Macromolecules **2000,** *33,* 5763−5765

Polyphosphazene−Polystyrene Copolymers: Block and Graft Copolymers from Polyphosphazene and Polystyrene Macromonomers

Robbyn Prange, Scott D. Reeves,[†] and Harry R. Allcock*

Department of Chemistry, The Pennsylvania State University, 152 Davey Laboratory, University Park, Pennsylvania 16802

Received March 30, 2000
Revised Manuscript Received June 23, 2000

The synthesis of hybrid block and graft copolymers of polyphosphazenes and polystyrene is a way to combine the attributes of both systems and to generate new combinations of properties. The chemical, physical, and mechanical properties of copolymers should be adjustable by varying the individual polymer components.[1−4] Thus, many of the valuable properties of the respective phosphazene and styrene homopolymers might be combined without sacrificing the overall solid state or solution properties.[2] Block or graft copolymers of polyphosphazenes and polystyrene may also improve the fire resistance of polystyrene.[1] The preparation of hybrid materials from polyphosphazenes and polystyrene, however, is a relatively unexplored area. Polystyrene/polyphosphazene grafted systems were synthesized by Gleria et al. using a radical initiation process,[5] and Wisian-Neilson and co-workers produced poly(methylphenylphosphazene)-*graft*-polystyrene by polymerizing styrene from deprotonated methyl groups along the phosphazene chain.[4] Here we report two methods for the preparation of graft and linear block copolymers that contain polyphosphazene and polystyrene moieties.

Traditionally, block copolymers have been synthesized via the sequential polymerization of different monomers. However, the limited number of compatible initiating monomers places restrictions on the number of copolymers that can be synthesized by this method. By contrast, telechelic polymers have provided additional routes for the production of a wide range of block and graft copolymers,[6] including those containing polyphosphazenes.[7] The reactive end groups present on telechelic polymers allow their utilization as platforms from which monomers can be polymerized or as linking groups which may react with other preformed polymer.[7−11] Thus, telechelic polymers have become an important building block in the synthesis of well-defined materials.

Two main approaches have been developed for the incorporation of reactive end groups into polymers synthesized via living processes,[6] including telechelic polyphosphazenes[7,12,13] and telechelic polystyrenes.[14−17] The first utilizes functionalized initiators. The second, which is the more promising current approach, involves quenching the active terminal sites on a living polymer with suitable electrophiles or nucleophiles. For example, the synthesis of telechelic polyphosphazenes involves the polymerization of halophosphoranimines, using a cationic initiator, to yield living cationic poly(dichlorophosphazene).[18] This species can then be terminated with nonhalogenated phosphoranimines to yield mono-, di-, or mixed telechelic polyphosphazenes[7,12,13] or block copolymers.[7,9] This method provides a way to synthesize polyphosphazenes with well-defined molecular weights, narrow polydispersities, and novel architectures.[3,7,18−21] In addition, these polymers can be used as macromonomers to produce new block and graft copolymers containing polyphosphazenes.

In this work, phosphine-terminated polystyrene (**1**) and vinylaniline-terminated polyphosphazene (**7**) were used in two separate studies to produce hybrid materials that contain polyphosphazene and polystyrene segments. The first approach utilized a novel polystyrene phosphoranimine (**2**) as a terminator for the living, cationic polymerization of $Cl_3P{=}NSiMe_3$ (Scheme 1). This methodology allows the synthesis of di- and triblock copolymers of polyphosphazene and polystyrene with controlled molecular weight and narrow polydispersities. In the second study, polystyrene-*graft*-polyphosphazene copolymers (**8**) were produced when a polyphosphazene, terminated with a vinyl aniline group (**7**), was addition-copolymerized with styrene by a free radical mechanism using AIBN as the initiator (Scheme 2).

Scheme 1 depicts the synthetic route used for the production of di- and triblock copolymers such as **5** and **6**. Polystyrene with a terminal phosphine unit (**1**) was prepared by quenching living polystyrene with Ph_2PCl.[21,22] The phosphine-terminated polystyrene was treated with N_3SiMe_3 to yield the novel polystyryl phosphoranimine, **2**, in quantitative yield. This species was used as a macromolecular terminator in the living polymerization of polyphosphazenes.[7,9,12,14] As illustrated in Scheme 1, triblock copolymers (**5**) were synthesized by the addition of 2.5 equiv of **2** to **3**. The termination process was monitored by ^{31}P NMR spectroscopy, which showed the disappearance of the PCl_3^+ terminal units at −8 ppm and the appearance of the new end groups at 5 ppm. Similarly, diblock copolymers, **6**, were prepared by the reaction of polyphosphazenes, containing only one terminal PCl_3^+ unit (**4**), with **2**.[24] Following termination, the chlorine atoms were replaced with trifluoroethoxide groups via reaction with a 1.5 M $NaOCH_2CF_3$ solution. Isolation of the polymer was accomplished via precipitation into water. In cases where multiple precipitations did not remove the excess polystyrene phosphoranimine (**2**), dialysis against THF was employed to remove the homopolymers. The block copolymers were isolated as white, hydrolytically stable materials after purification.

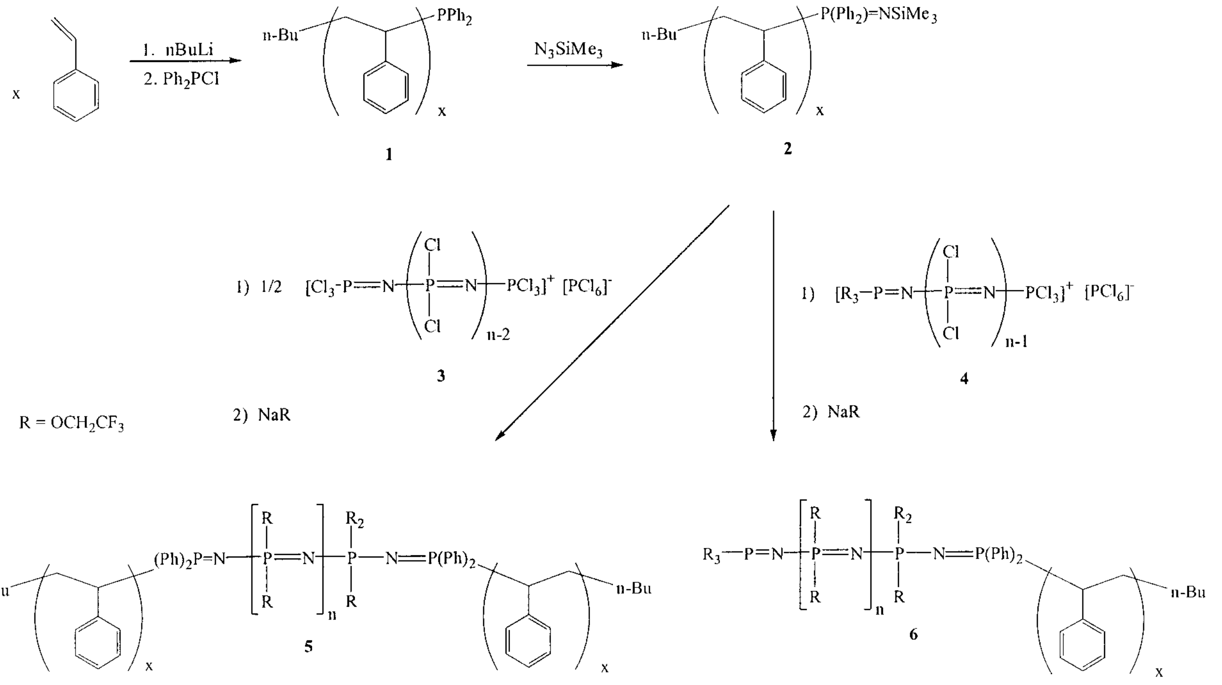
Graft copolymers (**8**) were prepared by the copolymerization of vinylaniline-terminated polyphosphazenes (**7**) with varying ratios of styrene (Scheme 2). The monotelechelic polyphosphazene, **7**, was produced by treatment of $(CF_3CH_2O)_3P{=}NSiMe_3$ with 2 mol equiv of PCl_5 at −78 °C in CH_2Cl_2 to generate the cationic species $[(CF_3CH_2O)_3P{=}N{-}PCl_3]^+[PCl_6]^-$. The formation of this salt was confirmed in situ by the presence of two doublets in the ^{31}P NMR spectrum for the $N{-}PCl_3^+$ and $(CF_3CH_2O)_3P{=}N$ units. The addition of a specific amount of $Cl_3P{=}NSiMe_3$ to the reaction mixture resulted in the formation of living poly(dichlorophosphazene), similar to **4**, with discrete chain lengths.[12,18,23] This living polymer was then quenched with 1.2 equiv

---

[†] Present address: Shipley Co., 455 Forest Street, Marlborough, MA 01752-3001.

10.1021/ma000573w CCC: $19.00

Scheme 1



Scheme 2

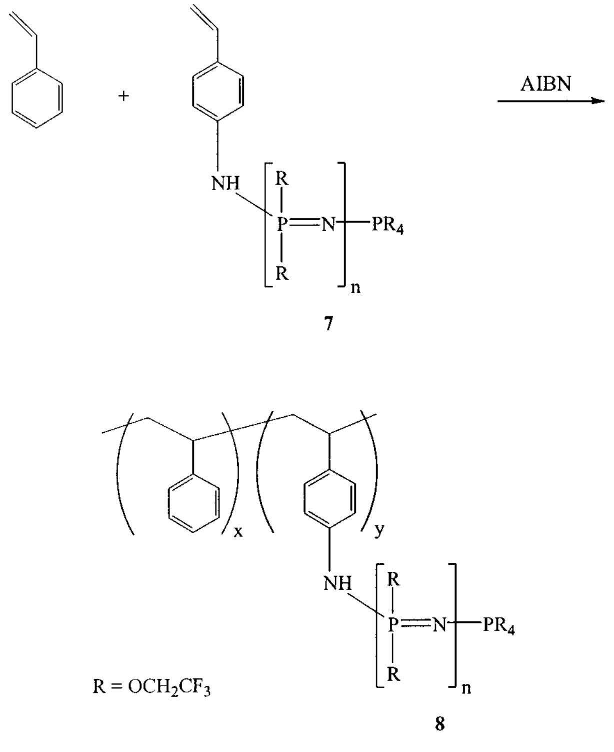


Table 1. Block Copolymers Synthesized via Initiation and Termination of Phosphine-Terminated Polystyrene

	prepolymer 2^a			copolymer		
polymer	M_n	PDI	phosphazene prepolymer^b M_n	calc M_n	found M_n^a	PDI^a
5a	2600	1.09	2400	5 600	8 100	1.21
5b	2600	1.09	4900	10 100	13 200	1.23
5c	5200	1.08	2400	12 800	14 700	1.17
5d	5200	1.08	4900	15 300	19 000	1.19
6a	2600	1.09	2400	5 000	7 100	1.21
6b	2600	1.09	4900	7 500	8 500	1.25
6c	5200	1.08	2400	7 600	9 300	1.13
6d	5200	1.08	4900	10 100	14 600	1.22

[a] Obtained by GPC vs polystyrene standards. [b] Calculated from the initial ratio of monomer to initiator at 100% conversion.

Table 2. Graft Copolymers Synthesized via Copolymerization of Styrene and 7

	prepolymer 7			copolymer	
polymer	M_n^a	PDI	wt % of **7**	M_n^a	PDI
8a	7 400	1.11	5	64 200	1.83
8b	7 400	1.11	10	72 500	1.64
8c	7 400	1.11	15	83 100	1.97
8d	10 300	1.09	5	80 900	2.01
8e	10 300	1.09	10	86 100	1.87
8f	10 300	1.09	15	102 000	1.94

[a] Obtained by GPC vs polystyrene standards.

of $CH_2CHC_6H_4{-}NH{-}(CF_3CH_2O)_2P{=}NSiMe_3$.[24,25] The termination of the living polymer was monitored by ^{31}P NMR spectroscopy which showed the formation of a new peak, from the $CH_2CHC_6H_4{-}NH{-}(CF_3CH_2O)_2P{=}N$ end group, near 5 ppm and the disappearance of the PCl_3^+ resonance at −8 ppm. The polymer was isolated via precipitation into water after the chlorine atoms were replaced by reaction with sodium trifluoroethoxide. The reactivity of the vinylaniline end unit on **7** was then utilized to synthesize polystyrene-*graft*-polyphosphazene copolymers, **8**, via a free radical polymerization. This was accomplished by refluxing a solution of **7**, AIBN, and styrene in THF for 48 h. The graft copolymers were isolated as finely divided solids in good yields after precipitation into water.

Multinuclear NMR, GPC, and elemental analysis were used to confirm the formation of the block (**5**, **6**) and graft (**8**) copolymers. Evidence for the structures of **5**, **6**, and **8** was provided by a comparison of the integration of the polyphosphazene to polystyrene peaks in the ^1H NMR spectra to elemental analysis. Analysis by GPC (Tables 1 and 2) also indicated the formation of copolymer as illustrated by the increase in molecular weight of the copolymer compared to that of the starting prepolymer. The molecular weight data obtained from the GPC give molecular weights different from those calculated due to the difference in hydrodynamic volume between the inorganic–organic copolymers and linear polystyrene. Further evidence that the macromolecules were indeed copolymers came from the GPC data where the refractive indices of the monomodal peaks for **5**, **6**, and **8** were of opposite polarity to that normally found for the single-substituent polymer $[N{=}P(OCH_2CF_3)_2]_n$.

This work demonstrates two methods for the preparation of polyphosphazene–polystyrene copolymers. The routes permit the production of both di- and triblock copolymers, with controlled molecular weights and narrow polydispersities, and graft copolymers that allow the molecular weight of the polyphosphazene chains and their density along the chain to be controlled.

Acknowledgment. We thank the National Science Foundation Polymers Program for the support of this work.

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

References and Notes

(1) Allcock, H. R.; Lampe, F. W. *Contemporary Polymer Chemistry*, 2nd ed.; Prentice Hall: New York, 1991.

(2) Mark, J. E.; Allcock, H. R.; West, R. *Inorganic Polymers*; Prentice Hall: New York, 1992.

(3) Allcock, H. R.; Reeves, S. D.; Nelson, J. M.; Crane, C. A.; Manners, I. *Macromolecules* **1997**, *30*, 2213.

(4) Wisian-Nelson, P.; Schaefer, M. A. *Macromolecules* **1989**, *22*, 2003.

(5) Gleria, M.; Bolognesi, D. J.; Graaskamp, J. M. *Macromolecules* **1987**, *20*, 469.

(6) Goethals, E. J. *Telechelic Polymers: Synthesis and Applications*; CRC Press: Boca Raton, FL, 1989.

(7) Prange, R.; Allcock, H. R. *Macromolecules* **1999**, *32*, 6390.

(8) Noshay, A.; McGrath, J. E. *Block Copolymer: Overview and Critical Survey*; Academic: New York, 1977.

(9) Nelson, J. M.; Primrose, P. A.; Hartle, T. J.; Allcock, H. R. *Macromolecules* **1998**, *31*, 947.

(10) Labeau, M.-P.; Cramail, H.; Deffieux, A. *Polym. Int.* **1996**, *41*, 453.

(11) Franta, E.; Rempp, P. F. *CHEMTECH* **1996**, *Jan*, 24.

(12) Allcock, H. R.; Nelson, J. M.; Prange, R.; Crane, C. A.; de Denus, C. R. *Macromolecules* **1999**, *32*, 5736.

(13) Allcock, H. R.; Laredo, W. R.; de Denus, C. R.; Prange, R., work in progress.

(14) Peters, M. A.; Belu, A. M.; Linton, R. W.; Dupray, L.; Meyer, T. J.; DeSimone, J. M. *J. Am. Chem. Soc.* **1995**, *117*, 3380.

(15) Cernohous, J. J.; Macosko, C. W.; Hoye, T. R. *Macromolecules* **1998**, *31*, 3759.

(16) Hirao, A.; Hayashi, M.; Nakahama, S. *Macromolecules* **1996**, *29*, 3353.

(17) Tohyama, M.; Hirao, A.; Nakahama, S.; Takenaka, K. *Macromol. Chem. Phys.* **1996**, *197*, 313.

(18) Allcock, H. R.; Crane, C. A.; Morrissey, C. T.; Nelson, J. M.; Reeves, S. D. *Report* **1996**, *96*, 21.

(19) Honeyman, C. H.; Manners, I.; Morrissey, C. T.; Allcock, H. R. *J. Am. Chem. Soc.* **1995**, *117*, 7035.

(20) Nelson, J. M.; Allcock, H. R.; Manners, I. *Macromolecules* **1997**, *30*, 3191.

(21) Allcock, H. R.; Nelson, J. M.; Reeves, S. D.; Honeyman, C. H.; Manners, I. *Macromolecules* **1997**, *30*, 50.

(22) Typical syntheses were accomplished with the use of 100 mL of THF at −78 °C. Styrene (2.0 g, 0.019 mol) was charged into the reaction vessel via a syringe. *n*-BuLi (0.24 mL, 1.6 M, 0.38 mmol) was then rapidly injected into the reaction vessel via a syringe through a septum, and a characteristic orange color gradually appeared over a few minutes. The reaction mixture was stirred for 2 h in THF to yield poly(styreneyllithium) with a $DP_n = 50$. The polymer was then quenched with chlorodiphenylphosphine (8.50 mg, 0.038 mmol) to form the polystyrene phosphine (**1**) as indicated by the clear, colorless reaction mixture. Examination of **1** by ^{31}P NMR spectroscopy indicated a single peak at −16.6 ppm assigned to the end-capped polymer. The phosphine-terminated polymer (**1**) was then treated with trimethylsilyl azide (4.4 mg, 0.038 mmol) to give the polystyrene functionalized phosphoranimine (**2**) in high yields with a characteristic peak at 35.8 ppm in ^{31}P NMR. For **2**: ^1H NMR: 7.13 (br, 4H, ArH), 6.58 (br, 1H, ArH), 4.31 (s, 0.16H, OCH_2CF_3), 1.5 (br, 3H, $CHCH_2$); ^{31}P NMR: 35.8: $M_n = 2600$ g/mol, PDI = 1.08, yield = 87%.

(23) Polymer **4** was produced by the interaction of 2 mol equiv of PCl_5 with $(CF_3CH_2O)_3P{=}NSiMe_3$ at −78 °C in CH_2Cl_2 to generate the salt $[(CF_3CH_2O)_3P{=}N{-}PCl_3]^+[PCl_6]^-$. The formation of this species was confirmed in situ by the presence of two doublets in the ^{31}P NMR spectrum for the $N{-}PCl_3^+$ and $(CF_3CH_2O)_3P{=}N$ units. Addition of a given amount of $Cl_3P{=}NSiMe_3$ to the reaction mixture resulted in the preparation of living poly(dichlorophosphazene)s, similar to **4**, with specific chain lengths. The length of the polyphosphazene chains were controlled by the ratio of $Cl_3P{=}NSiMe_3$ to PCl_5 in the synthesis of **3** and **4**.[12]

(24) The active ends of living polyphosphazene chains (**3**) can be diterminated, by the transfer of the cation from one end to the other, to form triblocks similar to **5**. However, if nonhalogen phosphoranimines, such as $(CF_3CH_2O)_3P{=}NSiMe_3$, are used to generate the initiating species for the living polymerization, then polymers similar to **4** are formed and only mono termination occurs to give diblocks (**6**).[12,21]

(25) $CH_2CHC_6H_4{-}NH{-}(CF_3CH_2O)_2P{=}NSiMe_3$ was synthesized following a previous reported method for the production of nonhalogenated phosphoranimines.[12] $Br(CF_3CH_2O)_2P{=}NSiMe_3$ was reacted with a stoichiometric amount of vinylaniline in the presence of triethylamine in THF at −78 °C. The phosphoranimine was obtained in good yield as a yellow oil after distillation.

MA000573W