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Synthesis of the First Organic Polymer/Polyphosphazene Block Copolymers: Ambient Temperature Synthesis of Triblock Poly(Phosphazene−ethylene oxide) Copolymers

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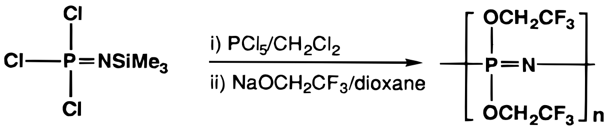
The recent development of an ambient temperature route for the synthesis of polyphosphazenes, $(N{=}PR_2)_n$, via the "living"/controlled cationic polymerization of phosphoranimines, e.g. $Cl_3P{=}NSiMe_3$ (**1**), provides an advanced method for the synthesis of these polymers with controlled molecular weights and narrow polydispersities.[1−5] This PCl_5-induced polymerization method (Scheme 1) is also useful for the production of a wide variety of polymeric phosphazene systems with controlled architectures, notably block *co*polyphosphazenes[3] and tri-arm star-branched phosphazenes.[4] These synthetic advances have raised the possibility that linear copolymeric macromolecules that contain blocks of phosphazene and organic units might be accessible.

Hybrid organic/phosphazene *graft* copolymers have been examined by numerous research groups. Neilson, Wisian-Neilson, and their co-workers reported the synthesis of *graft*-poly(phosphazene−styrene) comb polymers via the use of metalated samples of poly(methylphenylphosphazene), $[N{=}P(Ph)CH_2Li]_n$, to initiate the growth of polystyrene from $P{-}CH_2{-}$ side group units.[6] Similarly, poly(phosphazene−siloxane) graft copolymers have been synthesized via the lithiophosphazene-initiated anionic ring-opening polymerization of hexamethylcyclotrisiloxane, $[Me_2SiO]_3$, to form comb polymers with 10−20% grafting and up to 90 monomeric siloxane units (i.e., $CH_2(Me_2SiO)_{90}{-}SiMe_3$).[7,8] We have also made graft copolymeric systems by photolysis of poly[bis(methylphenoxy)phosphazene] in the presence of vinylpyridine or glycidyl methacrylate.[9] In addition, Gleria and co-workers reported the synthesis of graft copolymers synthesized via free radical methods.[10] However, to our knowledge the synthesis of well-defined, linear phosphazene−organic block copolymers has not been reported. As part of our continuing efforts to synthesize polyphosphazenes with controlled architectures, we report here the first synthesis of a phosphazene−organic multiblock copolymer.

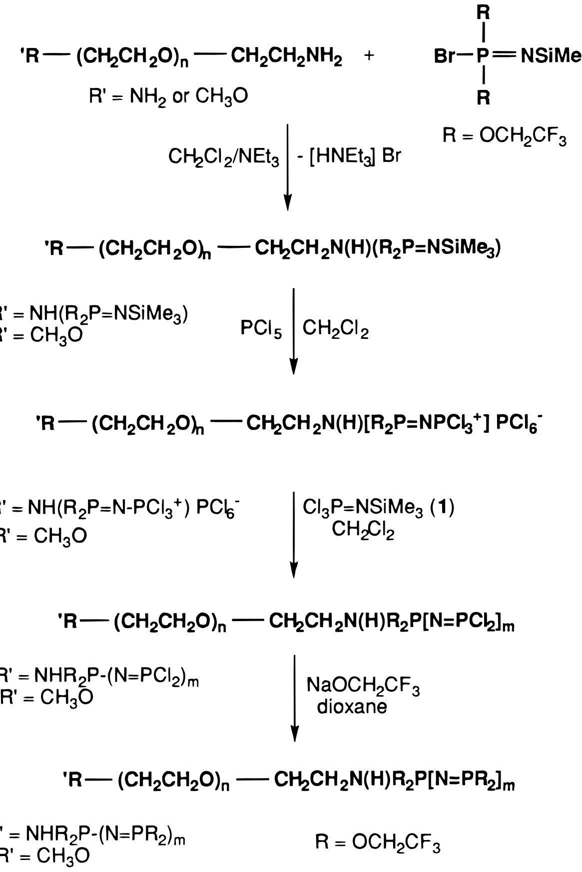
Previous studies, involving the polymerization behavior of $Cl_3P{=}NSiMe_3$ (**1**) have shown that this species is readily initiated by short chain ionic species such as $[Cl_3P{=}N{-}PCl_3]^+[PCl_6]^-$ to form linear poly(dichlorophosphazene) $[Cl_3P{=}N{-}(Cl_2P{=}N)_n{-}PCl_3]^+[PCl_6]^-$.[1,11,12] Recently, extensions of this methodology have yielded triarmed star-branched polyphosphazenes via the reaction of **1** with a small amount of a trifunctional cationic species.[4] This multifunctional initiator was synthesized by reaction of the tridentate primary amine $N(CH_2CH_2NH_2)_3$ 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**) and subsequent reaction of **3** with 6 molar equiv of PCl_5 at −78 °C in CH_2Cl_2, resulting in the formation of the trifunctional initiator $[N\{CH_2CH_2NH(CF_3CH_2O)_2P{=}N{-}PCl_3{}^+\}_3][PCl_6{}^-]_3$ (**4**). In view of these findings, attempts were made to incorporate short chain ionic species capable of initiating the phosphoranimine $Cl_3P{=}NSiMe_3$ (**1**) at the ends of commercially available amine-functionalized organic polymers, such as $NH_2(CH_2CH_2O)_n{-}CH_2CH_2{-}NH_2$, and the use of such macroinitiators for the development of block poly(phosphazene−ethylene oxide) polymers.

Scheme 1



1 **2**

Scheme 2



Thus, the commercially avaliable polymeric bidentate amine $NH_2{-}PEG{-}NH_2$ (PEG = $-CH_2CH_2O(CH_2CH_2O)_n{-}CH_2CH_2{-}$, $\bar{M}_n$ = 3400), was mixed with $(CF_3CH_2O)_2BrP{=}NSiMe_3$, in the presence of NEt_3, to produce the phosphoranimine **5** (see Scheme 2 for compounds **5**−**8**).[13] Subsequent reaction of **5** with 4 molar equiv of PCl_5 at −78 °C in CH_2Cl_2 resulted in the formation of the macroinitiator **6**. This macroinitiator was then treated with a 30-fold excess of $Cl_3P{=}NSiMe_3$

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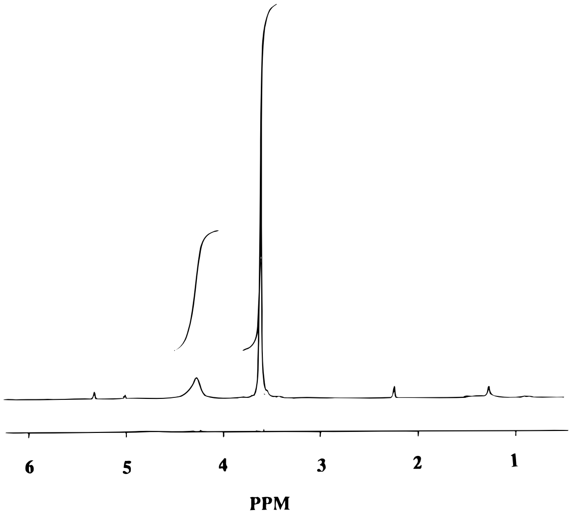

Figure 1. ^{1}H NMR spectrum of triblock copolymer **8** in CD_2Cl_2.

(**1**). 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) (**7**), based on a characteristic resonance at −17 ppm with loss of the doublet resonances for **6**. This product was treated with an excess of a sodium trifluoroethoxide/dioxane solution to replace the chlorine atoms by trifluoroethoxy groups and generate the hydrolytically stable block copolymer **8**. It should be noted that the amino PEG reagent is not 100% functionalized. The unfunctionalized polymer was removed during the purification.

Analysis of **8** by gel permeation chromatography (GPC) in THF indicated that it possessed an $\bar{M}_n$ of 1.5 × 10^4 and a polydispersity index (PDI = $\bar{M}_w/\bar{M}_n$) of 1.16 versus polystyrene standards. In addition, the refractive index of the GPC peak for **8** was found to be of opposite polarity to that commonly found for the trifluoroethoxy-substituted homopolymer $[N{=}P(OCH_2CF_3)_2]_n$ (**2**) and consistent with the GPC behavior for all-phosphazene block copolymers such as $[N{=}P(OCH_2CF_3)_2]_n{-}[N{=}PR_2]_m$ (R_2 = Ph(OCH_2CF_3), Me(Et), Me_2).[3] Further evidence for the structure of **8** is provided by comparison of the ^{1}H and ^{31}P NMR integration for the respective blocks ($n{:}2m$ = 2.95:1, Figure 1) with the elemental microanalysis results, which agree within experimental error.[14] The molecular weight of **8** was estimated by ^{1}H NMR to be 9.8 × 10^3. The discrepancy between the GPC and ^{1}H NMR estimated molecular weights may be due to an overestimation of molecular weight by GPC. Previous work has shown that GPC versus polystyrene standards may overestimate molecular weights for **2**.[15]

The observation that the resultant triblock copolymer **8** is soluble in THF, whereas the starting NH_2−PEG−NH_2 material is insoluble in THF solutions at 25 °C, provides added evidence for the proposed structure. Due to this insolubility, the molecular weight of the starting NH_2−PEG−NH_2 material was not determined by GPC.

Differential scanning calorimetry of **8** showed a depressed melting transition for the PEG segment at 38 °C. The PEG homopolymer melts between 54 and 58 °C. Small transitions were also present near the glass transition temperatures of **2** and poly(ethylene oxide) homopolymers.

By use of similar methodologies with the monodentate polymeric amine CH_3O−PEG−NH_2 (PEG = $-CH_2O(CH_2CH_2O)_n{-}CH_2CH_2{-}$, M_n = 5700), the macroinitiator **10** was synthesized and treated with $Cl_3P{=}NSiMe_3$ (**1**) (100:1 **1**:**10** ratio) to give block copolymer **11** (see Scheme 2 for **9**−**12**).[13] Treatment of **11** with an excess of sodium trifluoroethoxide resulted in the formation of the hydrolytically stable derivative **12**. Analysis of **12** by gel permeation chromatography (GPC) indicated that it possessed an $\bar{M}_n$ of 2.9 × 10^4 and a polydispersity index (PDI = $\bar{M}_w/\bar{M}_n$) of 1.4 versus polystyrene standards.

These results demonstrate that the “living” cationic polymerization of phosphoranimines via the use of macroinitiators should permit the synthesis of a wide variety of other phosphazene−organic block copolymers. The ability of poly(ethylene oxide) and phosphazene-based materials (e.g., $[N{=}P(OCH_2CH_2OCH_2CH_2OCH_3)_2]_n$, MEEP) to solvate metal salts is a characteristic that makes these copolymers attractive materials for use in solid-state batteries.[16] Preliminary examination of the MEEP analogues of the PEO−phosphazene triblock copolymer **8** complexed with lithium triflate ($LiSO_3CF_3$, 5−10 wt %) shows a range of room-temperature conductivities between 8 × 10^{-6} and 2 × 10^{-5} S cm^{-1} based on complex impedance analysis. These values are similar to those reported for MEEP complexed with similar amounts of $LiSO_3CF_3$[17] and are several orders of magnitude higher than for PEO at this temperature.[18,19] An additional interest in phosphazene/organic block copolymers is connected with their potential use as fire retardants in a wide range of organic polymer systems, and this aspect will be discussed in later publications.

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Supporting Information Available: Experimental details for **5**−**7** and **9**−**12** (4 pages). Ordering information is given on any current masthead page.

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(13) Experimental details for compounds **5**−**7** and **9**−**12** can be found in the Supporting Information.

(14) For **8**: ^{1}H NMR (CD_2Cl_2) δ 5.01 (s, $NHCH_2CH_2$), 4.23 (br s, CF_3CH_2O), 3.61 (br m, CH_2CH_2O), 2.20 (br s, $NHCH_2CH_2$), 1.41 (br s, $NHCH_2CH_2$); ^{31}P NMR (CD_2Cl_2) δ 7.5 (d, $^2J_{PP} =$ 51 Hz, $(CF_3CH_2O)_2P{=}N)$), −7.3 (s, $[N{=}P(OCH_2CF_3)]_n$); ^{13}C NMR (CD_2Cl_2) δ 124.6 (d of q, $^2J_{CF} = 310$ Hz, $^3J_{CP} = 9$ Hz, CF_3), 71.0 (s, CH_2CH_2O), 63.8 (d of q, $^2J_{CP} = 10$ Hz, $^3J_{CF} =$ 36 Hz, CH_2O), 35.0 (s, $NHCH_2CH_2$), 30.5 ppm (s, $NHCH_2CH_2$). GPC: $\bar{M}_n = 1.5 \times 10^4$ and PDI = 1.16. Anal. Calc.: C, 31.43; H, 4.14; N, 3.83. Found: C, 31.62; H, 4.70; N, 3.82.

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