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Synthesis of Triarmed-Star Polyphosphazenes via the "Living" Cationic Polymerization of Phosphoranimines at Ambient Temperatures†

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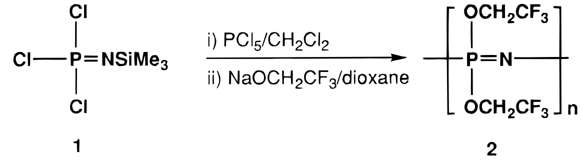
Star-type or hyperbranched polymers are of widespread interest due to their ability to impart properties or functionalities that are not currently accessible in conventional linear polymer systems.[1] The branched nature of these polymers alters properties, such as solubility and crystallinity, and provide an additional method for tuning macromolecular structures beyond those available for linear macromolecules. Linear polyphosphazenes, $(N{=}PR_2)_n$, have attracted considerable interest because of properties such as biocompatibility, thermooxidative stability, flame retardancy, elasticity, unusual surface properties, ionic conductivity, and electrooptical effects, depending on the specific side groups (R). This, together with their unique fundamental scientific aspects, has stimulated the synthesis and study of more than 700 different phosphazene-based polymers during the last 30 years.[2,3]

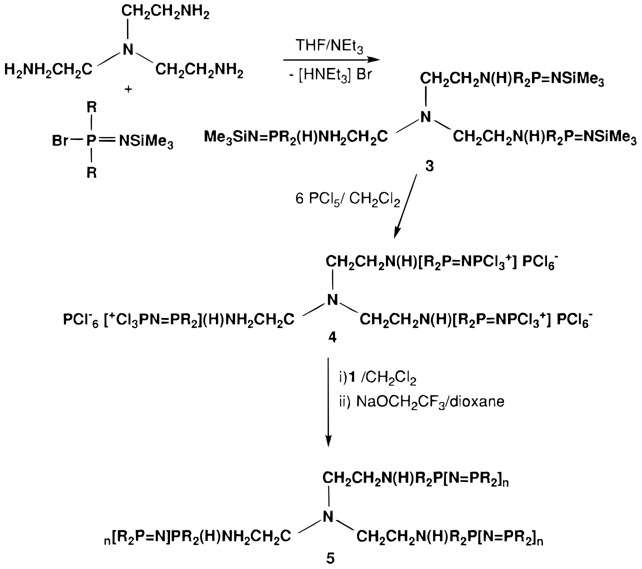
Recently, we reported a new method for the preparation of poly(dichlorophosphazene), $(N{=}PCl_2)_n$, via the reaction of the phosphoranimine $Cl_3P{=}NSiMe_3$ (**1**) with small amounts of PCl_5 at 25 °C (Scheme 1).[4] This improved method allows for the ambient temperature synthesis of poly(dichlorophosphazene), $(N{=}PCl_2)_n$, via a living cationic-induced polymerization, with molecular weight control.[5] This polymerization route also serves as an efficient method for the direct preparation of a variety of poly(organophosphazenes)[6] via the PCl_5-induced polymerization of *organo*phosphoranimines at ambient temperature. Recent extensions of this method have resulted in the development of phosphazene-based block copolymers.[7]

Previous studies, involving the reactivity of $Cl_3P{=}NSiMe_3$ (**1**), have shown that this species interacts with 2 equiv of PCl_5 to form $[Cl_3P{=}NPCl_3]^+[PCl_6]^-$ with the elimination of Me_3SiCl.[4,8] This ionic intermediate can then be induced to react with an additional equivalent of **1** to eliminate Me_3SiCl and form the short-chain cationic species $[Cl_3P{=}NPCl_2{=}NPCl_3]^+[PCl_6]^-$. Oligomeric products can be obtained by the addition of further equivalents of **1** to this species.[5] In view of these results, it appeared possible that the reaction of **1** with a small amount of an initiator that contained multiple $[R_3P{=}NPCl_3]^+[PCl_6]^-$-type sites could yield medium or high molecular weight star polymers. Cyclic phosphazenes such as the hexakis(aryloxy)cyclotriphosphazenes, $[N{=}P(p\text{-}OC_6H_4NH_2)_2]_3$, $[N{=}P(p\text{-}OC_6H_4COOH)_2]_3$, and $[N{=}P(p\text{-}OC_6H_4COCl)_2]_3$, have served as core units in the synthesis of a variety of organic-based hexaarmed star polymers, including poly(amino acids), nylon-6, and polystyrene/nylon-6 block copolymer systems.[9,10] Also, dendritic cyclotriphosphazene-based materials have recently been synthesized which are supported by alumina or molecular sieves.[11−13] However, to our knowledge, free-standing, totally phosphazene-based star polymer systems have not been described.

Scheme 1



Scheme 2



In this paper, we report the synthesis of triarmed phosphazene-based star polymers via the cationic-induced polymerization of phosphoranimines at ambient temperatures. This method results in the synthesis of star polymers with molecular weight control and low polydispersity indices.

Phosphoranimines such as $(CF_3CH_2O)_2BrP{=}NSiMe_3$ have been shown to readily undergo substitution reactions in the presence of alkoxides or amines, to produce $(CF_3CH_2O)_2RP{=}NSiMe_3$ species (R = RO or RNH).[14,15] With this in mind, the tridentate primary amine $N(CH_2CH_2NH_2)_3$ was mixed with $(CF_3CH_2O)_2BrP{=}NSiMe_3$, in the presence of NEt_3 to produce the trifunctional phosphoranimine $N\{CH_2CH_2NH(CF_3CH_2O)_2P{=}NSiMe_3\}_3$ (**3**). Subsequent reaction of **3** with 6 molar equiv of PCl_5 at −78 °C in CH_2Cl_2 resulted in the formation of the trifunctional cationic species $[N\{CH_2CH_2NH(CF_3CH_2O)_2P{=}NPCl_3{}^+\}_3]\,[PCl_6{}^-]_3$ (**4**) (Scheme 2). Species **4** was then treated with a 30-fold excess (per reactive site) of $Cl_3P{=}NSiMe_3$ (**1**) in CH_2Cl_2. After 3 h at 25 °C, examination of the reaction mixture by ^{31}P NMR spectroscopy revealed the complete conversion of **1** to a new form of poly(dichlorophosphazene), $(N{=}PCl_2)_n$, based on a characteristic resonance at −17 ppm with loss of the doublet resonances for **4**. Also detected was a doublet resonance at ca. 8.2 ppm, as well as triplet resonances at −14.5 and −15.5 ppm, consistent with the presence of the star polymer $N\{CH_2CH_2NH(CF_3CH_2O)_2P{=}NPCl_2N{=}PCl_2[N{=}PCl_2]_n\}_3$ (Figure 1). Integration of the ^{31}P NMR resonances associated with the star polymer were consistent with theoretical values based on the initial reactant ratio of **1**:**4**. This product was treated with an excess of sodium trifluoroethoxide to replace the chlorine atoms by trifluoroethoxy groups and generate the hydrolytically stable star polymer N{CH2-

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† Dedicated to John James Nelson.

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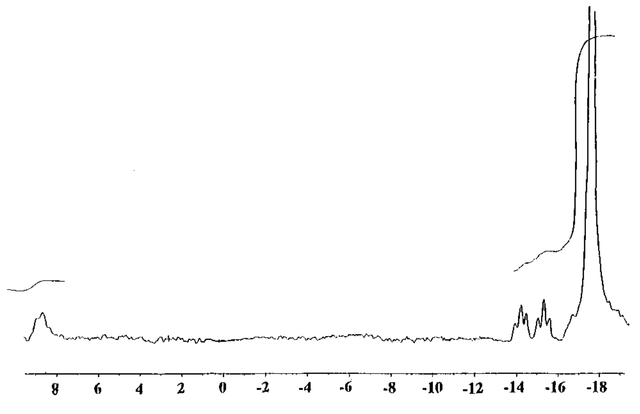

Figure 1. ^{31}P NMR spectrum of $N\{CH_2CH_2NH(CF_3CH_2O)_2P{=}NPCl_2N{=}PCl_2[N{=}PCl_2]_n\}_3$ in CH_2Cl_2.

Table 1. Star Polymer Molecular Weights

M:I/reactive site	reaction time (h)	$M_n \times 10^{-3}$ found[a]	found[b]	calcd[c]	PDI
10:1	0.66	12.6	9.1	9.1[d]	1.05
15:1	1	17.0	13.0	13.0	1.02
30:1	3	20.6	23.7	23.7	1.03
50:1	6	35.3	NA	38.3	1.03
100:1	14	41.6	NA	74.8	1.36

[a] Molecular weights by GPC following replacement of Cl by $NaOCH_2CF_3$. [b] Molecular weights by end group analysis using ^{31}P NMR spectroscopy. [c] Calculated at 100% conversion. [d] $M_n = 8.1 \times 10^3$ by ^1H NMR integration based on a core:trifluoroethoxy ratio of 1:8.5.

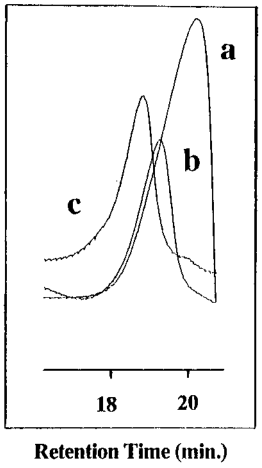

Figure 2. GPC chromatograms of star polymer **5** synthesized from (a) 10:1 **1**:**4** ratio, (b) 15:1 **1**:**4** ratio, and (c) 30:1 **1**:**4** ratio.

$CH_2NH(CF_3CH_2O)_2P[N{=}P(OCH_2CF_3)_2]_n\}_3$ (**5**). Analysis of **5** by gel permeation chromatography (GPC) indicated that it possessed an M_n of 2.1×10^4 and a polydispersity index (PDI = M_w/M_n) of 1.03 versus polystyrene standards. The molecular weights of these star polymers can be controlled by variation of monomer:initiator ratios (Table 1). End-group analysis by ^{31}P NMR spectroscopy was also used to provide molecular weight estimates in cases where the end-group unit $[-NP(OCH_2CF_3)_2NH-]$ was detectable.

Preliminary comparisons of the physical properties of low molecular weight samples of **5** with the linear analogue $[N{=}P(OCH_2CF_3)_2]_n$ (**2**) of comparable molecular weight (1.2×10^4) revealed that, while the linear polymer is a crystalline white fibrous material which readily forms films, the triarmed star polymer **5** is a pale yellow, viscous gum. The corresponding star and linear polymers with molecular weights higher than 1.7×10^4 show similar physical characteristics. In addition, GPC chromatograms for **5** with M_n above 2.1×10^4 appear to underestimate the molecular weight and provide indirect evidence for the branched nature of **5**. Efforts are currently focused on the further development of phosphazene star polymers and on structural studies, including light scattering.

Experimental Section. Materials. 2,2,2-Trifluoroethanol, sodium metal, and tris(2-aminoethyl)amine were obtained from Aldrich and were used without further purification. Phosphorus pentachloride (Aldrich) was sublimed under vacuum. Sodium trifluoroethoxide[16] and $(CF_3CH_2O)_2BrP{=}NSiMe_3$[14] were synthesized and purified by literature procedures. Dichloromethane (Aldrich) was dried and distilled from CaH_2 and then from P_2O_5 into the reaction flask.

Preparation of $N(CH_2CH_2NH(CF_3CH_2O)_2P{=}NSiMe_3)_3$ (3). A mixture of $(CF_3CH_2O)_2BrPNSiMe_3$[14] (16 g, 40.4 mmol) and NEt_3 (4.08 g, 40.4 mmol) in THF (200 mL) was cooled to −78 °C. To this solution $N(CH_2CH_2NH_2)_3$ (1.96 g, 13.4 mmol) was added dropwise over a 20 min period. The reaction mixture was stirred at −78 °C for 1 h and then warmed to room temperature. All volatiles were removed in vacuo to produce an orange oil. Distillation under high vacuum (170 °C, 0.2 mmHg) produced **3** as a pale-yellow oil. For **3**: Yield 9.01 g (60%). ^1H NMR ($CDCl_3$): $\delta = 4.23$ (q, $^3J_{HF} = 16$ Hz, 4H, CH_2O), 3.05 (br m, $^2J_{HH} = 12$ Hz, 2H, CH_2NH), 2.5 (br t, $^2J_{HH} = 11$ Hz, 2H, NCH_2), 1.23 (br s, 1H, NH), 0.03 ppm (d, $^4J_{PH} = 1$ Hz, 9H, $SiCH_3$). ^{31}P NMR ($CDCl_3$): $\delta = -0.7$ ppm. ^{13}C NMR ($CDCl_3$): $\delta = 124.6$ (q of d, $^2J_{CF} = 310$ Hz, $^3J_{CP} = 9$ Hz, CF_3), 61.8 (d of q, $^2J_{CP} = 10$ Hz, $^3J_{CF} = 36$ Hz, CH_2O), 55.2 (d, $^2J_{PC} = 9$ Hz, CH_2NH), 39.4 (s, NCH_2), 2.5 ppm (d, $^3J_{PC} = 1$ Hz, $SiCH_3$). MS (CI, isobutane): $m/z = 1092$ (MH^+, 17%), 1076 ($M^+ - Me$, 15%), in good agreement with isotopic abundance calculations. Anal. Calcd: C, 29.70; H, 4.91; N, 9.02. Found: C, 28.81; H, 4.61; N, 9.37.

Preparation of $N[CH_2CH_2NH(CF_3CH_2O)_2P{=}NPCl_3^+]_3[PCl_6^-]_3$ (4). To a stirred solution of PCl_5 (4.0 g, 19 mmol) in CH_2Cl_2 (200 mL) at −78 °C was added **3** (3.5 g, 3.2 mmol) dropwise over a period of 20 min. The reaction mixture was stirred at −78 °C for 1 h and allowed to warm to room temperature. After solvent removal in vacuo, the remaining residue was washed with hexane (4 × 100 mL) to produce **4** as a light yellow solid. For **4**: Yield 4.5 g (70%). ^{31}P NMR ($CDCl_3$): $\delta = 17.7$ (d, $^2J_{PP} = 51$ Hz, $(CF_3CH_2O)_2P{=}N)$), 7.6 (d, $^2J_{PP} = 51$ Hz, Cl_3PN), −297 ppm (s, PCl_6^-).

Polymerization of $Cl_3P{=}NSiMe_3$ (1) by $N[CH_2CH_2NH(CF_3CH_2O)_2P{=}NPCl_3^+]_3$ $[PCl_6^-]_3$ (4) in Solution. General Procedure. To a stirred solution of **4** (0.10 g, 4.6×10^{-2} mmol) in CH_2Cl_2 (1.5 mL) at 25 °C was added **1** (0.90 g, 4.10 mmol). After 3 h all of the initial monomer **1** had reacted, as evidenced by the disappearance of the ^{31}P NMR resonance for **1** at −54 ppm and the presence of a new resonance at −17.6 ppm for $[N{=}PCl_2]_n$. For $N\{CH_2CH_2NH(CF_3CH_2O)_2P{=}NPCl_2N{=}PCl_2[N{=}PCl_2]_n\}_3$: ^{31}P NMR (CH_2Cl_2): $\delta = 8.2$ (d, 1P, $^2J_{PP} = 29$ Hz, $(CF_3CH_2O)_2P{=}N$), −14.5, −15.5 (t, 2P, $^2J_{PP} = 40$ Hz, $(CF_3CH_2O)_2P{=}NPCl_2N{=}PCl_2(N{=}PCl_2)_n]$), −17.6 ppm (br s, 28P, $[N{=}PCl_2]_n$). All volatile species were removed at reduced pressure. The residue was then dissolved in 10 mL of dioxane and treated with 2.5 M sodium trifluoroethoxide (10 mmol) in dioxane (4 mL). The mixture was then refluxed for 1 h and stirred at 25 °C for 24 h to produce the macromolecule $N[CH_2$-

$CH_2NH(CF_3CH_2O)_2P{=}NP(OCH_2CF_3)_2(N{=}P(OCH_2CF_3)_2)_n]_3$ (**5**). Polymer **5** was then precipitated into deionized water (3×) and hexane (2×). For **5**: Yield 90%. ^{31}P NMR (CH_2Cl_2): $\delta = -6.9$ ppm. ^{1}H NMR ($CDCl_3$): $\delta = 4.23$ (q, $^3J_{HF} = 16$ Hz, 2H, CH_2O), 3.05 (br m, $^2J_{HH} = 12$ Hz, 2H, CH_2NH), 2.5 (br t, $^2J_{HH} = 11$ Hz, 2H, NCH_2), 1.23 (br s, 1H, NH), 0.03 ppm (d, $^4J_{PH} = 1$ Hz, 9H, $SiCH_3$). GPC: $M_n = 2.1 \times 10^4$ and PDI = 1.03. Anal. Calcd: C, 19.80; H, 1.61; N, 5.79. Found: C, 19.62; H, 1.50; N, 5.41.

In order to control the molecular weight, the ratio of monomer to initiator was varied by changing the amount of monomer while keeping all other amounts constant (see Table 1).

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