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Polyphosphazene Block Copolymers via the Controlled Cationic, Ambient Temperature Polymerization of Phosphoranimines

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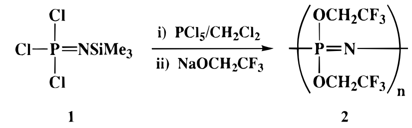
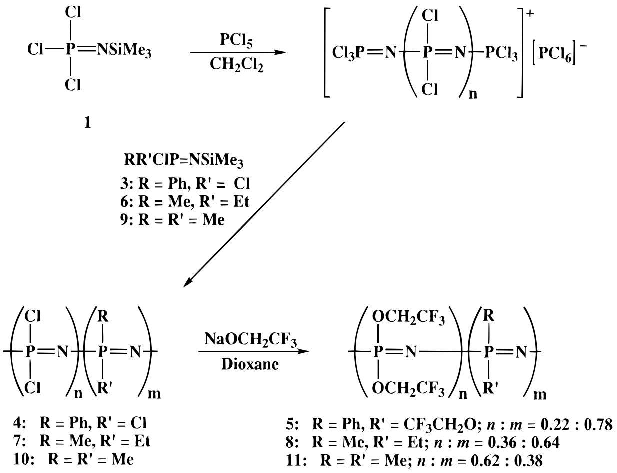
Introduction. The recent discovery of an ambient temperature route to polyphosphazenes via the “living” cationic polymerization of the phosphoranimine $Cl_3P{=}NSiMe_3$ (**1**)[1,2] provides an advanced method with molecular weight control and narrow polydispersities for the synthesis of poly(dichlorophosphazene). This is a critical intermediate in the synthesis of most poly(organophosphazenes) (e.g. **2**; Scheme 1).[3,4] This “living” cationic polymerization method has also been used for the direct synthesis of poly(organophosphazenes) by the PCl_5-induced polymerization of mono- and disubstituted organophosphoranimines, such as $PhCl_2P{=}NSiMe_3$ (**3**) at ambient temperatures (ca. 25−35 °C).[5] The presence of “living” active sites at the termini of the polymer chains, produced via reaction of **1** with PCl_5, offered the possibility for the formation of block copolymers either with other phosphazene monomers or with organic monomers. Thus, this new method may be applicable to the production of a wide variety of phosphazene copolymers with controlled architectures.

Polyphosphazene copolymers have been synthesized previously by a variety of methods. Random copolymers are accessible via the thermal ring-opening copolymerization of cyclotriphosphazenes, such as $(NPCl_2)_3$ with *non-gem* $N_3P_3(R)_3Cl_3$ (R = Me, Ph), $N_3P_3(R)X_5$ (R = Ph, X = Cl, F), and *gem* or *non-gem* $N_3P_3(R_2)X_4$ (R = Ph, X = Cl, F), as developed in our laboratories.[6−8] Also, Neilson, Wisian-Neilson, and co-workers[9] reported that phosphazene random copolymers could be synthesized by the thermal condensation polymerization of mixed *N*-silylphosphoranimines. In addition, block copolymers have been synthesized by Matyjaszewski and co-workers via the anionic polymerization of *N*-silylphosphoranimines, such as $(CF_3CH_2O)_3P{=}NSiMe_3$ and $(CH_3OCH_2CH_2O)(CF_3CH_2O)_2P{=}NSiMe_3$, at 133 °C.[10,11] However, due to the presence of two possible leaving groups in one of the initial monomers (e.g. $CH_3OCH_2CH_2O$ and CF_3CH_2O), this approach yields block copolymers where one of the block segments contains a mixture of side groups. Polyphosphazene block copolymers produced via this route have molecular weights which approach M_n of 4.3×10^4 with polydispersity indices of 1.4−2.3.

Scheme 1



Scheme 2



Although more than 700 phosphazene polymers have been synthesized via the macromolecular nucleophilic substitution reactions of poly(dichlorophosphazene),[3,4,6,8] phosphazene block copolymers that can be tailored by this method have not been reported previously. In this communication, we describe the ambient temperature synthesis of polyphosphazene block copolymers via the controlled cationic polymerization of phosphoranimines. This new route provides block copolymers with controlled molecular weights and narrow polydispersities. Macromolecular halogen replacement reactions carried out on these species allow a variety of derivative polymers to be synthesized.

Results and Discussion. In an earlier publication we described the reactions of the phosphoranimine $Cl_3P{=}NSiMe_3$ (**1**) with small quantities of PCl_5 to give “living” poly(dichlorophosphazene) $(N{=}PCl_2)_n$. Further addition of **1** to this species resulted in resumed polymerization to give higher molecular weight $(N{=}PCl_2)_n$.[2] Therefore, it seemed likely that the subsequent addition of other phosphoranimines might result in the formation of block copolymers (Scheme 2). Thus, in the present work, a reaction of **1** with PCl_5 in CH_2Cl_2 in a 10:1 ratio at 25 °C resulted in the formation of $(N{=}PCl_2)_n$ over a time span of 3 h. A portion of this reaction mixture was treated with $NaOCH_2CF_3$, to produce $[N{=}P(OCH_2CF_3)_2]_n$ (**2**) as a control with an M_n of 9.6×10^3 (PDI = 1.11 by GPC). Addition of a second phosphoranimine, $PhCl_2P{=}NSiMe_3$ (**3**), to the remaining portion of $(N{=}PCl_2)_n$ (in a 4:1 ratio with respect to **1**) at 25 °C, resulted in the polymerization of **3** to form $\{[N{=}PCl_2]_n[N{=}PPh(Cl)]_m\}$ (**4**) as monitored by ^{31}P NMR spectroscopy over a period of one week. Subsequent treatment of this reaction mixture with $NaOCH_2CF_3$ replaced the chlorine atoms by trifluoroethoxy groups to yield the air- and water- stable block copolymer $\{[N{=}P(OCH_2CF_3)_2]_n[N{=}PPh(OCH_2CF_3)]_m\}$ (**5**). Analysis of this product by GPC suggested an M_n of 1.6×10^4 (PDI = 1.13), consistent with the formation of block copolymer **5** (see Figure 1). The refractive index of the single GPC peak for **5** was of opposite polarity to that found for **2**, and this is indirect evidence that the product is a copolymer rather than two separate homopolymers. Analysis of polymer **5** by ^{31}P NMR spectroscopy indicated the presence of characteristic peaks for both $[N{=}P(OCH_2CF_3)_2]_n$ at −6.9 ppm and $[N{=}PPh(OCH_2CF_3)]_m$ at 3.1 ppm. Further evidence for the structure of **5** comes from a comparison of the ^1H and ^{31}P NMR integration for the respective blocks (n:m = 0.22:0.78), with the elemental analysis results, which agree within experimental error.[12]

Other studies were conducted in an attempt to detect switching groups between the phosphazene blocks.

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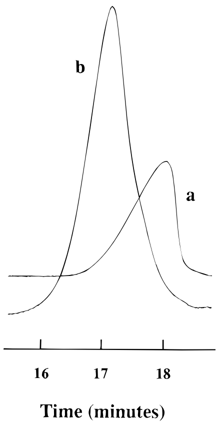

Figure 1. A GPC chromatogram comparison of a polymerization of $Cl_3P{=}NSiMe_3$ initiated with PCl_5 in a 10:1 ratio: (a) after macromolecular substitution with $NaOCH_2CF_3$ to result in $[N{=}P(OCH_2CF_3)_2]_n$ (**2**); (b) after the addition of $PhCl_2P{=}NSiMe_3$ followed by macromolecular substitution with $NaOCH_2CF_3$ to form $\{[N{=}P(OCH_2CF_3)_2]_n[N{=}PPh(OCH_2CF_3)]_m\}$ (**5**).

Reactions of the phosphoranimine $Me(Et)ClP{=}NSiMe_3$ (**6**) with samples of “living” poly(dichlorophosphazene), produced via treatment of **1** with PCl_5 in CH_2Cl_2, resulted in the formation of the block copolymer $\{[N{=}PCl_2]_n[N{=}PMe(Et)]_m\}$ (**7**). Examination of polymer **7** by ^{31}P NMR spectroscopy revealed the presence of characteristic resonances for $[N{=}PMe(Et)]_m$ at ca. 20 ppm and for $[N{=}PCl_2]_n$ at ca. −17 ppm. Also present in this ^{31}P NMR spectrum were multiplet resonances at 26.3 and −14.5 ppm, which are attributed to the presence of switching groups that link the two phosphazene blocks. In an attempt to confirm the nature of these linkage groups, a short-chain phosphazene cation, $[Cl_3P{=}N{-}PCl_2{=}N\text{-}PMe(Et){=}N{-}PMe(Et)Cl]^+$ $[PCl_6]^-$ (**7a**), was synthesized by successive additions of **5** to $[Cl_3P{=}N{-}PCl_3]^+$ $[PCl_6]^-$.[13] Analysis of **7a** by ^{31}P NMR spectroscopy showed resonances at 27.1 and −14.1 ppm assigned to the junction $-PCl_2$ and $-PMe(Et)$ groups, respectively.[14]

The synthesis of **7** via reaction of **1** with PCl_5 (ca. 8:1 **1**:PCl_5) in CH_2Cl_2 at 25 °C followed by addition of an equimolar (with respect to **1**) amount of **6** resulted in the production of a low molecular weight form of **7**. The low molecular weight of the resultant block species is attributed to the inability of **6** to undergo complete polymerization in CH_2Cl_2 solutions.[5] Treatment of the low molecular weight block copolymer $\{[N{=}PCl_2]_n[N{=}PMe(Et)]_m\}$ with $NaOCH_2CF_3$ produced the trifluoroethoxy derivative $\{[N{=}P(OCH_2CF_3)_2]_n[N{=}PMe(Et)]_m\}$ (**8**). Species **8** was found by GPC analysis to have an M_n of 8.0×10^3 (PDI = 1.39). This can be compared with the M_n value of 6.7×10^3 (PDI = 1.14) found for the portion of the initial sample of $(N{=}PCl_2)_n$ treated with $NaOCH_2CF_3$ to produce $[N{=}P(OCH_2CF_3)_2]_n$ (**2**) before the addition of **6**. As reported for **5**, GPC chromatograms of **8** were opposite in refractive index polarity with respect to $[N{=}P(OCH_2CF_3)_2]_n$ (**2**).

To obtain higher conversions of **6** to polymer, monomer **6** was treated with a more concentrated solution of $(N{=}PCl_2)_n$ in CH_2Cl_2 (synthesized via the reaction of **1** with PCl_5 in a 20:1 ratio respectively) at 25 °C. These slight variations in synthetic procedure produced a sample of **7** which, after chlorine replacement by $NaOCH_2CF_3$, yielded **8** with an M_n of 1.6×10^4 (PDI = 1.19 by GPC). For comparison, a portion of the initial $(N{=}PCl_2)_n$ sample, before addition of **6**, was found to have an M_n of 1.2×10^4 (PDI = 1.06 by GPC after chlorine replacement by $NaOCH_2CF_3$). As with the previously mentioned lower molecular weight sample of **8**, GPC chromatograms of this sample of **8** were opposite in refractive index polarity with respect to $[N{=}P(OCH_2CF_3)_2]_n$ (**2**). Furthermore, a comparison of the ^1H NMR integration for the respective blocks (n:m = 0.36:0.64) for **8** corresponds with elemental analysis results.[12]

In addition, treatment of “living” samples of $(N{=}PCl_2)_n$ (synthesized via the reaction of **1** with PCl_5 in a 20:1 ratio respectively) with $Me_2ClP{=}NSiMe_3$ (**9**) at 25 °C yielded $\{[N{=}PCl_2]_n[N{=}PMe_2]_m\}$ (**10**). Subsequent macromolecular substitution with $NaOCH_2CF_3$ resulted in the formation of $\{[N{=}P(OCH_2CF_3)_2]_n[N{=}PMe_2]_m\}$ (**11**) with $M_n = 1.6 \times 10^4$ and PDI = 1.14 (as compared to an initial sample of $(N{=}PCl_2)_n$ substituted with $NaOCH_2CF_3$ to form **2** with $M_n = 1.3 \times 10^4$ and PDI = 1.04). Again, the GPC chromatograms of **11** were negative in polarity relative to **2**. Interestingly, the polymeric species **11** is soluble in THF, which is in sharp contrast to $(N{=}PMe_2)_n$, which is insoluble in that solvent.[15,16] Examination of the block copolymer **11** in THF by ^1H and ^{31}P NMR spectroscopy indicated the presence of the bis(trifluoroethoxy)- and dimethylphosphazene blocks in a ratio of n:m = 0.62:0.38.[12] The solubility data, together with the NMR and GPC data, strongly suggest that the $(N{=}PMe_2)_m$ block is covalently bonded to the $[N{=}P(OCH_2CF_3)_2]_n$ block.

Thus, phosphazene block copolymers can be synthesized by the cationic polymerization of phosphoranimines. Although the copolymers reported here are of only modest molecular weight, variations in the initiator to $Cl_3P{=}NSiMe_3$ ratio allow the length of the first block to be extended. It is the monomer reactivity during formation of the second block that needs to be enhanced. Current work is focused on extending the scope of this process and on the examination of the properties of these block copolymers.[17]

Experimental Section. Sodium trifluoroethoxide ($NaOCH_2CF_3$), $[Cl_3P{=}N{-}PCl_3]^+[PCl_6]^-$,[13] and the phosphoranimines $Cl_3P{=}NSiMe_3$ (**1**),[1,13] $PhCl_2P{=}NSiMe_3$ (**3**),[13] $Me(Et)ClP{=}NSiMe_3$,[5] (**5**) and $Me_2ClP{=}NSiMe_3$ (**7**)[16−18] were synthesized via methods reported previously. Phosphorus pentachloride and CH_2Cl_2 were purified as described elsewhere.[25] Glassware was dried overnight in an oven or flame dried under vacuum before use. All reactions were performed under an atmosphere of dry argon or nitrogen. NMR spectra, obtained on a Bruker WM-360 NMR spectrometer, and gel permeation chromatography (GPC) measurements were performed as described elsewhere.[2,5] Elemental analyses were obtained by Quantitative Technologies Inc., Whitehorse, NJ.

General Synthetic Method. Synthesis of 5. To a stirred solution of PCl_5 (ca. 0.19 g, 0.91 mmol) in 20 mL of CH_2Cl_2 was added **1** (2.00 g, 8.95 mmol), and the resultant reaction mixture was stirred at 25 °C. After complete conversion of **1** to poly(dichlorophosphazene), as determined by ^{31}P NMR spectroscopy (ca. 3 h; for $(N{=}PCl_2)_n$; ^{31}P-NMR (CH_2Cl_2) $\delta = -17.4$ ppm), a portion of the reaction mixture was treated with $NaOCH_2CF_3$ in dioxane to produce the trifluoroethoxy derivative $[N{=}P(OCH_2CF_3)_2]_n$ (**2**). For **2**, GPC: $M_n = 9.6 \times 10^3$ and PDI = 1.11. To the remainder of the reaction solution was added 4.72 g (17.8 mmol) of $PhCl_2P{=}NSiMe_3$ (**3**), and the resultant mixture was stirred for 1 week with occasional monitoring by ^{31}P

NMR spectroscopy. After complete conversion of **3** to polymer, all volatiles were removed at reduced pressure. Treatment of the resultant $\{[N{=}PCl_2]_n[N{=}PPh(Cl)]_m\}$ (**4**) with $NaOCH_2CF_3$ in dioxane produced $\{[N{=}P(OCH_2CF_3)_2]_n[N{=}PPh(OCH_2CF_3)]_m\}$ (**5**), thus permitting molecular weight determination by GPC. For **4**, GPC: $M_n = 1.6 \times 10^4$ and PDI = 1.13. ^{31}P-NMR (CH_2Cl_2): δ = 3.1 (s, $[N{=}PPh(OCH_2CF_3)]_m$), −6.9 ppm (s, $[N{=}P(OCH_2CF_3)_2]_n$). Anal. Calcd: C, 37.75; H, 2.82; N, 6.20. Found: C, 37.48; H, 2.75; N, 5.89.

Synthesis of 8. The synthesis of **8** was performed in a manner analogous to the preparation of copolymer **5**. A control "living" sample of $(N{=}PCl_2)_n$ was treated with $NaOCH_2CF_3$ to produce **2**. For **2**, GPC: $M_n = 1.3 \times 10^4$ and PDI = 1.06. Addition of $Me(Et)ClP{=}NSiMe_3$ (**6**) to the remaining $(N{=}PCl_2)_n$ and subsequent reaction with $NaOCH_2CF_3$ yielded **8**. For **8**, ^{31}P-NMR (CH_2Cl_2): δ = 20.0 (s, $[N{=}PMe(Et)]_m$), −6.9 ppm (s, $[N{=}P(OCH_2CF_3)_2]_n$). GPC: $M_n = 1.6 \times 10^4$ and PDI = 1.19. Anal. Calcd: C, 28.02; H, 4.62; N, 9.74. Found: C, 27.19; H, 5.09; N, 8.80.

Synthesis of 11. The synthesis of **11** was also carried out in a manner analogous to the preparation of copolymer **5**. A "living" sample of $(N{=}PCl_2)_n$ was treated with $NaOCH_2CF_3$ to produce **2**. For **2**, GPC: $M_n = 1.3 \times 10^4$ and PDI = 1.04. Addition of $Me_2ClP{=}NSiMe_3$ (**9**) to the remaining $(N{=}PCl_2)_n$ and subsequent reaction with $NaOCH_2CF_3$ resulted in **8**. For **11**; ^{31}P-NMR (CH_2Cl_2): δ = 7.1 (br s, $[N{=}PMe_2]_m$), −6.9 ppm (s, $[N{=}P(OCH_2CF_3)_2]_n$). GPC: $M_n = 1.6 \times 10^4$ and PDI = 1.14.

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(12) There is some discrepancy with respect to the length of the blocks formed. For block copolymer **5**, the values obtained from GPC analysis imply a block length of approximately 40 $N{=}P(OCH_2CF_3)_2$ repeating units linked to a block of 29 $N{=}PPh(OCH_2CF_3)_2$ units. However, NMR and elemental analysis suggest $n{:}m$ = 0.22:0.78. Therefore, if a DP_n = 20 is assumed for $N{=}P(OCH_2CF_3)_2$ (from calculations based on the initial $Cl_3P{=}NSiMe_3$ to PCl_5 ratio), then a block of 20 $N{=}P(OCH_2CF_3)_2$ units linked to a block of approximately 71 $N{=}PPh(OCH_2CF_3)_2$ units is suggested. Similar results were obtained for block copolymers **8** and **11**. For the higher molecular weight form of **8**, GPC analysis suggested 49 $N{=}P(OCH_2CF_3)_2$ units linked to 45 $N{=}PMe(Et)$ units (compared to $n{:}m$ = 0.36:0.64). For **11** by GPC analysis, 53 $N{=}P(OCH_2CF_3)_2$ units linked to 40 $N{=}PMe_2$ units is implied (compared to $n{:}m$ = 0.62:0.38).

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(14) For $[Cl_3P{=}N{-}PCl_2{=}N{-}PMe(Et){=}N{-}PMe(Et)Cl]^+[PCl_6]^-$ (**7a**); ^{31}P-NMR (CH_2Cl_2): δ = 55.1 (d, $^2J_{PP}$ = 40 Hz, $-N{=}\mathit{P}Me(Et)Cl$), 27.1 (m, $^2J_{PP}$ = 39 Hz, $-N{-}\mathit{P}Me(Et){=}$), −14.1 (m, $^2J_{PP}$ = 43 Hz, $-N{-}\mathit{P}Cl_2{=}$), −24.9 (d, $^2J_{PP}$ = 43 Hz, $-N{=}\mathit{P}Cl_3$), and −297 ppm (s, $\mathit{P}Cl_6^-$).

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