (22).

Preparation of (7)

The polymerization of **5** into **7** was carried out by using a similar procedure as those outlined above. The quantities used in this preparation are: **5** (0.74 g, 7.4 × 10^{-1} mmol). Yield: 0.40 g (54%). ^{1}H NMR ($CDCl_3$) δ: 8.48–7.10 (m(broad), 33H, aromatic and N=C*H*), 3.2 (m(broad), 15H, N(*Me*)), 1.26 (m, 3H, C*H*-CH_2). ^{31}P NMR ($CDCl_3$) δ: 18.06 (d, *P*(N(Me)N=CH-C_6H_4N)$_2$), 13.7 (t, $^2J_{P\text{-}N\text{-}P}$ = 54.9 Hz, P(OR)N(Me)N=CH-C_6H_4N). Intrinsic viscosity: 1.35 cm^3 g^{-1} (benzene), indicating a molecular weight of approximately 15 000 (22).

Results and discussion

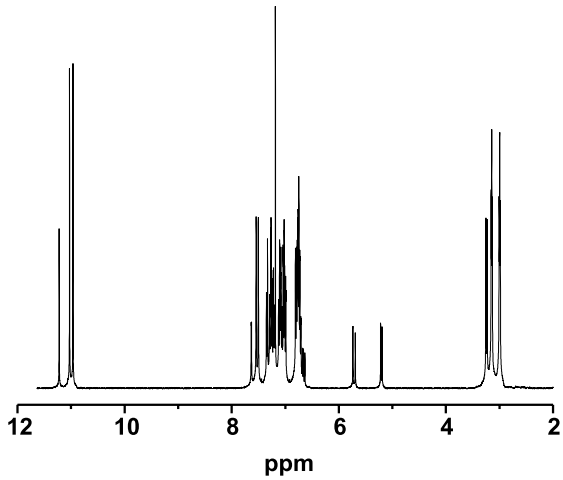
Synthesis and spectroscopy of the cyclophosphazene derivatives 3 to 5

The cyclophosphazene $N_3P_3Cl_5$[O-C_6H_4-*p*-C_6H_4-*p*-CH=CH_2] (**2**) has been shown previously by Inoue and co-workers (13 to 15) and by us (22) to be an excellent monomer in terms of its ease of preparation, hydrolytic stability, and ready polymerizability. It is readily prepared by the reaction of $N_3P_3Cl_6$ (**1**) with 4-hydroxy-4′-vinyl biphenyl in the presence of triethylamine as the hydrogen chloride scavenger (Scheme 2).

The presence of five reactive P—Cl bonds allows **2** to be used as a precursor for further reactions with nucleophiles. Accordingly the reaction of **2** with 10 equiv of *N*-methylhydrazine results in the complete substitution of the chlorine atoms, affording N_3P_3[N(Me)NH_2]$_5$[O-C_6H_4-*p*-C_6H_4-*p*-CH=CH_2] (**3**). in an excellent yield (Scheme 3). This reaction is regio-specific; the *N*-methyl end of the difunctional reagent is found to exclusively attach to the phosphorus atom. Such behavior has also been noted earlier in the reactions of *N*-methylhydrazine with acyclic phosphorus(V) halides, such as P(O)Cl_3 or PhP(O)Cl_2 (23–26). The most important feature of the reaction of **2** with *N*-methylhydrazine is that the product (**3**) still contains five reactive groups in the form of peripheral -NH_2 units. Also, the polymerizable vinyl group remains intact in the conversion of **2** to **3**.

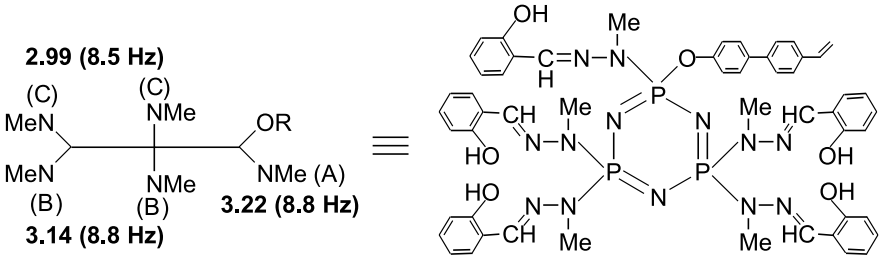
The condensation of **3** with 5 equiv of *o*-hydroxybenzaldehyde proceeds in boiling ethanol to afford the hydrazone **4**. Similarly condensation of **3** with pyridine-2-carboxaldehyde affords the hydrazone **5** (Scheme 4). Both of these cyclophosphazene derivatives contain a multi-site coordination environment in the form of the imino nitrogens, the cyclophosphazene ring nitrogen atoms, and the phenoxy oxygen (or the pyridyl nitrogen). The FAB-MS of **3**, **4**, and **5** show prominent parent ion peaks at 555, 1076, and 1001 respectively. The ^{1}H NMR spectrum of **3** shows the presence of the terminal -NH_2 groups as indicated by the appearance of a broad resonance at 3.2 ppm. This signal disappears upon the conversion of **3** into the hydrazones **4** and **5**. Interestingly, in the case of **4**, three hydroxy signals are seen as sharp singlets at 11.21, 11.01, and 10.95 ppm, respectively. The C*H*=N protons of **4** resonate at 7.55, 7.50, and 7.35 ppm. The vinyl protons appear as an AMX multiplet for all the three compounds **3**, **4**, and **5**. A representative ^{1}H NMR spectrum for compound **4** is given in Fig. 1. The presence (absence) of second order virtual coupling effects are helpful in the assignment of individual N-CH_3 chemical shifts. As can be seen from Fig. 2, in each of the compounds **3**, **4**, and **5**, three types of N-CH_3 resonances are expected. The most downfield N-CH_3 resonance is readily assigned to =P(OR)[N(CH_3)N=CHR′], because of the chemical shift, as well as the absence of virtual coupling effects. The other two

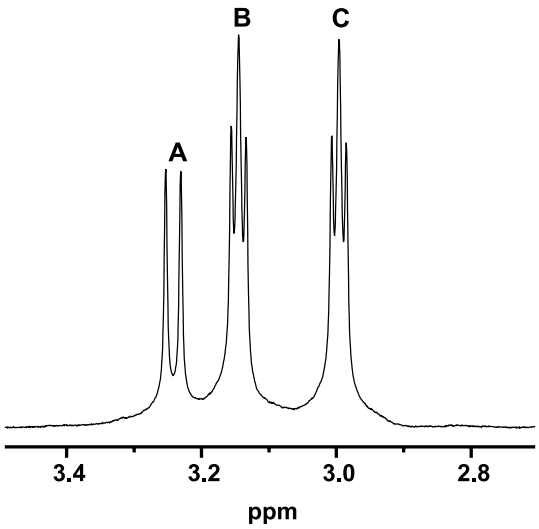
Fig. 1. ^{1}H NMR spectrum of compound **4**.



N-CH_3 resonances (Types B and C) show pronounced virtual coupling; these resonances are seen as virtual triplets with an intense central line. B and C themselves can be distinguished from each other. Thus the more shielded signal (C) is assigned as arising from the substituent flanked by the aryloxy group. Such effects have been well demonstrated in other situations among cyclophosphazenes (27).

Fig. 2. Virtual coupling effects in the N-Me region of the ^{1}H NMR of **4**.





Scheme 5.

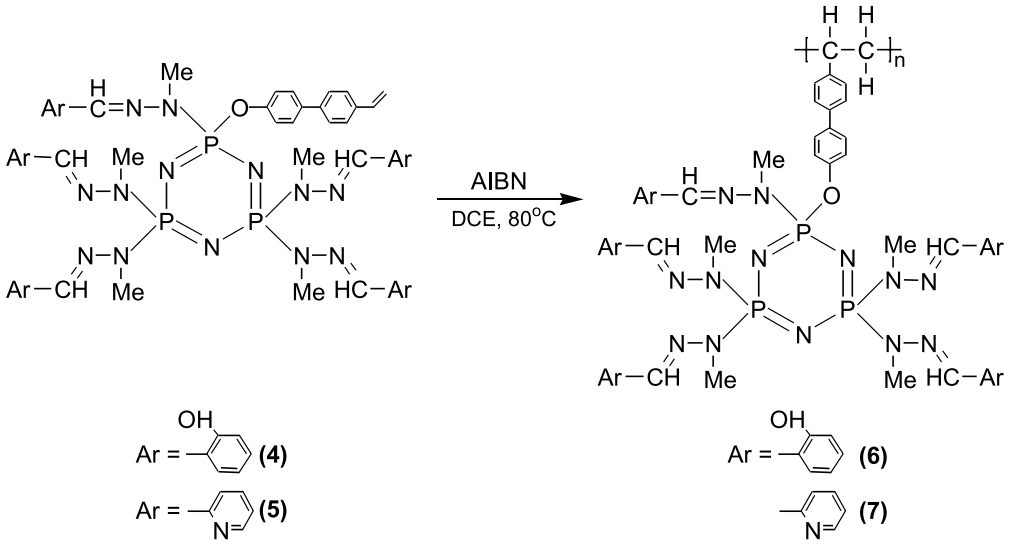


Table 1. ^{31}P NMR data for compounds **2**–**7**.

Compound	δ P(OR)(R) ν_A	δ P(R_2) ν_X	$^2J_{P\text{-}N\text{-}P}$ Hz
2	12.3	22.5	58.2
3	22.4	29.4	40.4
4	14.0	16.4	58.2
5	13.7	18.1	56.6
6	13.9	16.4	58.3
7	13.7	18.1	54.9

The ^{31}P NMR spectra of **3**, **4**, and **5** are of the AX_2 type. The chemical shift and coupling constant data for compounds **2**–**7** are summarized in Table 1. An interesting observation is that the conversion of the hydrazide **3** to the hydrazones **4** and **5** is accompanied by an upfield shift of the signals, along with a concomitant increase in the $^2J_{P\text{-}N\text{-}P}$ values.

Homopolymerization of 4 and 5

The compounds **4** and **5** can be readily homopolymerized in dichloroethane by using AIBN as the initiator to afford polymers **6** and **7** (Scheme 5). These polymers are obtained in their pure form by several re-precipitations, by dissolving in dichloroethane and using *n*-hexane as a non-polar solvent. The final dried products are air-stable powders soluble in a variety of organic solvents such as dichloromethane, tetrahydrofuran, etc. Dilute solution viscosity studies on **6** and **7** reveal that they have intrinsic viscosities of 1.29 and 1.35 $cm^3\ g^{-1}$, respectively, as measured in benzene. This suggests that these polymers have an MW of approximately 15 000 (22).

^{1}H NMR spectra of **6** and **7** show the complete disappearance of the AMX multiplet due to the vinyl protons and a broadening of other signals. The ^{31}P NMR spectra of **6** and **7** are of the AX_2 type, and the signal positions are unchanged vis-à-vis **4** and **5**. This strongly suggests that the cyclophosphazene moiety remains intact and does not suffer any degradation during the polymerization reaction.

Thermogravimetric analysis of the polymers **6** and **7** reveal that these are fairly robust polymers. Both of these polymers have similar degradation profiles. An initial decomposition leads to a char yield of approximately 68.5% at 400°C for **6** and 61.6% for **7**. Four further gradual decompositions occur. Even at 800°C, however, the char yields are fairly high (49.6% (**6**) and 45.9% (**7**)). Differential scanning calorimetric studies reveal that polymers **6** and **7** have high glass transition temperatures (T_g) viz., 139.4 and 119.6°C, respectively.

Conclusion

In conclusion, we have prepared new cyclophosphazene ligands containing hydrazone linkages and have successfully converted them into soluble and thermally stable polymeric systems, retaining the ligand framework as pendant groups. The metalation studies of these ligands are being pursued.

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