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# New Initiators for the Ring-Opening Thermal Polymerization of Hexachlorocyclotriphosphazene: Synthesis of Linear Poly(dichlorophosphazene) in High Yields[1]

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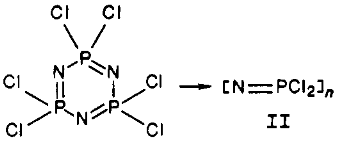
ABSTRACT: Ring-opening thermal polymerization of hexachlorocyclotriphosphazene ($N_3P_3Cl_6$) has been investigated at 250 °C and at 1.333-Pa pressure using chlorocyclotriphosphazenes $N_3P_3Cl_5(N{=}PPh_3)$ and $N_3P_3Cl_{6-n}(NMe_2)_n$ ($n$ = 2–4), salt hydrates, triphenylphosphine, and benzoic acid as initiators. The linear poly(dichlorophosphazene) products are phenoxylated, and the phenoxy polymers are characterized by gel permeation chromatography and dilute solution viscometry. Among the various initiators investigated, $CaSO_4{\cdot}2H_2O$ brings about a high conversion (>60%) of $N_3P_3Cl_6$ to the linear $[NPCl_2]_n$ polymer which possesses a high molecular weight ($>5 \times 10^6$). The rationale for the choice of the initiators and possible mechanism(s) of polymerization is discussed. Several mixed substituent polymers, $[NP(OPh)_x(OC_6H_4Me\text{-}p)_{2-x}]_n$ and $[NP(OPh)_x(OCH_2CF_3)_{2-x}]_n$, have been prepared and their thermal properties evaluated.

## Introduction

Linear poly(organophosphazenes) possess several unusual properties.[2] These polymers are prepared generally by the nucleophilic substitution reactions of poly(dichlorophosphazene), $[NPCl_2]_n$, which is in turn synthesized by the ring-opening polymerization of hexachlorocyclotriphosphazene (I, eq 1). The ring-opening polymerization can be effected by heating $N_3P_3Cl_6$ (I) with or without solvents at elevated temperatures[2-6] or by irradiating the sample with $^{60}Co$ $\gamma$-rays;[7,8] polymerization can also be brought about by electron impact in the ionization chamber of a mass spectrometer.[9] The thermal polymerization is the best method available for the synthesis of $[NPCl_2]_n$ linear polymer. Very recently, a combination of Raman spectroscopy and laser light scattering has been employed to monitor the melt and solution polymerizations of $N_3P_3Cl_6$ (I).[10] Apparently, bulk thermal polymerization of I is a complex process, and despite the numerous studies on the use of a variety of catalysts for the polymerization, it has been difficult to achieve consistently high yields of the soluble polymer possessing desired molecular mass characteristics.[5,11] We have investigated the effect of several salt hydrates, substituted chlorocyclophosphazenes $N_3P_3Cl_5(N{=}PPh_3)$ and $N_3P_3Cl_{6-n}(NMe_2)_n$ ($n$ = 2–4), triphenylphosphine, and benzoic acid on the thermal polymerization of I and found that calcium sulfate dihydrate initiated polymerization affords reasonably high yields of soluble linear polymer (II) with a high molecular weight. The results of these studies are presented in this paper.



I

II

## Results and Discussion

**Rationale for the Choice of Initiators.** Triphenylphosphine is a good chlorine abstracting reagent[12] and is known to form ionic salts with halogen compounds.[13] Since the thermal polymerization of $N_3P_3Cl_6$ involves ionic species in the initiation step,[2,5,14] $PPh_3$ can act as an initiator. High percentage conversion of $N_3P_3Cl_6$ to polymer is observed when benzoic acid is used as an initiator[15] but the solubility and the molecular mass characteristics of the resulting polymer have not been examined. Therefore, a detailed study of the polymerization of $N_3P_3Cl_6$ using either benzoic acid or $PPh_3$ is undertaken.

The presence of traces of water in the polymerization tube affects the polymerization process considerably.[16,17] In the present study, water has been introduced as salt hydrates which are easy to handle. Besides, the stoichiometric ratio of the substrate and initiator concentrations can be readily varied. The metal ion may also influence the polymerization process as discussed later.

Synthetic, kinetic,[18,19] and $^{35}Cl$ nuclear quadrupole resonance studies[20] reveal that *trans*-$N_3P_3Cl_3(NMe_2)_3$ contains ionizable P–Cl bonds; an X-ray crystallographic study of this compound shows that one of the PCl bonds is longer than the other two P–Cl bonds.[21] It has been proposed that the chlorine atom attached to phosphorus bearing the $NPPh_3$ group in $N_3P_3Cl_5(N{=}PPh_3)$ possesses considerable ionic character.[19,22] These compounds should thus be capable of initiating the polymerization process. The effects of bis- and tetrakis(dimethylamino) derivatives have been investigated to compare the results with those obtained by using the tris(dimethylamino) derivative.

**Polymerization of $N_3P_3Cl_6$ with Various Initiators.** In the absence of an initiator, the polymerization of highly purified $N_3P_3Cl_6$ (see Experimental Section) is extremely slow; at 220 °C, the starting material is recovered almost unchanged after 72 h. At 250 °C, the polymerization proceeds to an extent of ~35% after 8 h, but the yield of the soluble polymer is very low (5% based on $N_3P_3Cl_6$). The results obtained in the thermal polymerization of $N_3P_3Cl_6$ using various initiators are presented in Tables I and II. Although the data are admittedly limited, it may be concluded that there is an optimum concentration of each initiator as well as reaction time at which a maximum yield of the soluble polymer (>60% in some instances) can be obtained. Beyond these optimum limits, cross-linking sets in and the yield of soluble polymer decreases drastically. Reproducibility in terms of yield of the soluble polymer for a particular duration of polymerization is best achieved by using the same batch of $N_3P_3Cl_6$ for each initiator. With different batches of $N_3P_3Cl_6$, the yields slightly differ (±5%) with respect to time of reaction. Comparison of results obtained with different initiators and different batches of $N_3P_3Cl_6$ are thus valid in relative terms even though the absolute values may vary slightly from batch to batch.

Although a high yield of soluble polymer is obtained using benzoic acid or $N_3P_3Cl_5(N{=}PPh_3)$ as the initiator, the viscosity data indicate that the molecular weight of the resulting polymer is very low (Table III). With triphenylphosphine as the initiator, not only is the conversion to the soluble polymer poor but also the molecular weight

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**Table I**
**Results of Polymerization of $N_3P_3Cl_6$ Using $PPh_3$, $PhCO_2H$, $N_3P_3Cl_5(NPPh_3)$, and $N_3P_3Cl_{6-n}(NMe_2)_n$ ($n$ = 2–4) as Initiators at 250 °C**

| initiator | amt of initiator, mol % | reaction time, h | recovered cyclics,[a] % | polymer,[a] % soluble | polymer,[a] % insoluble |
|---|---|---|---|---|---|
| nil | nil | 72[b] | 100 | 0 | 0 |
| | nil | 8 | 66 | 4 | 30 |
| $PPh_3$[c] | 3 | 8 | 83 | 17 | 0 |
| | | 12 | 71 | 27 | 2 |
| | 5 | 4 | 83 | 17 | 0 |
| | | 10 | 77 | 20 | 3 |
| | 7.5 | 6.5 | 77 | 21 | 2 |
| | | 9 | 27 | 16 | 57 |
| $PhCO_2H$[d] | 3 | 6 | 77 | 23 | 0 |
| | | 8 | 26 | 3 | 71 |
| | 5 | 5 | 59 | 39 | 2 |
| | | 5.5 | 32 | 24 | 44 |
| | 7 | 4 | 35 | 64 | 1 |
| | | 4.5 | 24 | 42 | 34 |
| $N_3P_3Cl_5(NPPh_3)$[e] | 3 | 120 | 46 | 54 | 0 |
| | 3.5 | 120 | 33 | 65 | 2 |
| | 3.8 | 120 | 16 | 68 | 16 |
| $N_3P_3Cl_3(NMe_2)_3$[e] | 4 | 24 | 55 | 45 | 0 |
| | 5 | 24 | 48 | 52 | 0 |
| | 6 | 24 | 42 | 43 | 15 |
| *trans*-$N_3P_3Cl_4(NMe_2)_2$[e] | 5 | 24 | 68 | 29 | 3 |
| *cis*-$N_3P_3Cl_2(NMe_2)_4$[e] | 5 | 18 | 39 | 38 | 23 |
| | | 24 | 20 | 0 | 80 |

[a] Error involved is ±3%. [b] At 220 °C. [c] 3 g of $N_3P_3Cl_3$ was used. [d] 2 g of $N_3P_3Cl_6$ was used. [e] 5 g of $N_3P_3Cl_6$ was used.

**Table II**
**Details of Polymerization of $N_3P_3Cl_6$[a] in the Presence of Salt Hydrates at 250 °C**

| salt hydrate | amt of salt hydrate in mg | amt of salt hydrate in mol % | amt of water present, mol % | reaction time, h | recovered cyclics,[b] % | polymer,[b] % soluble | polymer,[b] % insoluble | intrinsic viscosity,[c] dL/g |
|---|---|---|---|---|---|---|---|---|
| $CaSO_4{\cdot}2H_2O$ | 9 | 0.10 | 0.2 | 6 | 94 | 6 | 0 | 1.1 |
| | | | | 14 | 34 | 64 | 2 | 2.8 |
| | 17 | 0.20 | 0.4 | 3 | 96 | 4 | 0 | |
| | | | | 6 | 93 | 7 | 0 | 0.1 |
| | | | | 9 | 67 | 33 | 0 | 0.8 |
| | | | | 12 | 43 | 56 | 1 | |
| | | | | 14 | 32 | 66 | 2 | 1.6 |
| | 44 | 0.50 | 1.0 | 3 | 94 | 6 | 0 | 0.1 |
| | | | | 6 | 90 | 10 | 0 | |
| | | | | 9 | 65 | 35 | 0 | |
| | | | | 14 | 30 | 57 | 13 | |
| | 87 | 1.00 | 2.0 | 4.5 | 75 | 20 | 5 | |
| | | | | 6 | 50 | 30 | 20 | |
| | | | | 7 | 45 | 2 | 53 | |
| $MgSO_4{\cdot}7H_2O$ | 7 | 0.06 | 0.4 | 14 | 72 | 26 | 2 | 0.4 |
| $BaCl_2{\cdot}2H_2O$ | 24 | 0.20 | 0.4 | 14 | 44 | 44 | 12 | 0.8 |
| $CuSO_4{\cdot}5H_2O$ | 10 | 0.08 | 0.4 | 14 | 47 | 38 | 15 | 0.8 |
| $NiSO_4{\cdot}7H_2O$ | 9 | 0.06 | 0.4 | 14 | 22 | 55 | 23 | 1.2 |
| $CoSO_4{\cdot}7H_2O$ | 8 | 0.06 | 0.4 | 14 | 29 | 53 | 18 | 0.9 |

[a] For each experiment, 5 g of $N_3P_3Cl_6$ was used. [b] Error involved is ±3%. [c] For the derivatized polymer, $[NP(OPh)_2]_n$, in benzene at 25 °C.

**Table III**
**Molecular Mass Characteristics[a] of $[NP(OPh)_2]_n$ Derived from $[NPCl_2]_n$ Obtained by Using Various Initiators**

| initiator | intrinsic viscosity at 25 °C,[b] dL/g | $\bar{M}_w$[d] | $\bar{M}_n$[e] | polydispersity $D = \bar{M}_w/\bar{M}_n$ |
|---|---|---|---|---|
| $PPh_3$ | 0.1 | $5.3 \times 10^5$ | $4.3 \times 10^4$ | 12 |
| $PhCO_2H$ | 0.1[c] | $3.2 \times 10^6$ | $5.8 \times 10^4$ | 55 |
| $N_3P_3Cl_5(N{=}PPh_3)$ | 0.4 | $>5.0 \times 10^6$ | $2.3 \times 10^5$ | ~20 |
| *trans*-$N_3P_3Cl_3(NMe_2)_3$ | 0.9 | $>5.0 \times 10^6$ | $1.5 \times 10^6$ | ~6 |
| $CaSO_4{\cdot}2H_2O$ | 2.8 | $>5.0 \times 10^6$ | $>5.0 \times 10^6$ | ~2 |

[a] GPC measurements. [b] In benzene. [c] At 30 °C. [d] Weight-average molecular weight. [e] Number-average molecular weight.

is low. With $CaSO_4{\cdot}2H_2O$ as the initiator, the intrinsic viscosity of the derivatized polymer $[NP(OPh)_2]_n$ can be as high as 2.8 dL/g.[23] The intrinsic viscosities of the derivatized polymers obtained by changing the initiator concentration ($CaSO_4{\cdot}2H_2O$) and the duration of the polymerization are given in Table II. For the same amount of initiator (0.2 mol %), intrinsic viscosity increases with time of polymerization, but as the concentration of the initiator increases from 0.1 to 0.2 mol % for a fixed reaction time (6 h), intrinsic viscosity decreases sharply. This decrease in intrinsic viscosities signifies a decrease in the molecular weight of the polymer. The possible reason for this behavior is discussed later while we deal with the mechanism of the polymerization.

The gel permeation chromatograms (GPC) for the derivatized polymers are shown in Figure 1, and weight-average and number-average molecular weights calculated are presented in Table III. It can be readily seen that the polymer obtained by using $CaSO_4{\cdot}2H_2O$ shows a narrower

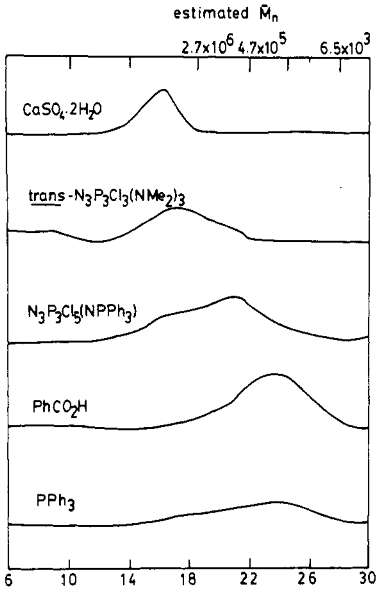

**Figure 1.** Gel permeation chromatograms for the derivatized polymers, $[NP(OPh)_2]_n$, prepared from the linear $[NPCl_2]_n$ obtained by the polymerization of $N_3P_3Cl_6$ using various initiators.

distribution of molecular weights compared to the distribution for polymers obtained by using other initiators.

In order to make a comparative study of the effect of $CaSO_4{\cdot}2H_2O$ initiator with other salt hydrates, experiments have been carried out with copper, nickel, cobalt, magnesium, and barium salt hydrates (see Table II). With all these initiators, the formation of the soluble polymer is always accompanied by an appreciable amount of an insoluble polymer. The molecular weight of the resulting polymer is also lower than that obtained by using $CaSO_4{\cdot}2H_2O$.

**Mechanism of Polymerization of $N_3P_3Cl_6$ Using Various Initiators.** It is generally agreed that the initiation step in the thermal polymerization of $N_3P_3Cl_6$ is either the dissociation of a P–Cl bond or ring opening to yield a phosphazenium cation which undergoes chain growth.[2] Polymerization of $N_3P_3Cl_6$ in the presence of the chlorocyclophosphazenes, $N_3P_3Cl_5(N{=}PPh_3)$ and $N_3P_3Cl_{6-n}(NMe_2)_n$ ($n$ = 2–4), involves the former process; mesomeric electron release from the exocyclic nitrogen atom facilitates the ionization of chlorine at a PCl(R) (R = $N{=}PPh_3$ or $NMe_2$) center.[25] The rate of polymerization with the dimethylamino derivatives varies in the order bis < tris < tetrakis. This trend parallels the increasing ease of heterolysis of the P–Cl bond(s) in these compounds and further supports the proposed mechanism. It must however be stressed that with the tetrakis(dimethylamino) derivative as the initiator, the insoluble polymer is obtained in an appreciable quantity (Table I). The very slow polymerization of $N_3P_3Cl_6$ with $N_3P_3Cl_5(N{=}PPh_3)$ as the initiator may be due to an adverse steric effect imposed by the $NPPh_3$ group in the propagation step.

The mechanism proposed for the polymerization of $N_3P_3Cl_6$ in the presence of water envisages the cleavage of the ring and the formation of the acyclic species $ClP(O){=}NPCl_2{=}NPCl_2{=}NH$. The higher the amount of water present in the system, the higher will be the concentration of hydrogen chloride. If an appreciable amount of hydrogen chloride is present, the termination of the growing chain will be favored. Therefore, the molecular weight of the polymer formed decreases with increasing concentration of water.[16] When salt hydrates are used for the polymerization of $N_3P_3Cl_6$, the metal ion can also influence the polymerization to a significant extent by coordinating to the phosphazene unit via the skeletal nitrogen atom(s).[26-29] Often ring- or chain-cleaved product is formed as a result of this type of interaction.[30,31] Since the extent of interaction of $Cu^{2+}$, $Ni^{2+}$, $Co^{2+}$, or $Mg^{2+}$ ions with the skeletal nitrogen would be certainly stronger than that between $Ca^{2+}$ ions and the phosphazene chain, cleavage reactions are more likely to occur with the salt hydrates of Cu, Ni, Co, and Mg, resulting in the formation of low molecular weight polymers (Table II).

**Table IV**
**Thermal Properties of Poly(organophosphazenes)**

| polymer | $T_g$, °C | 10% wt loss, °C | 30% wt loss, °C |
|---|---|---|---|
| $[NP(OPh)_2]_n$ | −9 | 360 | 400 |
| $[NP(OPh)_{1.7}(OC_6H_4Me\text{-}p)_{0.3}]_n$ | −34 | 355 | 390 |
| $[NP(OPh)_{1.2}(OC_6H_4Me\text{-}p)_{0.8}]_n$ | −37 | 330 | 380 |
| $[NP(OPh)(OC_6H_4Me\text{-}p]_n$ | −29 | 350 | 400 |
| $[NP(OPh)_{0.7}(OC_6H_4Me\text{-}p)_{1.3}]_n$ | −34 | 350 | 390 |
| $[NP(OPh)_{0.4}(OC_6H_4Me\text{-}p)_{1.6}]_n$ | −39 | 295 | 370 |
| $[NP(OC_6H_4Me\text{-}p)_2]_n$ | −3 | 335 | 375 |
| $[NP(OPh)_{1.5}(OCH_2CF_3)_{0.5}]_n$ | −25 | 325 | 350 |
| $[NP(OPh)_{1.3}(OCH_2CF_3)_{0.7}]_n$ | −31 | 285 | 320 |
| $[NP(OPh)_{0.6}(OCH_2CF_3)_{1.4}]_n$ | −33 | 285 | 315 |
| $[NP(OCH_2CF_3)_2]_n$ | −67 | 275 | 315 |

The mode of action of $PPh_3$ as an initiator for the polymerization of $N_3P_3Cl_6$ is not clear. It may function in a manner analogous to $BCl_3$ and open up the P–N ring in the initiation step.[6] Benzoic acid initiated polymerization of $N_3P_3Cl_6$ may also proceed by a mechanism involving the cleavage of the phosphazene ring as originally proposed by Gimblet.[15]

**Reactions of $[NPCl_2]_n$ with a Mixture of Alkoxides and Aryl Oxides.** It has been shown that by using 0.1 mol % $CaSO_4{\cdot}2H_2O$ as the initiator and carrying out the polymerization reaction for 14 h, the yield of the soluble $[NPCl_2]_n$ polymer having a high molecular weight can be maximized (~60%). The $[NPCl_2]_n$ polymer prepared under these conditions is used in all subsequent experiments to study its reactivity toward alkoxide/aryl oxides and for the preparation of mixed substituent polymers, $[NP(OPh)_x(OR)_{2-x}]_n$ (R = $C_6H_4Me$-$p$ or $CH_2CF_3$; $0 < x < 2$). The compositions of the mixed substituent polymers have been established from the integrated intensities of the appropriate peaks in their $^1H$ NMR (60 MHz) spectra[32] and confirmed in a few instances by combustion analysis.[33] The reactivity of $[NPCl_2]_n$ toward sodium phenoxide or $p$-cresoxide is the same. When a mixture of the aryl oxides is used, the compositions of the mixed substituent polymers are solely determined by the stoichiometric ratio of the aryl oxides. When a mixture of sodium phenoxide and trifluoroethoxide is used, trifluoroethoxide is consumed completely. The $^{31}P$ NMR spectra of the polymers $[NP(OPh)_2]_n$, $[NP(OPh)_{1.3}(OCH_2CF_3)_{0.7}]_n$ and $[NP(OPh)_{0.6}(OCH_2CF_3)_{1.4}]_n$ showed broad peaks in the region $\delta$ −18.3, −11.0 to −15.0, and −19.7 to −22.3, respectively.[34]

The thermal properties of several poly(organophosphazenes) are presented in Table IV. The glass transition temperature ($T_g$) of mixed phenoxy-$p$-cresoxy polymers is lowered up to −39 °C compared to the values for the homopolymers. For phenoxytrifluoroethoxy polymers, the $T_g$ values are intermediate between those of the homopolymers and remain almost constant over a wide range of the ratio of the alkoxy and the aryloxy substituents.

## Conclusions

Several Lewis acids and a host of other compounds have been found to catalyze the polymerization of I.[2,6,11] Each of them has its merits and demerits. One commonly encountered disadvantage is the difficulty of obtaining soluble polymers with high molecular weights even though the polymerization rate can be enhanced and the yield of soluble polymer can be high as found in the case of $BCl_3$-catalyzed polymerization.[6] In the present study, the utility of salt hydrates and cyclotriphosphazenes containing readily ionizable P–Cl bonds as initiators for the polymerization of $N_3P_3Cl_6$ has been established. These two approaches should prove useful in further studies to optimize and control the polymerization reaction with the aim of obtaining a maximum yield of soluble linear polymer with desired molecular mass characteristics. Among the several initiators tried by us, $CaSO_4 \cdot 2H_2O$ appears to be promising in affording consistently high yields of soluble polymer with a high molecular weight.

## Experimental Section

**Materials.** The solvents were purified by conventional procedures. Light petroleum employed had a boiling range of 60–80 °C.

Pure hexachlorocyclotriphosphazene, $N_3P_3Cl_6$, was prepared by a standard method.[2a] It was repeatedly recrystallized from light petroleum (at least thrice) and sublimed in vacuum (13.33 Pa) at 55–60 °C. The sublimate was carefully removed to a weighing bottle inside a glovebag filled with dry nitrogen. It was stored in a desiccator and used within 12–24 h. All the operations were carried out in the absence of moisture. These stringent precautions were found to be essential to get reproducible results.

Triphenylphosphine and salt hydradtes ($CaSO_4 \cdot 2H_2O$, $MgSO_4 \cdot 7H_2O$, $CuSO_4 \cdot 5H_2O$, $NiSO_4 \cdot 7H_2O$, $CoSO_4 \cdot 7H_2O$, and $BaCl_2 \cdot 2H_2O$) were used as supplied (BDH, AR grade). The cyclophosphazene derivatives, $N_3P_3Cl_5(N{=}PPh_3)$[35] and $N_3P_3Cl_{6-n}(NMe_2)_n$ ($n$ = 2–4),[36] were prepared by methods reported previously. These compounds were purified by vacuum sublimation (120, 90, 80, and 100 °C, respectively) at 13.33-Pa pressure; they were stored in a desiccator and used within 12–24 h. Benzoic acid (AR grade) was purified by sublimation (55–60 °C/13.33 Pa).

**Instrumental Methods.** A thermoregulated electrically heated oven was used for the polymerization of $N_3P_3Cl_6$; the oven could be maintained at the desired temperature with an accuracy of ±3 °C.

The viscosity of the phenoxy polymer, $[NP(OPh)_2]_n$, was determined in benzene solution by using a Cannon-Ubbelohde viscometer. Gel permeation chromatograms were obtained by using a Waters Assoc. HPLC/GPC 401 instrument equipped with a refractive index detector. The column used was packed successively with $\mu$-styragel of pore size $10^5$, $10^4$, and $10^3$ Å. The solvent used was THF with a flow rate of 1 mL/min. Polystyrene standards were used for calibration.

Thermogravimetric analyses in static air were carried out on a ULVAC SINKU Model TA-1500 analyzer. The low-temperature differential thermal analyses were carried out by using a Stanton Redcroft analyzer in the temperature range −150 to 25 °C. The heating rate employed in both cases was 10 °C $min^{-1}$. For some of the samples, differential scanning calorimetric experiments were carried out on a Du Pont 990 thermal analyzer fitted with a 910 DSC accessory module. The heating rate employed was 20 °C $min^{-1}$.

**Polymerization of $N_3P_3Cl_6$. General Methodology.** Cyclindrical glass tubes (20-mm outer diameter and 20-cm length) fitted with a $B_{14}$ cone having a constriction 5 cm from the top (to facilitate sealing in vacuum) were used for polymerization of $N_3P_3Cl_6$. The tubes were thoroughly washed with double-distilled water; they were dried at 110 °C (24 h) and at 250 °C (>120 h). The tubes were closed with a stopcock and cooled. Known quantities of rigorously purified $N_3P_3Cl_6$ and the initiator were introduced into the tube. The tube was degassed (1.333 Pa) and sealed under vacuum. The sealed tube was suspended in an oven at the required temperature. The tube was removed from the oven and cooled. The residual (unpolymerized) cyclic oligomers slowly crystallized. The tube was broken, and the contents along with glass pieces were placed in a 100-mL round-bottomed flask. The contents were extracted repeatedly with hot light petroleum (4 × 80 mL) until no more cyclic oligomers were extracted. The petroleum insoluble material was extracted several times with hot THF (4 × 80 mL). The yield of insoluble polymer was then determined by knowing the amounts of (i) soluble polymer (THF extract), (ii) cyclic oligomers (petroleum extract), and (iii) $N_3P_3Cl_6$ initially used for the polymerization. All of the above operations were carried out in an atmosphere of dry nitrogen.

The experimental details for the polymerization of $N_3P_3Cl_6$ with several initiators are summarized in Tables I and II.

**Derivatization of Linear $[NPCl_2]_n$.** The soluble polymers obtained as above were phenoxylated. Sodium phenoxide was prepared by the reaction of sodium with phenol (1:1.1 molar ratio) in boiling THF. The stoichiometry of $[NPCl_2]_n$ to sodium phenoxide was 1:4. Tetra-$n$-butylammonium bromide (50% by weight to $[NPCl_2]_n$) as a phase-transfer catalyst[37] was added to the reaction mixtures to ensure the replacement of all the chlorine atoms. The whole mixture was heated under reflux for 12 h. Most of the solvent from the mixture was removed under vacuum and the remaining material poured into water (~800 mL); the phenoxy polymer $[NP(OPh)_2]_n$ precipitated out. The aqueous layer was decanted, and the polymer was extracted several times with hot water to remove sodium chloride and unreacted sodium phenoxide. The polymer was further purified for physical measurements by dissolving it in THF and pouring the solution into an excess of methanol. The dissolution–precipitation sequence was repeated and the precipitated polymer was extracted with methanol for 3 days in a Soxhlet apparatus to remove traces of occluded phenol if any. The polymer was dried over phosphorus pentoxide in a vacuum oven at 50 °C. The yield of the purified polymer was generally 60–70% (based on $[NPCl_2]_n$ linear polymer).

**Synthesis of Mixed Substituents Polymers.** The required amounts of sodium phenoxide or trifluoroethoxide were prepared separately and mixed before the addition of chloro polymer, $[NPCl_2]_n$. The procedure for the synthesis and purification of mixed substituent polymers is the same as that described above for $[NP(OPh)_2]_n$. Precipitation of polymers containing mixed aryloxy substituents was carried out in methanol; for the precipitation of mixed phenoxytrifluoroethoxy polymers, light petroleum was used.

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**Registry No.** $PPh_3$, 603-35-0; $PhCO_2H$, 65-85-0; $N_3P_3Cl_5(NPPh_3)$, 16151-27-2; $N_3P_3Cl_3(NMe_2)_3$, 3721-13-9; *trans*-$N_3P_3Cl_4(NMe_2)_2$, 1081-87-4; *cis*-$N_3P_3Cl_2(NMe_2)_4$, 963-05-3; $CaSO_4$, 7778-18-9; $MgSO_4$, 7487-88-9; $BaCl_2$, 10361-37-2; $CuSO_4$, 7758-98-7; $NiSO_4$, 7786-81-4; $CoSO_4$, 10124-43-3; poly(dichlorophosphazene), 26085-02-9; poly(hexachlorocyclotriphosphazene) (homopolymer), 25231-98-5.

## References and Notes

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# Polymerization of Monomers Containing Functional Silyl Groups. 3. Anionic Living Polymerization of (4-Vinylphenyl)dimethylsilane

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ABSTRACT: Anionic polymerization of (4-vinylphenyl)dimethylsilane was investigated at −78 °C in THF or THF–pentane mixture with oligo($\alpha$-methylstyryl)dilithium, -disodium, or -dipotassium. Under such conditions, the polymerization of this monomer proceeded as a living system. Polymers of predictable molecular weights and of narrow molecular weight distributions ($\bar{M}_w/\bar{M}_n$ = 1.08–1.19) were obtained in quantitative yields. The living polymer thus obtained can initiate further polymerization of styrene to afford a new type of block copolymer, poly[styrene-*b*-(4-vinylphenyl)dimethylsilane-*b*-styrene].

## Introduction

It is well-known that silicon hydrides add to olefins, acetylenes, and carbonyl compounds in the presence of either radical initiators or, more commonly, certain transition metals and their complexes.[1] The hydrogens of silicon hydrides can readily be displaced by both electrophiles and nucleophiles.[2] Many of these reactions are of great value in organic synthesis. The preparation of a silicon hydride containing polymer has attracted special interest in this regard, because the silicon hydride on the polymer may undergo a wide variety of the above-mentioned reactions by which important and versatile specialty functions may be introduced into the polymer.

Extensive studies have appeared on the synthesis and application of poly(methylsiloxanes) and their copolymers with dimethylsiloxane units where the Si–H bonds are present in the main chains. It was reported mostly in patents that they were prepared either by the hydrolysis of $CH_3SiHCl_2$ or by the ring-opening polymerization of cyclic oligomers of $\overline{-[CH_3Si(H)O]_n-}$.

In contrast, the polymers having silicon hydrides in the side chains are less widely known. In the presence of transition metals, the polymerizations of vinyldialkyl- and vinyldiarylsilanes proceeded via polyaddition mechanism in preference to the occurrence of vinyl polymerization. As a result, linear polymers represented as $-(SiR_1R_2CH_2CH_2)_n-$ with no SiH groups were obtained.[3,4] On the other hand, it was reported that radical and $VCl_3$–$Al(C_2H_5)_3$-initiated polymerizations of vinylsilanes and 4-substituted styrenes with SiH group resulted in the polymers with polyvinylic structures assigned on the basis of their IR and NMR spectra.[5,6] The vinyl reactivity of (4-vinylphenyl)dimethylsilane was also discussed from its radical polymerization behavior.[7] In these systems, however, there are still some possibilities that the addition of the SiH group to the vinyl bond might occur, because radical initiators used in the polymerization also play a role as hydrosilylation catalysts.[1] Accordingly, a linear polymer

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