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Telechelic Syntheses of the First Phosphazene Siloxane Block Copolymers

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Polyphosphazenes, $[R_2P{=}N]_n$, and poly(organosiloxanes), $[R_2Si{-}O]_n$ are two of the most widely studied inorganic−organic polymer systems.[1,2] Each polymer type has its own unique set of physical properties together with advantages and disadvantages for practical applications. However, polyphosphazenes allow access to a wider variety of side group structures, and this facilitates the design and synthesis of a broad range of materials. The development of hybrid polymers, which combine the advantages of polyphosphazenes and polysiloxanes, could stimulate advances in both fundamental science and technology.[3]

We report here two methods for the synthesis of the first linear A−B, A−B−A, and B−A−B copolymer systems containing polyphosphazenes and polysiloxanes. These synthetic routes produce new hybrid materials that expand the characteristics and properties of both systems beyond those now available.

Approaches that incorporate organosiloxanes and polyphosphazenes into one material have been reported.[4] However, none of these combine the attributes of the two inorganic backbone systems into linear phosphazene−siloxane block copolymers. The absence of such structures is a consequence of synthetic problems associated with monomer-based routes, such as widely differing monomer reactivities and polymerization mechanisms or solvent incompatibilities. The synthesis of block copolymers through preformed telechelic polymers is a method that alleviates many of these problems and has been used for a number of organic block copolymer systems.

The "living" cationic polymerization of phosphoranimines is an effective method for the production of well-defined phosphazene polymers with controlled architectures.[5] This synthetic route has recently been extended to yield triarm star-branched polyphosphazenes,[6] phosphazene−phosphazene and phosphazene−organic based block copolymers,[7] and, most recently, mono-, di-, and mixed telechelic polyphosphazenes.[8] We have now utilized these methods to develop two routes for the synthesis of novel, well-defined phosphazene−siloxane block copolymers. These routes provide a way to control the chain length of the individual polymeric components. Thus, many of the valuable characteristics of the respective homopolymers, such as thermal and oxidative stability, can now be imparted to the copolymer without sacrificing the material's overall properties.[3]

Scheme 1

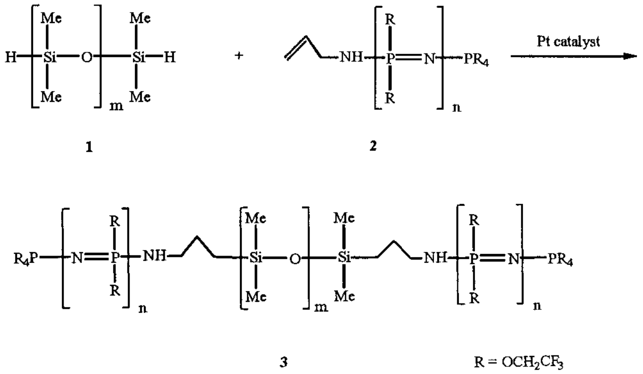

Table 1. Molecular Weight and Molecular Weight Distribution of Di- and Triblock Copolymers of Phosphazenes and Siloxanes

polymer	siloxane MW[a]	phosphazene MW[b]	copolymer MW calcd[c]	copolymer MW GPC[d]	copolymer MW PDI[d]
3a	6000	2800	11 600	12 203	1.13
3b	6000	5200	17 200	20 367	1.07
3c	6000	7400	19 400	24 363	1.17
8a	1600	2430	5 630	10 938	1.05
8b	1600	4800	8 000	14 749	1.07
8c	1600	7290	10 490	21 698	1.09
9a	1600	9720	11 320	17 494	1.13
9b	1600	14580	16 180	28 529	1.13

[a] Reported by Aldrich and Gelest. [b] Calculated from the initial ratio of monomer to PCl_5 initiator at 100% conversion. [c] According to the starting molecular weights of the individual blocks of phosphazene and siloxane. [d] Obtained by GPC vs polystyrene standards.

The first route developed for the synthesis of phosphazene−siloxane copolymers utilizes hydrosilylation chemistry to couple monotelechelic polyphosphazenes with commercially available dihydride-terminated poly(dimethylsiloxane) (PDMS) (**1**) ($H{-}[Me_2SiO]_{80}{-}SiMe_2H$, $M_n = 6000$). As shown in Scheme 1, phosphazene-*block*-siloxane-*block*-phosphazene copolymers were produced by treatment of **1** with monoallyl functional polyphosphazene[8] (**2**) in the presence of a divinyldisiloxane:Pt catalyst at 66 °C.[11,12] The progress of the reaction was monitored by infrared spectroscopy, which showed the disappearance of the Si−H stretch at 2100 cm^{-1} over a 12 h period. The polymer was isolated as an adhesive, off-white material in good yield. Analysis of **3** by gel permeation chromatography (GPC) indicated that well-defined block copolymers with polydispersities below 1.17 (Table 1) had been prepared. Further evidence for the structure of **3** was provided by a comparison of the ^1H and ^{31}P NMR integrations for the respective blocks with the elemental analysis results, which agreed within experimental error.

Scheme 2 depicts the second approach for the preparation of di- and triblock copolymers, such as **8** and **9**. A PDMS with a terminal phosphoranimine unit (**5**) was prepared from monohydroxy PDMS (**4**) ($CH_3(CH_2)_3[Me_2SiO]_{20}Me_2Si(CH_2)_3OCH_2CH_2OH$, $M_w = 1600$) and $Br(CF_3CH_2O)_2P{=}NSiMe_3$.[11] This species was obtained in good yield as a viscous, colorless oil with a ^{31}P NMR resonance at −15 ppm in contrast to the $Br(CF_3CH_2O)_2P{=}NSiMe_3$ resonance which appears at −34 ppm. The lack of a halogen group on **5** enables it to act as a terminating species in the living polymerization of polyphosphazenes by quenching the cationic ends of the chain.[12] Thus, living poly(dichlorophosphazene) (**6**) was terminated with a slight excess of **5,** followed by subsequent reaction with sodium trifluoroethoxide to yield the hydrolytically stable, trifluoroethoxy-substituted siloxane-*block*-phosphazene-*block*-siloxane copolymers (**8**). Similarly, diblock

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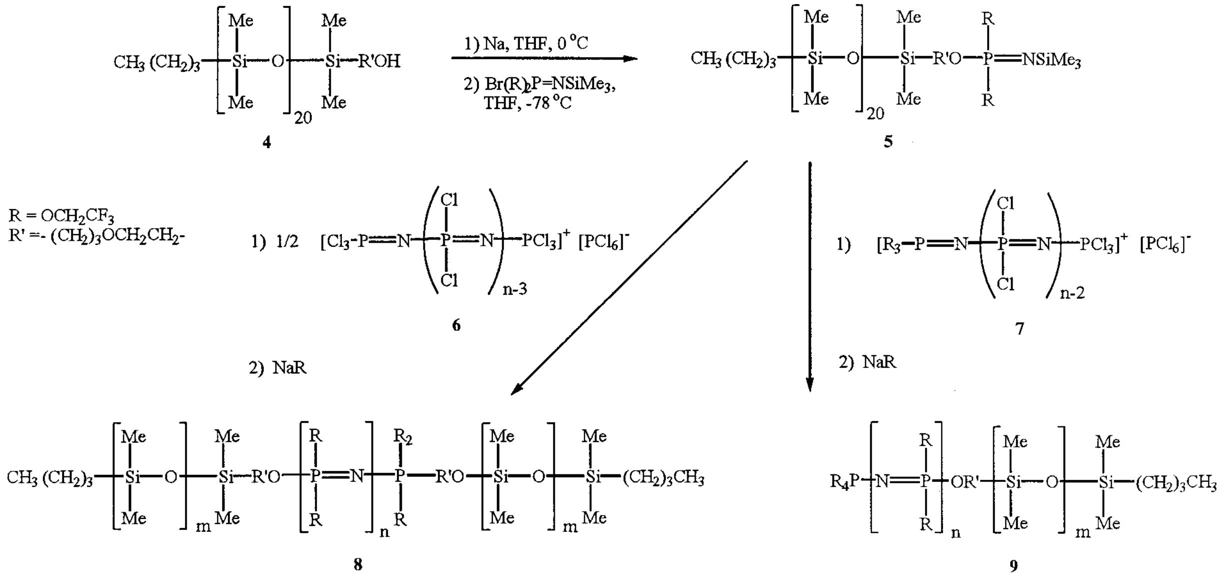
Scheme 2



copolymers (**9**) were synthesized by termination of living monotelechelic poly(dichlorophosphazene) chains (**7**) with a slight excess of **5**, followed by subsequent reaction with sodium trifluoroethoxide.[7] In all instances, ^{31}P NMR spectroscopy was used to monitor the termination of the living polymerization process. This was indicated by the disappearance of the PCl_3^+ resonance at +8 ppm and the subsequent appearance of a new resonance at −2 ppm following the addition of **5**. Replacement of the chlorine atoms with sodium trifluoroethoxide was also confirmed by ^{31}P NMR spectroscopy, which revealed a resonance at −6 ppm for the substituted $[(CF_3CH_2O)_2P{=}N]_n$ polymer with no trace of unsubstituted $[Cl_2P{=}N]_n$ at −17 ppm. Any excess PDMS present in the product was easily removed by successive washing with CH_2Cl_2 to yield well-defined polymers with narrow polydispersities (Table 1). The physical properties of the block copolymers ranged from adhesive, off-white gums to white crystalline solids as the molecular weight of the polyphosphazene block increased.

The refractive indices of the monomodal GPC peaks for **3**, **8**, and **9** were of opposite polarity to that normally found for the single-substituent polymer $[(CF_3CH_2O)_2P{=}N)]_n$. This is a further indication that the macromolecules are block copolymers.[7] Multinuclear NMR and elemental analysis also confirmed the formation of the block copolymers.

These results demonstrate that a wide variety of di- and triblock phosphazene−siloxane copolymers are accessible with controlled molecular weights, narrow polydispersities, and a wide range of different organic side groups on the phosphazene component. These synthetic methods produce polymers in quantitative yields with little or no contamination by the homopolymers. In addition, the molecular weights of both polymeric units can be varied, and this provides a way to further fine-tune the chemical and physical properties of the copolymers. Work aimed at the further development of this area and the examination of the properties of these hybrid materials is in progress.

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Supporting Information Available: Experimental Section. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) Mark, J. E.; Allcock, H. R.; West, R. *Inorganic Polymers*; Prentice Hall: Englewood Cliffs, NJ, 1992. (b) Allcock, H. R. In *Inorganic and Organometallic Polymers II*; Wisian-Neilson, P., Allcock, H. R., Wynne, K. J., Eds.; ACS Symposium Series 572; American Chemical Society: Washington, DC, 1994; Chapter 17.

(2) Yigor, I.; McGrath, J. E. *Polysiloxane Containing Copolymers: A Survey of Recent Development; Advances in Polymer Science*; Springer-Verlag: New York, 1988; Vol. 86.

(3) Allcock, H. R.; Lampe, F. W. *Contemporary Polymer Chemistry*, 2nd ed.; Prentice Hall: Englewood Cliffs, NJ, 1990.

(4) (a) Allcock, H. R.; Coggio, W. D.; Archibald, R. S.; Brennan, D. J. *Macromolecules* **1989**, *22*, 3571. (b) Allcock, H. R.; Kuharcik, S. E.; Nelson, C. J. *Macromolecules* **1996**, *29*, 3686. (c) Allcock, H. R.; Smith, D. E. *Chem. Mater.* **1995**, *7*, 1469. (d) Wisian-Neilson, P.; Islam, M. S. *Macromolecules* **1989**, *22*, 2026.

(5) (a) Honeyman, C. H.; Manners, I.; Morrissey, C. T.; Allcock, H. R. *J. Am. Chem. Soc.* **1995**, *117*, 7035. (b) Allcock, H. R.; Crane, C. A.; Morrissey, C. T.; Nelson, J. M.; Reeves, S. D.; Honeyman, C. H.; Manners, I. *Macromolecules* **1996**, *29*, 7740. (c) Allcock, H. R.; Nelson, J. M.; Reeves, S. D.; Honeyman, C. H.; Manners, I. *Macromolecules* **1997**, *30*, 50.

(6) Nelson, J. M.; Allcock, H. R. *Macromolecules* **1997**, *30*, 1854.

(7) (a) Allcock, H. R.; Reeves, S. D.; Nelson, J. M.; Crane, C. A. *Macromolecules* **1997**, *30*, 2213. (b) Nelson, J. M.; Allcock, H. R.; Manners, I. *Macromolecules* **1997**, *30*, 3191. (c) Nelson, J. M.; Primrose, P. A.; Hartle, T. J.; Allcock, H. R. *Macromolecules* **1998**, *31*, 947.

(8) Allcock, H. R.; Nelson, J. M.; Prange, R.; Crane, C. A.; deDenus, C. R. *Macromolecules*, in press.

(9) (a) Speier, J. L. *Adv. Organomet. Chem.* **1979**, *17*, 407. (b) Allcock, H. R.; Smith, D. E.; Kim, Y. B. *Macromolecules* **1994**, *27*, 5206.

(10) Monoallyl-terminated polyphosphazenes (**2**) of various weights were prepared according to a previously described method.[8] Dihydride-terminated PDMS (**1**) ($M_n = 6000$) was purchased from Gelest and gave a $M_n = 12572$ (PDI = 1.73) by GPC vs polysytrene standards. A general procedure for the synthesis of **3a** is given. Monoallyl polyphosphazene (**2**) with a $M_w = 2800$ (1 g, 0.36 mmol) was dissolved in 20 mL of THF. To this solution was added 3 g of **1** (0.5 mmol) and 10 mg of divinyldisiloxane:Pt catalyst at 66 °C. The progress of the reaction was monitored by infrared spectroscopy, which showed the disappearance of the Si−H stretch at 2100 cm^{-1} over a 12 h period.

(11) $CH_3(CH_2)_3[Me_2SiO]_{20}Me_2Si(CH_2)_3OCH_2CH_2OH$ (**4**) ($M_n = 1600$) was purchased from Aldrich and gave a $M_n = 5730$

(PDI = 1.17) by GPC vs polystyrene standards. The PDMS phosphoranimine, **5**, was prepared by reacting **4** ($M_n = 1600$) (1.00 g, 0.625 mmol) with sodium metal in the presence of THF (100 mL) to afford the sodium salt. This solution was then reacted at −78 °C with an excess of $Br(CF_3CH_2O)_2P{=}NSiMe_3$ (0.37 g, 0.94 mmol) and NEt_3 (1 mL) in THF (100 mL). The reaction mixture was stirred at −78 °C for 1 h, warmed to room temperature, and then filtered to remove salts. A clear, colorless oil was obtained as the product (**5**), as indicated by a ^{31}P NMR resonance at −15.37 ppm, after removal of solvents and excess $Br(CF_3CH_2O)_2P{=}NSiMe_3$ in vacuo.

(12) It is well-known that the active ends of living polyphosphazene chains (**6**) can be di-end-capped due to the transfer of the cation from one end to the other. However, if nonhalogen species, such as $(CF_3CH_2O)_3P{=}NSiMe_3$, are used to initiate the living polymerization, then polymers similar to **7** are formed, and only mono-end-capping is observed.[7,8]

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