Properties of Poly(phosphazene−siloxane) Block Copolymers Synthesized via Telechelic Polyphosphazenes and Polysiloxane Phosphoranimines

Harry R. Allcock* and Robbyn Prange†

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

Received January 17, 2001

ABSTRACT: Linear A−B, A−B−A, and B−A−B block copolymers containing polyphosphazenes and polysiloxanes were synthesized and characterized. Two methods were used in the synthesis of these novel block copolymers. The first utilized hydrosilylation chemistry to couple monotelechelic polyphosphazenes with commercially available dihydride-terminated poly(dimethylsiloxane) (PDMS). The second involved the termination of living poly(dichlorophosphazene) chains with phosphoranimine-terminated PDMS. The semicrystalline, hydrophobic copolymers, $[(CF_3CH_2O)_2P{=}N]_x{-}[(Me)_2Si{-}O]_y$, and the water-soluble copolymers, $[(CH_3OCH_2CH_2OCH_2CH_2O)_2P{=}N]_x{-}[(Me)_2Si{-}O]_y$, were prepared by the linkage of either hydrophobic or hydrophilic organic groups to the polyphosphazene backbone. These materials, with a polyphosphazene content from 19 to 73 mol % (43−90 wt %) were obtained with controlled molecular weights that ranged from 5600 to 108 900 Da. The syntheses, characterization, and physical properties of the linear polyphosphazene−polysiloxane block copolymers are reported.

Introduction

The living, cationic polymerization of phosphoranimines is a broadly applicable and effective method for the production of well-defined polyphosphazenes with controlled architectures. Over the past 5 years this ambient temperature polymerization route has yielded well-defined polyphosphazenes,[1−3] phosphazene−phosphazene copolymers,[4] and triarmed branched polyphosphazenes.[5] More recently, the utilization of *trisorgano*phosphoranimines has resulted in the direct synthesis of telechelic polyphosphazenes and block copolymers of polyphosphazenes with organic and organosilicon polymers.[6−9]

The development of *trisorgano*phosphoranimines and their use in the preparation of telechelic polyphosphazenes have opened up a new area of polyphosphazene research. Telechelic polymers are attractive precursors for the preparation of phosphazene-containing block and graft copolymers. The reactive end groups on these polymers can be employed to produce (a) block copolymers through coupling reactions with other preformed polymers or (b) graft copolymers when homo- or copolymerized with functional monomers.[10] For example, telechelic polymers were used to prepare linear block copolymers of polyphosphazenes with poly(ethylene oxide),[9] polystyrene,[7] and poly(dimethylsiloxane).[8] Graft copolymers of polyphosphazenes with polystyrene or polynorbornene were also synthesized through the copolymerization of olefinic monomers with an unsaturated terminal group on monotelechelic polyphosphazenes.[7,11] As a result, the development of the living cationic polymerization of polyphosphazenes and the synthesis of telechelic polyphosphazenes have proved to be a vital step in the production of advanced polyphosphazenes and hybrid phosphazene-containing materials.

An important objective of our current research is to explore the synthesis and properties of hybrid polyphosphazene block copolymers that contain nonphosphazene segments. Polyphosphazene−polysiloxane hybrid systems are of particular interest due to their anticipated surface and bulk characteristics. Copolymers that combine polyphosphazenes with polysiloxanes could, in principle, produce tailorable materials with unique combinations of properties.[12,13] Potential applications include nonburning elastomers, viscosity modifiers, coatings, solid polymer electrolytes, and biomedical materials.[12]

A few phosphazene−siloxane hybrid materials have been reported in the past. For example, Wisian-Neilson et al. prepared polyphosphazene-*graft*-siloxane materials with 10−20% oligomeric siloxane grafts via the ring-opening polymerization of hexamethylcyclotrisiloxane, $[Me_2SiO]_3$, from lithiated sites along a poly(methylphenylphosphazene) chain.[14] Allcock et al. prepared macromolecules with a polyphosphazene backbone and a variety of organosilicon side groups.[15−17] However, these polymers do not combine *poly*phosphazenes and *poly*siloxanes into one continuous backbone. Recent advances in the living cationic polymerization of polyphosphazenes have allowed the preparation of linear block copolymers of polyphosphazenes with polyorganosiloxanes, as we reported in a recent communication.[8] Here, we describe in more detail the synthesis, characterization, and physical properties of a series of linear polyphosphazene−polysiloxane block copolymers.

Results and Discussion

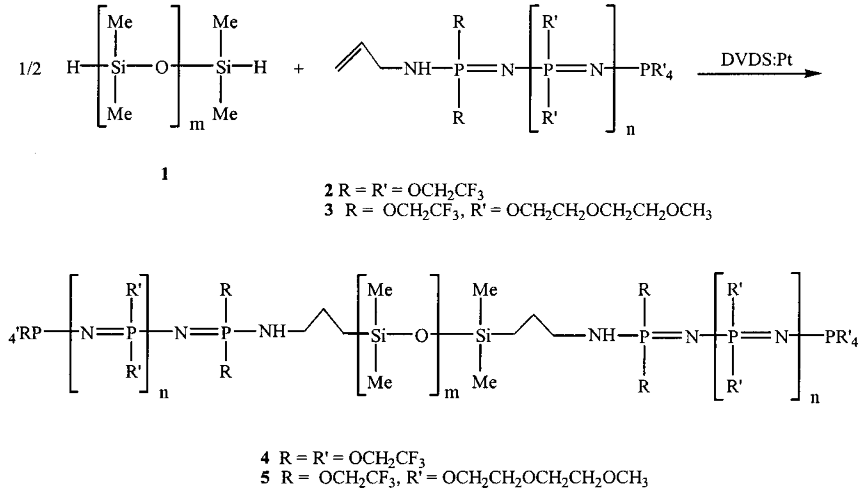
Polyphosphazene-*block*-polysiloxane-*block*-polyphosphazene via Hydrosilylation Chemistry (4, 5). Hydrosilylation reactions involve the addition of a silicon hydride unit across a carbon−carbon double bond. Reactions of this type are often catalyzed by hexachloroplatinic acid (Speier's catalyst)[18] or 1,3-divinyltetramethyldisiloxane−platinum complex (Karstedt's catalyst).[19] Hydrosilylation chemistry has become

---

† Present address: The Dow Chemical Company, 1707 Building, Midland, MI 48674.

10.1021/ma010088g CCC: $20.00

Scheme 1



1

2 R = R' = OCH_2CF_3
3 R = OCH_2CF_3, R' = $OCH_2CH_2OCH_2CH_2OCH_3$

4 R = R' = OCH_2CF_3
5 R = OCH_2CF_3, R' = $OCH_2CH_2OCH_2CH_2OCH_3$

one of the most important methods for the formation of silicon−carbon bonds.[20] Academic and industrial research has exploited this reaction for the production of copolymers, dendrimers, and siloxane elastomers.[21]

Our research has utilized hydrosilylation chemistry to produce linear block copolymers of polyphosphazenes and polysiloxanes. Preformed telechelic polyphosphazenes with allyl terminal units (**2**, **3**) were prepared by the polymerization of $Cl_3P{=}NSiMe_3$ from an allyl functional cationic initiator, $[CH_2{=}CHCH_2{-}NH{-}(CF_3CH_2O)_2P{=}N{-}PCl_3]^+[PCl_6]^-$, followed by replacement of the chlorine atoms with the appropriate organic group.[6] Hydrosilylation chemistry was then used to couple the allyl functionality to the ends of hydride-terminated polysiloxanes. As illustrated in Scheme 1, the addition of the silicon hydride unit to the double bond of the terminal allyl unit on the preformed polyphosphazenes (**2, 3**) was catalyzed by a divinyltetramethyldisiloxane−platinum complex (DVDS:Pt). The chain lengths of the starting polysiloxane (**1**) and the polyphosphazene (**2, 3**) were varied in order to study the effects of block length on the properties of the final copolymers. In addition, both hydrophobic, $[(CF_3CH_2O)_2P{=}N]_x{-}[(Me)_2Si{-}O]_y$ (**4**), and hydrophilic, $[(CH_3OCH_2CH_2OCH_2CH_2O)_2P{=}N]_x{-}[(Me)_2Si{-}O]_y$ (**5**), block copolymers were synthesized by changing the organic side groups in the starting polyphosphazene.

The platinum-catalyzed hydrosilylation reaction between the monoallyl-terminated polyphosphazene and the silicon hydride-terminated PDMS was slow even in the presence of excess allyl-terminated polyphosphazene. However, all reactions were complete within 48 h and yielded block copolymers with narrow polydispersities. The progress of the hydrosilylation reaction was monitored by infrared spectroscopy, which showed the disappearance of the Si−H stretch near 2150 cm^{-1} over a 48 h period (Figure 1), which indicated complete addition of the silicon hydride across the carbon−carbon double bond of the allyl-terminated polyphosphazene.

The progress of the hydrosilylation reaction was also monitored by gel permeation chromatography (GPC), as shown in Figure 2. Curves c and d show the GPC traces of the starting polysiloxane (**1**) and the polyphosphazene polymer (**3**), respectively. Curve b of Figure 2 was obtained from the product of the hydrosilylation reaction after 16 h. The bimodal distribution suggests that two products with distinct molecular weights were obtained. The major peak represents a low molecular weight diblock copolymer, which is a product from an incomplete hydrosilylation reaction. The higher molecular weight peak is the triblock polymer (**5**) in which both terminal Si−H units on **1** have undergone a hydrosilylation reaction with an allyl group on **3**. The monomodal GPC trace of the final hydrosilylated product (**5**) is shown in curve a of Figure 2.

The properties of the block copolymers are dependent not only on the phosphazene content but also on the nature of the side groups linked to the polyphosphazene. Polymers **4a**−**4h** (Scheme 1 and Table 1), which contain trifluoroethoxy side groups, were isolated as off-white adhesive materials when the phosphazene content was below 39 mol % (63 wt %) and as white solids when the phosphazene content was above 46 mol % (74 wt %). These polymers are soluble in tetrahydrofuran, methylene chloride, and acetone but are insoluble in water, methanol, pentane, and hexanes. Polymers **5a**−**d** (Scheme 1 and Table 1), with methoxyethoxyethoxy side groups, were obtained as tan viscous gels in moderate yields after isolation via dialysis. These polymers are soluble in water, methanol, acetone, methylene chloride, and tetrahydrofuran but are insoluble in hexanes and pentane.

Macromolecular Phosphoranimines as a Terminating Species: Synthesis of Tri- and Diblock Copolymers (8, 10). We have shown that the active ends of a living polyphosphazene chain, $[Cl_3P{=}N{-}(Cl_2P{=}N)_n{-}PCl_3]^+[PCl_6]^-$ (**7**), can be terminated by the addition of a *trisorgano*phosphoranimine ($R_3P{=}NSiMe_3$).[6] Since the positive charge on the PCl_3 is delocalized to both ends of the macromolecule, di-end-capped polyphosphazenes are produced.[6] A mono-end-capped polyphosphazene is produced when a living polyphosphazene chain with only one terminal PCl_3 group, $[(CF_3CH_2O)_3P{=}N{-}(Cl_2P{=}N)_n{-}PCl_3]^+[PCl_6]^-$ (**9**), is quenched by the addition of a *trisorgano*phosphoranimine.[6] This termination principle has been utilized with (a) monomeric phosphoranimines for the production of telechelic polyphosphazenes and (b) non-phosphazene polymers terminated with a phosphoranimine group for the direct synthesis of block copolymers.[7,8] Furthermore, the monomer- and polymer-based *trisorgano*phosphoranimines can be employed as initiators in the polymerization of halogenated phosphoranimines.[6,9] Here, we have expanded this approach to synthesize a number

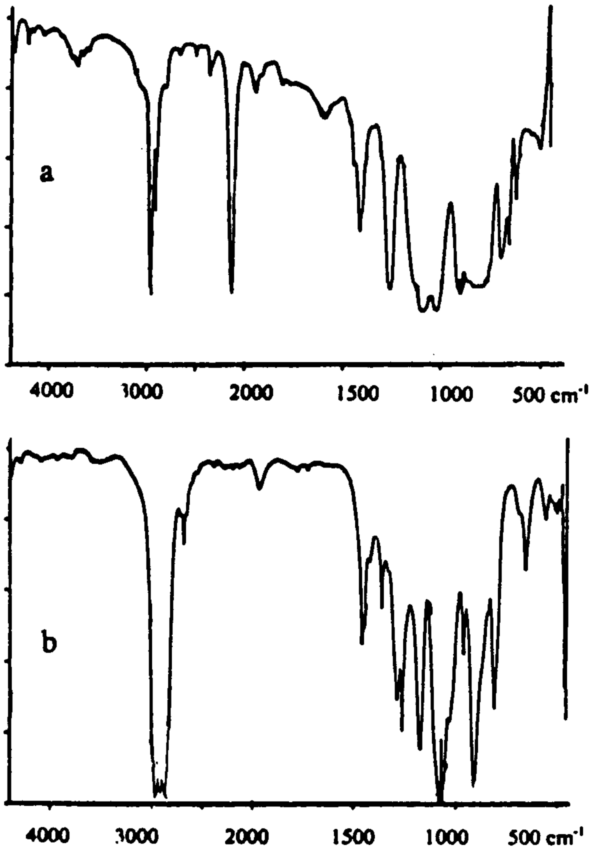


Figure 1. IR spectra of (a) the initial Karstedt-catalyzed hydrosilylation reaction mixture and (b) after 48 h.

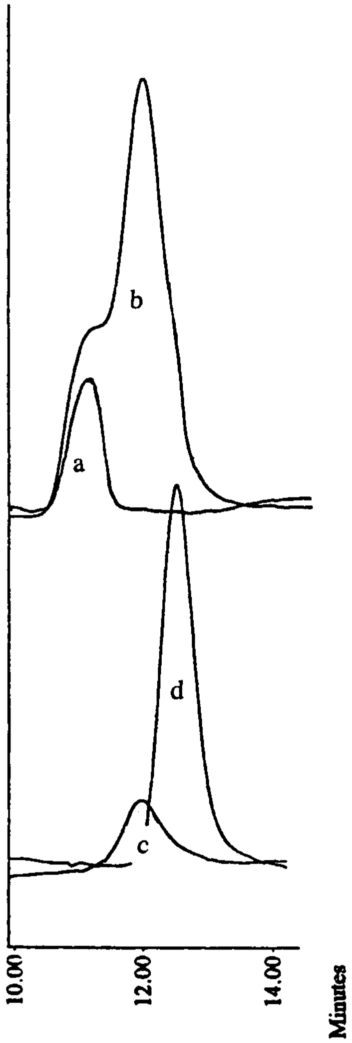


Figure 2. GPC traces of the Karstedt-catalyzed hydrosilylation reaction, Scheme 1. The GPC curves represent (a) the final triblock copolymer **5a** after 48 h, (b) the incomplete hydrosilylation products **5a** after 16 h, (c) the starting PDMS polymer **4**, and (d) the starting polyphosphazene **3a**.

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

	siloxane	polyphosphazene			copolymer M_n		
polymer	MW[a] ($\times10^{-4}$)	MW[b] ($\times10^{-4}$)	mol %	wt %	calcd[c] ($\times10^{-4}$)	GPC[d] ($\times10^{-4}$)	PDI[d]
4a	0.60	0.28	22	48	1.16	1.22	1.13
4b	0.60	0.52	35	63	1.64	2.04	1.07
4c	0.60	0.78	44	72	2.16	2.44	1.17
4d	0.60	1.01	51	77	2.62	3.31	1.22
4e	1.77	1.01	26	54	3.76	3.33	1.21
4f	1.77	2.48	46	74	6.71	6.69	1.26
4g	1.77	4.56	61	85	10.89	10.43	1.29
4h	2.40	1.01	20	46	4.35	4.12	1.30
4i	2.40	2.48	39	63	7.36	7.29	1.28
5a	0.60	0.33	22	52	1.26	1.32	1.24
5b	0.60	0.61	35	67	1.82	2.13	1.16
5c	0.60	0.89	44	75	2.38	2.41	1.19

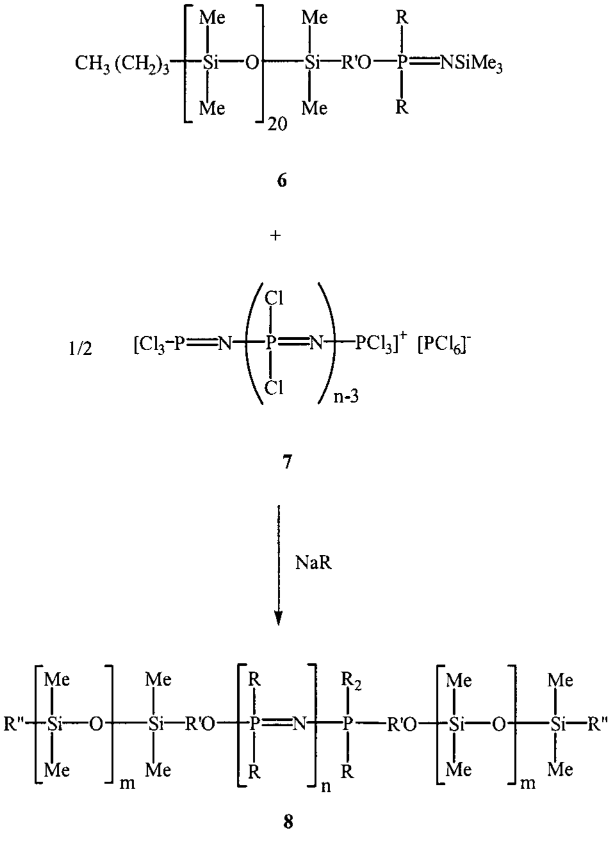
[a] Reported by Aldrich and Gelest. [b] MW listed is for one phosphazene block and was calculated from the initial ratio of monomer to PCl_5 initiator at 100% conversion. [c] According to the starting molecular weights of the individual blocks of phosphazene and siloxane. [d] M_n obtained by GPC vs polystyrene standards.

of di- and triblock copolymers of polyphosphazenes with polysiloxanes.

A monophosphoranimine-terminated PDMS (**6**) was prepared and utilized as a terminator for the living cationic polymerization of polyphosphazenes. Thus, as shown in Scheme 2, triblock copolymers (**8**) were prepared by terminating living poly(dichlorophosphazene) (**7**) with a slight excess of **6**. Subsequent replacement of the chlorine atoms with trifluoroethoxy groups yielded hydrolytically stable, hydrophobic polysiloxane-*block*-polyphosphazene-*block*-polysiloxane species (**8**). Similarly, diblock copolymers (**10**) were synthesized by the termination of living monotelechelic poly(dichlorophosphazene) (**9**) with a slight excess of **6**, followed by the subsequent replacement of the chlorine atoms by treatment with trifluoroethoxide (Scheme 3). The physical properties of these block copolymers ranged from off-white adhesive gums (<40 mol % or <70 wt %) to white crystalline solids as the weight percent of the polyphosphazene block increased.

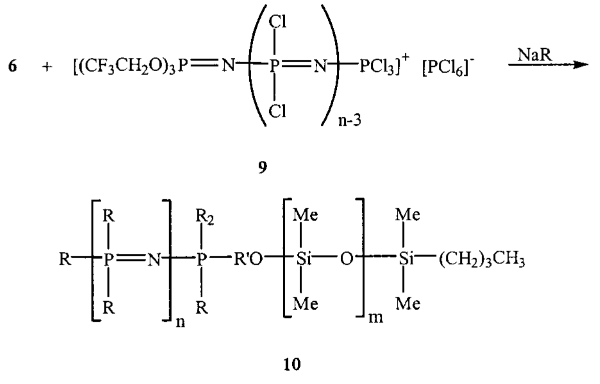
In all instances, ^{31}P NMR spectroscopy was used to monitor the termination of **7** and **9** by **6**. The terminal PCl_3^+ units on **7** and **9** appear near +8 ppm, which is indicative of living polyphosphazene chains. After the polymer chains were terminated with **6**, this resonance disappeared, and a new one appeared near −2 ppm, representative of the new end group.[6] Replacement of the chlorine atoms by trifluoroethoxy groups was also confirmed by ^{31}P NMR spectroscopy which revealed a resonance near −7 ppm for the substituted copolymer, $[(CF_3CH_2O)_2P{=}N]_n$, with no trace of nonsubstituted or partly substituted polyphosphazene, $[Cl_2P{=}N]_n$, near −17 ppm or $[(CF_3CH_2O)(Cl)P{=}N]_n$ near −12 ppm. ^{1}H NMR spectroscopy was used to verify the percentage of polyphosphazene incorporated in the fully substituted

Scheme 2



$R = OCH_2CF_3$, $R' = -(CH_2)_3OCH_2CH_2-$, $R'' = (CH_2)_3CH_3$

Scheme 3



$R = OCH_2CF_3$, $R' = -(CH_2)_3OCH_2CH_2-$

block copolymers by comparing the integration of the Me to OCH_2CF_3 protons. In all cases the ^1H NMR integration was in agreement with elemental analysis.

Molecular Weights and Polydispersities. Analysis of polymers **4**, **5**, and **8** by gel permeation chromatography (GPC) indicated that well-defined block copolymers with narrow polydispersities had been prepared. As shown in Table 1, the percentage of polyphosphazene incorporated in copolymers **4** and **5** was varied from 20 to 61 mol % (46−85 wt %) by controlling the molecular weight of the starting polymers (**1, 2, 3**). The percentage of polyphosphazene incorporated in copolymers **8** and **10** was also varied by adjusting the molecular weight of the starting polymers. The molecular weights of copolymers **8** and **10**, as estimated by GPC, are listed in Table 2. The incorporation of polyphosphazene into these copolymers ranged from 19 to 73 mol % (43 to 90 wt %).

Tables 1 and 2 also show the increased molecular weights of the block copolymers compared to the initial polymer components, an indication that block copolymers were indeed formed. The discrepancy between the calculated and experimentally obtained GPC molecular weights may be due to differences in the hydrodynamic volume of these block copolymers vs linear polystyrene standards.[2,4] Further evidence that block copolymers were formed comes from the refractive indices of the monomodal GPC peaks. The refractive indices of copolymers **4, 8,** and **10** were of opposite polarity to that normally found for the single-substituent polymer $[(CF_3CH_2O)_2P{=}N]_n$. This refractive index trend is consistent with the GPC behavior of phosphazene−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) and is reliable evidence that block copolymers have been formed.[2,4]

Thermal Analysis. Analysis of the thermal transitions in a copolymer is a way to determine whether the individual components of the copolymer have formed a homogeneous solid or have become phase-separated. The thermograms of a phase-separated copolymer usually show transitions representative of each component of the material. However, when a copolymer forms a homogeneous mixture, a thermal transition representative of the new material is often detected. Phase separation in block copolymers is determined by factors that include interfacial tension between polymer chains, copolymer composition, surface energy, compatibility of the individual blocks in the copolymer, and the flexibility of the polymeric backbone. The glass transition temperature (T_g) and melting temperature (T_m) of a polymer is thus a reflection of the macromolecular chain motion and the amount of free volume in the polymer. Polyphosphazenes and polysiloxanes are two polymers that possess extremely flexible backbones, resulting in low thermal transitions. For example, $[(CF_3CH_2O)_2P{=}N]_n$ has a T_g of −66 °C, $T(1) = 65{-}83$ °C, and T_m at 242 °C while $[(Me)_2Si{-}O]_n$ has a $T_g = -123$ °C, $T_c = -92$ °C, and $T_m = -29$ °C.[13,22]

The thermal transitions of copolymers **4, 8**, and **10** were determined by DSC and are listed in Table 3. Although the thermal transitions of these copolymers suggest that phase separation occurred, the T_g's and T_m's corresponding to the polyphosphazene and polysiloxane blocks were affected by the overall composition of the copolymer. In all the copolymers, the T_m corresponding to the PDMS block was typical of the one detected in poly(dimethylsiloxane).[13,22] However, the $T(1)$ of the polyphosphazene block was slightly lower than typical values for poly[bis(trifluoroethoxy)phosphazene] homopolymer.[13] Specifically, copolymers **4** and **8** gave glass transition, melting, and crystallization temperatures typical of polysiloxanes.[13] This is probably a result of high molecular weight polysiloxane segments and/or the large mole percent of polysiloxane incorporated in the copolymer (>50 mol %). The thermal transitions of the diblock copolymers **10** were quite different from the triblock copolymers, with T_g's substantially higher than those detected for copolymers **4** and **8**. This is probably a reflection of the incorporation of a short poly(dimethlysiloxane) block along with an increased polyphosphazene incorporation. Thus, the behavior of these polymers more closely resembles that

Table 2. Molecular Weight and Molecular Weight Distribution of Di- and Triblock Copolymers of Phosphazenes and Siloxanes Synthesized via Phosphoranimine Terminated Polysiloxanes

		polyphosphazene			copolymer M_n		
polymer	siloxane MW[a] ($\times 10^{-4}$)	MW[b] ($\times 10^{-4}$)	mol %	wt %	calcd[c] ($\times 10^{-4}$)	GPC[d] ($\times 10^{-4}$)	PDI[d]
8a	0.16	0.24	19	43	0.56	1.09	1.05
8b	0.16	0.48	32	60	0.80	1.47	1.07
8c	0.16	0.73	41	70	1.05	2.17	1.09
8d	0.16	0.97	48	75	1.30	2.23	1.11
8e	0.47	0.73	24	44	1.66	1.84	1.19
8f	0.47	0.97	32	51	1.90	2.73	1.32
8g	0.47	1.46	48	61	2.39	3.27	1.08
10a	0.16	0.48	48	75	0.64	0.98	1.10
10b	0.16	0.73	58	82	0.89	1.32	1.09
10c	0.16	0.97	65	86	1.13	1.75	1.13
10d	0.16	1.46	73	90	1.62	2.85	1.13

[a] Reported by Aldrich and Gelest. [b] MW listed is for one phosphazene block and was 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] M_n obtained by GPC vs polystyrene standards.

Table 3. Contact Angle and Thermal Transitions in the Block Copolymers

			thermal transitions[a]			
polymer	wt % phosphazene	contact angle (deg)	T_g	T_c	T_m[b]	$T(1)$[c]
4a	48	61	−130	−103	−52	39
4b	63	72	−125	−104	−60	39
4c	72	80	−131	−104	−52	40
4d	77	86	−105	*d*	−51	54
4e	54	78	−131	−104	−52	52
4f	74	82	−131	−104	−52	39
4g	85	79	−123	*d*	−56	29
4h	46	71	−132	−104	−52	49
8a	43	61	−104	*d*	−52	53
8b	60	72	−103	*d*	−52	34
8c	70	74	−105	*d*	−55	50
8d	75	74	−104	*d*	−57	43
8e	44	79	−121	*d*	−54	37
8f	51	81	−119	*d*	−53	−37
8g	61	81	−122	*d*	−50	35
10a	75	61	−80	*d*	−60	40
10b	82	69	−63	*d*	*d*	45
10c	86	69	−54	*d*	*d*	43
10d	90	72	−59	*d*	−23	20

[a] Measured by DSC and recorded in °C. [b] Melting transition corresponding to the polysiloxane block. [c] Thermal transition corresponding to the polyphosphazene block undergoing a transition to a hexagonal mesophase. [d] Not detected.

of a polyphosphazene with a short oligomeric siloxane end group vs symmetric block copolymers.

DSC curves of **4e**, **4f**, **4g**, and **10d** are shown in Figure 3. As discussed above, the thermograms of the copolymers containing high molecular weight PDMS, **4e** and **4f**, gave curves very similar to that of pure poly(dimethylsiloxane). The $T(1)$ corresponding to the polyphosphazene block was lower than that of poly[bis(trifluoethoxy)phosphazene] homopolymer. However, it does correspond to a decrease in molecular weight. Copolymer **4g**, with a phosphazene content of 61 mol % (85 wt %), also gave similar T_g, T_m, and $T(1)$ values. However, a crystallization temperature typical of polysiloxanes was not detected for this copolymer, perhaps a consequence of the high polyphosphazene content. Copolymer **10d**, with a polyphosphazene content of 73 mol % (90 wt %) and a PDMS molecular weight of only 1600 Da, gave a dramatically increased T_g of −59 °C compared to copolymers **4e**−**4g** ($T_g = -131$, -131, and -123 °C).

Contact Angles. The contact angle of water on a surface can be used to define the hydrophobicity of the material. However, in copolymeric materials complications often arise due to macromolecular reorientation and/or phase separation of the components.[23,24] Similar problems exist for obtaining contact angle measurements of polysiloxanes. For example, the contact angle of a poly(dimethylsiloxane) film that has not been cross-linked ranges from 50° to 60°.[25] However, the contact angle increases significantly if the siloxane film is heated or cross-linked. The contact angle of water on a poly(dimethylsiloxane) cured or cross-linked film ranged from 95° to 113°.[25,26] This range is an indication that the polymer chains remain flexible, allowing significant interaction between the polar water molecules and the surface of the polymer. Although the increase in contact angle on heating is not fully understood, it is believed to be a result of (a) the removal of adsorbed water from the polymer and/or (b) the condensation of surface hydroxyl groups.[26] These reasons are often used to explain why preformed poly(dimethlysiloxane) elastomers give high contact angles without having been cross-linked.[26]

Copolymers **4, 8,** and **10** have the potential to be mechanically stable, hydrophobic films with high contact angles, without the need for additional cross-linking. Thus, contact angles of water on the surface of copolymers **4**, **8,** and **10** were measured and are shown in Table 3. The contact angles for the block copolymers **4, 8,** and **10** depend on the composition of the polymer. For example, water contact angles on polymer **10** increased from 69° to 80° with increasing polyphosphazene content. This trend is similar to those seen with polymers **4a**−**4d** where the contact angle ranged from 71° to 89° and with increasing polyphosphazene content. Polymers **4e**−**4g** gave contact angles between 78° and 80°, but the values did not increase linearly with increasing polyphosphazene content. We believe that this lack of a trend is due to the high molecular weight of the polysiloxane segment of polymers **4e**−**4g**, which, despite similar polyphosphazene content, gave films that were generally less mechanically stable than those for polymers **4a**−**4d**. Contact angle measurements were not obtained for **4i** due to its poor film-forming properties, again a result of a high molecular weight polysiloxane segment. A trend in contact angle measurements was not detected for polymer **8** and is believed to be a result of the low molecular weight of the polysiloxane segments. In general, the instability of the contact angle of water on these polyphosphazene−polysiloxane films may be a result of the two hydrophobic segments competing for the surface region with one retreating

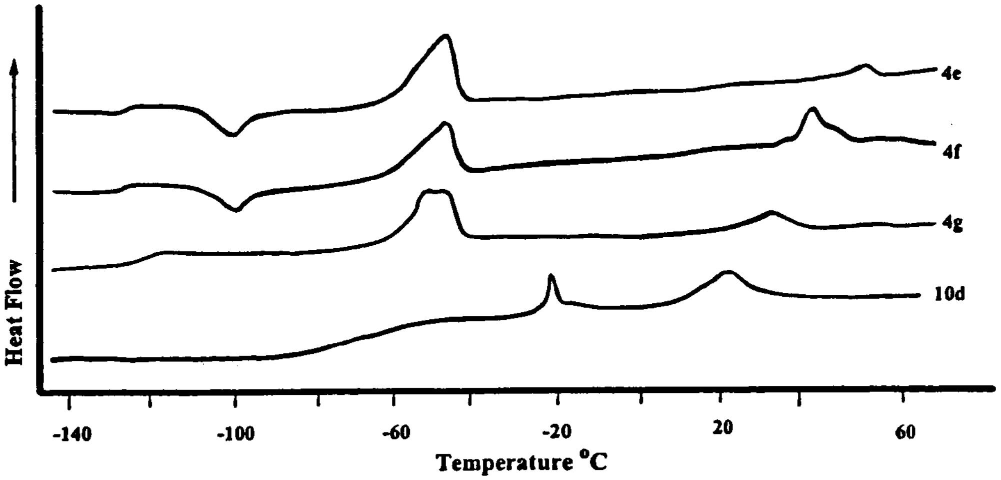


Figure 3. DSC traces of copolymers **4e**, **4f**, **4g**, and **10d**.

over time from the water droplet into the bulk polymer. This type of reorganization is often detected in phase-separated copolymer systems that contain blocks of poly(dimethylsiloxane),[27,28] especially when the poly(dimethylsiloxane) block is of low molecular weight.[29]

Conclusions

The development of hybrid polyphosphazene−polysiloxane materials is an area with considerable potential for use in both research and technology. We have described two synthetic methods for the preparation of linear block copolymers that contain segments of polyphosphazenes and polysiloxanes. These routes offer a way to synthesize a wide variety of A−B, A−B−A, and B−A−B. This work also demonstrates the feasibility of producing materials with controlled changes in both the block copolymer ratios and the type of side groups along the phosphazene chains.

Experimental Section

Materials. Lithium bis(trimethylsilyl)amide (97%), 2,2,2-trifluoroethanol (99+%), sodium metal, CaH_2 (90−95%), benzophenone (99%), and *n*-BuLi (1.6 M in hexanes) were purchased from Aldrich and used without further purification. Monohydroxy-terminated PDMS (M_n = 4670) and hydride-terminated poly(dimethylsiloxane)s (M_n = 580, 6000, 17 500, 24 000) were obtained from Aldrich and were used without further purification. Silanol-terminated PDMS (M_n = 4200) was purchased from Gelest and used without further purification. Karstedt's catalyst, a 2.1−2.4% Pt(0)−1,1,3,3-tetramethyldisiloxane complex in a solution of xylene, was purchased (Aldrich or Gelest) and was used without further purification. Phosphorus pentachloride (98%, Aldrich) was purified by sublimation under vacuum prior to use. 2-(2-Methoxyethoxy)-ethanol (Aldrich, 99%) was distilled from CaH_2 before use. Vinylaniline (Aldrich, 90%) were distilled before use. $Cl_3P{=}NSiMe_3$, $Br(CF_3CH_2O)_2P{=}NSiMe_3$, and $CH_2CHCH_2NH{-}(CF_3CH_2O)_2P{=}NSiMe_3$ were synthesized and purified by literature procedures.[6] Tetrahydrofuran and toluene (EM Science) were distilled from sodium−benzophenone ketyl under an atmosphere of dry argon. Dichloromethane (Aldrich) was dried and distilled from CaH_2. All glassware was dried overnight in an oven or flame-dried under vacuum before use. The reactions were performed using standard Schlenk techniques or in an inert atmosphere glovebox (Vacuum Atmospheres) under an atmosphere of dry argon or nitrogen.

Equipment. ^1H, ^{13}C, and ^{31}P spectra were recorded on a Bruker WM-360 NMR spectrometer operated at 360, 146, and 90.27 MHz, respectively. ^1H and ^{13}C NMR spectra are referenced to solvent signals while ^{31}P NMR chemical shifts are relative to 85% phosphoric acid as an external reference, with positive shift values downfield from the reference. All chemical shifts are reported in ppm while coupling constants are in hertz. Molecular weights were estimated using a Hewlett-Packard HP 1090 gel permeation chromatograph equipped with an HP-1047A refractive index detector and with American Polymer Standards AM gel 10 mm 10^4 Å columns. After calibrating with polystyrene standards (Polysciences), samples were eluted at 40 °C with a 0.1 wt % solution of tetra-*n*-butylammonium nitrate (Acros) in THF (OmniSolv) at a flow rate of 1 mL/min. Elemental analysis was obtained from Quantitative Technologies Inc. Differential scanning calorimetry was carried out using Perkin-Elmer DSC 7 equipment and an empty aluminum pan as a reference. Samples (10−15 mg) were examined in aluminum pans under an atmosphere of dry nitrogen. The samples were heated to 150 °C to remove traces of solvents and were then cooled rapidly to −150 °C. The measurements were preformed at an advancing heating rate of 20 °C/min. Surface contact angles were measured with the use of a Rame-Hart contact angle goniometer. Dust-free films were prepared by solution casting onto glass slides from a concentrated THF solution. The values reported are accurate to within 1 deg and represent an average of five measurements.

General Procedure for the Preparation of Phosphazene-*block*-siloxane-*block*-phosphazene Copolymers (4, 5). A general procedure for the synthesis of **4a** is given. Monoallylpolyphosphazene (**2, 3**) (MW = 2800, 2 g, 0.71 mmol) was dissolved in 20 mL of THF. To this solution was added 3 g of dihydride-terminated PDMS (**1**) (MW = 6000, 0.5 mmol) and a catalytic amount of DVDS:Pt (10 mg) at 66 °C. The progress of the reaction was monitored by infrared spectroscopy, which showed the disappearance of the Si−H stretch near 2150 cm^{-1} over a 48 h period or less. The polymer was obtained as an adhesive, off-white solid after precipitation into water (3 times).

For **4a**: ^1H NMR (CD_3COCD_3): 4.63−4.51 (br s, 32H, $[(CF_3\mathit{CH_2}O)_2P{=}N]_8$), 4.37 (t, *J* = 7.19, 8H, $-CH_2NH-[(CF_3\mathit{CH_2}O)_2P{=}N]$), 3.42 (br s, 8H, $-CH_2\mathit{CH_2CH_2}NH-$), 1.60 (br s, 2H, NH), 0.74 (br s, 4H, $-Si\mathit{CH_2}CH_2CH_2NH-$), 0.12 (br s, 486 H, $[\mathit{Me_2}SiO]_{80}\mathit{Me_2}Si$). ^{31}P NMR (CD_3COCD_3): −7.24 (s, $[(CF_3CH_2O)_2P{=}N]_{20}$), −2.43 (d, *J* = 65.76 Hz, $-(CF_3CH_2O)_2P{=}N-$). ^{13}C NMR (CD_3COCD_3): 122.23 (q, *J* = 266.78 Hz, $OCH_2\mathit{CF_3}$), 63.72 (q, *J* = 43.02, $O\mathit{CH_2}CF_3$), 24.52 ($CH_2\mathit{CH_2}CH_2-Si$), 25.39 ($\mathit{CH_2}CH_2CH_2-Si$), 13.26 ($CH_2CH_2\mathit{CH_2}-Si$), 0−1.40 (m, $[\mathit{Me_2}SiO]_{80}\mathit{Me_2}Si$). Elemental analysis for polymer entry **1**: Calcd C, 26.32; H, 4.96; Si, 19.55; P, 6.18; F, 22.64. Found C, 26.13; H, 4.86; Si, 20.01; P, 5.98; F, 21.19. Elemental analysis for polymer entry **4a**: Calcd C, 25.63; H, 4.61; Si, 17.49; P, 3.32; F, 12.16. Found C, 25.13; H, 4.71; Si, 17.53; P, 3.01; F, 11.83. Contact angle for polymer **4a** = 61, **4b** = 72, **4c** = 80, and **4d** = 86. Yield for polymer **4a** = 76%, **4b** = 87%, **4c** = 86%, and **4d** = 79%.

For **5a**:^{1}H NMR (CD_3COCD_3): 4.63−4.51 (br s, 32H, $[(CF_3CH_2O)_2P{=}N]_8$), 4.37 (t, $J = 7.19$, 8H, $-CH_2NH-[(CF_3CH_2O)_2P{=}N]$), 3.42 (br s, 8H, $-CH_2CH_2CH_2NH-$), 1.60 (br s, 2H, NH), 0.74 (br s, 4H, $-SiCH_2CH_2CH_2NH-$), 0.12 (br s, 486 H, $[Me_2SiO]_{80}Me_2Si$). ^{31}P NMR (CD_3COCD_3): −7.24 (s, $[(CF_3CH_2O)_2P{=}N]_{20}$), −2.43 (d, $J = 65.76$ Hz, $-(CF_3CH_2O)_2P{=}N-$). ^{13}C NMR (CD_3COCD_3): 122.23 (q, $J = 266.78$ Hz, OCH_2CF_3), 63.72 (q, $J = 43.02$, OCH_2CF_3), 24.52 ($CH_2CH_2CH_2-Si$), 25.39 ($CH_2CH_2CH_2-Si$), 13.26 ($CH_2CH_2CH_2-Si$), 0−1.40 (m, $[Me_2SiO]_{80}Me_2Si$). Elemental analysis for polymer entry **5a**: Calcd C, 26.9; H, 5.10; N, 2.70; F, 22.6. Found C, 27.3; H, 5.80; N, 2.70; F, 22.9. Yield for polymer **5a** = 67%, **5b** = 58%, and **5c** = 63%.

Preparation of $CH_3(CH_2)_3-[Me_2SiO]_{20}-Me_2Si-(CH_2)_3-OCH_2CH_2O-(CF_3CH_2O)_2P{=}NSiMe_3$ (6). A general procedure for the production of **4** is given. $CH_3(CH_2)_3[Me_2SiO]_{20}Me_2Si(CH_2)_3OCH_2CH_2OH$ (MW = 1600) was purchased from Aldrich and gave a $M_n = 5730$ and PDI = 1.17 by GPC analysis vs polystyrene standards. The phosphoranimine was prepared by reacting $CH_3(CH_2)_3[Me_2SiO]_{20}Me_2Si(CH_2)_3OCH_2CH_2OH$ (1.00 g, 0.625 mmol) with an excess of sodium metal (18 mg, 0.625 mmol) 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) 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 after removal of solvents and excess $Br(CF_3CH_2O)_2P{=}NSiMe_3$ in vacuo.

For **6**: Yield: 1.04 g (83%). ^{1}H NMR ($CDCl_3$): 0.072 (br s, 126H, $[Me_2SiO]_{20}Me_2Si$), 0.553 (m, $J = 3.21$ Hz, 4H, $CH_2-[Me_2SiO]_{20}Me_2Si$), 0.903 (t, $J = 6.78$ Hz, 3H, CH_3CH_2-), 1.31−1.35 (m, 4H, $-CH_2CH_2CH_2-$), 1.65 (quin, $J = 4.69$ Hz, 2H, CH_3CH_2-), 3.46 (t, $J = 6.89$ Hz, 2H, $-CH_2O-$), 3.54 (t, $J = 4.27$ Hz, 2H, $-CH_2CH_2O-$), 3.73 (t, $J = 4.29$ Hz, 4H, $-CF_3CH_2O-$). ^{31}P NMR ($CDCl_3$): −15.56 (s). ^{13}C NMR ($CDCl_3$): 0−1.40 (m, $[Me_2SiO]_{20}Me_2Si$), 14.17, 14.72 (s, CH_2-Si), 18.43 (s, CH_3), 24.00 (s, CH_3CH_2), 25.95, 26.82 (s, $CH_2CH_2CH_2$), 62.60, 72.60, 74.50 (s, $CH_2-O-CH_2CH_2-O-$), 63.33 (q, $J = 37.41$ Hz, OCH_2CF_3), 124.37 (q, $J = 273.10$, OCH_2CF_3).

Preparation of Siloxane-*block*-phosphazene-*block*-siloxane Copolymer (8). A general procedure for **8a** is given. A solution of 20 mg (0.10 mmol) of PCl_5 in 10 mL of CH_2Cl_2 was placed in a flask and was stirred for 1 h. A solution of $Cl_3P{=}NSiMe_3$ (0.11 g, 0.5 mmol) in 2 mL of CH_2Cl_2 was then added to the flask to produce **7**. The reaction mixture was monitored by ^{31}P NMR spectroscopy until complete conversion of $Cl_3P{=}NSiMe_3$ to polymer had occurred. An excess of **6** (0.40 g, 0.2 mmol) was then added to quench the living polymer chain. The reaction mixture was allowed to stir for 8 h, at which time all volatiles were removed under reduced pressure. The end-capped poly(dichlorophosphazene) was redissolved in 20 mL of THF, and then the chlorine atoms were substituted at 25 °C with a 2-fold excess of 1.5 M sodium trifluoroethoxide, per chlorine atom.. The derivatized polymer (**8**) was then recovered via precipitation into deionized water (3 times). Residual siloxane homopolymer was removed by successive washing with CH_2Cl_2.

For **8a**: ^{1}H NMR (CD_3COCD_3): 0.02 (br s, 252 H, $[Me_2SiO]_{20}Me_2Si$), 0.97 (br s, 6 H, CH_3CH_2), 1.14 (br s, 12 H, $-CH_2CH_2CH_2-$), 3.80−3.88 (m, 8 H, $-CH_2CH_2O$), 4.53 (br s, 32 H, $[(CF_3CH_2O)_2P{=}N]_8$), 4.34 (m, 4 H, $CH_2CH_2O-[(CF_3CH_2O)_2P{=}N]_1$). ^{31}P NMR ($CD_3COCD_3$): −7.50 (s, $[(CF_3CH_2O)_2P{=}N]_{10}$), −3.84 (d, $J = 67.92$, $-(CF_3CH_2O)_2P{=}N-$). ^{13}C NMR (CD_3COCD_3): 0.81−2.43 (m, $[Me_2SiO]_{20}\ Me_2Si$), 14.17, 14.66 (s, CH_2-Si), 18.40 (s, CH_3), 23.91 (s, CH_3CH_2), 24.93, 26.80 (s, $CH_2CH_2CH_2$), 62.15, 72.48, 74.42 (s, $CH_2-O-CH_2CH_2-O-$), 63.61 (q, $J = 38.74$, OCH_2CF_3), 122.71 (q, $J = 268.92$, OCH_2CF_3). Elemental analysis for polymer entry **8a**: Calcd C, 26.99; H, 5.32; Si, 21.60; P, 5.48; F, 20.10. Found C, 26.63; H, 5.31; Si, 21.50; P, 5.42; F, 19.23. Contact angle for polymer **8a** = 61, **8b** = 72, **8c** = 74, **8d** = 74 **8e** = 79, **8f** = 81, and **8g** = 81. Yields for polymer **8a** = 83%, **8b** = 90%, **8c** = 81%, **8d** = 78%, **8e** = 77%, **8f** = 81%, and **8g** = 73%.

Preparation of Phosphazene-*block*-siloxane Copolymers (10). A general procedure for the synthesis of **10a** is given. To a stirred solution of PCl_5 (0.104 g, 0.5 mmol) in CH_2Cl_2 (100 mL) at −78 °C was added 0.25 mmol of $(CF_3CH_2O)_3P{=}NSiMe_3$ via syringe to produce the cationic initiator $[(CF_3CH_2O)_3P{=}N-PCl_3]^+[PCl_6]^-$. This solution was then used to polymerize 2.25 g of $Cl_3P{=}NSiMe_3$ (10 mmol) for the production of living monofunctional polyphosphazene, $[(CF_3CH_2O)_3P{=}N-(Cl_2P{=}N)_n-PCl_3]^+[PCl_6]^-$ (**9**), which was quenched with an excess of **6** (1 g, 0.5 mmol). The solvent was then removed, the polymer was redissolved, and then the chlorine atoms were replaced via macromolecular substitution with $NaOCH_2CF_3$ to render the hydrolytically stable block copolymer **10a**. ^{31}P NMR spectroscopy confirmed the presence of the reaction mixture intermediates and the desired product.

For **9**: ^{31}P NMR (CD_3COCD_3): 7.50 (d, $J = 51.2$ Hz, $PCl_3{}^+$), −5.08 (d, $J = 63.2$ Hz, $(CF_3CH_2O)_3P{=}N$), − 17.60 (br s, $[Cl_2P{=}N]_{n-2}$).

For **10a**:^{1}H NMR (CD_3COCD_3): 0.024 (br s, 126 H, $[Me_2SiO]_{20}Me_2Si$), 4.79−4.81 (b, 80 H, OCH_2CF_3). ^{31}P NMR (CD_3COCD_3): −6.13 (s, $[(CF_3CH_2O)_2P{=}N]_{10}$), −4.24 (d, $J = 67.92$ Hz, $-(CF_3CH_2O)_2P{=}N$). ^{13}C NMR (CD_3COCD_3): 0.23−1.62 (m, $[Me_2SiO]_{20}Me_2Si$), 13.87, 13.47 (s, CH_2-Si), 17.99 (s, CH_3), 23.43 (s, CH_3CH_2), 24.68, 26.41 (s, $CH_2CH_2CH_2$), 61.79, 72.38, 74.02 (s, $CH_2-O-CH_2CH_2-O-$), 63.12 (q, $J = 38.74$ Hz, 20 C, OCH_2CF_3), 123.79 (q, $J = 268.92$, OCH_2CF_3). Elemental analysis for polymer entry **11a**; Calcd C, 22.95; H, 3.23; Si, 9.45; P, 9.60; F, 35.18. Found C, 23.13; H, 3.31; Si, 9.45; P, 9.42; F, 34.23. Contact angle for polymer **10a** = 79, **10b** = 81, **10c** = 84, and **10d** = 82. Yields for polymer **10a** = 76%, **10b** = 82%, **10c** = 85%, and **10d** = 88%.

Acknowledgment. We thank the National Science Foundation Polymers Program, Grant DMR-9812389, for the support of this work.

References and Notes

(1) Honeyman, C. H.; Manners, I.; Morrissey, C. T.; Allcock, H. R. *J. Am. Chem. Soc.* **1995**, *117*, 7035.
(2) Allcock, H. R.; Nelson, J. M.; Reeves, S. D.; Honeyman, C. H.; Manners, I. *Macromolecules* **1997**, *30*, 50.
(3) Allcock, H. R.; Crane, C. A.; Morrissey, C. T.; Nelson, J. M.; Reeves, S. D.; Honeyman, C. H.; Manners, I. *Macromolecules* **1996**, *29*, 7740.
(4) Allcock, H. R.; Reeves, S. D.; Nelson, J. M.; Crane, C. A.; Manners, I. *Macromolecules* **1997**, *30*, 2213.
(5) Nelson, J. M.; Allcock, H. R. *Macromolecules* **1997**, *30*, 1854.
(6) Allcock, H. R.; Nelson, J. M.; Prange, R.; Crane, C. A.; de Denus, C. R. *Macromolecules* **1999**, *32*, 5736.
(7) Prange, R.; Reeves, S. D.; Allcock, H. R. *Macromolecules* **2000**, *33*, 5763.
(8) Prange, R.; Allcock, H. R. *Macromolecules* **1999**, *32*, 6390.
(9) (a) Nelson, J. M.; Primrose, P. A.; Hartle, T. J.; Allcock, H. R. *Macromolecules* **1998**, *31*, 947. (b) Allcock, H. R.; Prange, R.; Hartle, T. J. *Macromolecules* **2001**, *34*, 5463.
(10) Goethals, E. J. *Telechelic Polymers: Synthesis and Applications*; CRC Press: Boca Raton, FL, 1989.
(11) Allcock, H. R.; Laredo, W. R.; de Denus, C. R.; Prange, R. *Macromolecules* **2001**, *34*, 2757.
(12) Mark, J. E.; Allcock, H. R.; West, R. *Inorganic Polymers*; Prentice Hall: Englewood Cliffs, NJ, 1992.
(13) Allcock, H. R.; Lampe, F. W. *Contemporary Polymer Chemistry*, 2nd ed.; Prentice Hall: Englewood Cliffs, NJ, 1991.
(14) Wisian-Neilson, P.; Islam, M. S. *Macromolecules* **1989**, *22*, 2026.
(15) Allcock, H. R.; Brennan, D. J.; Dunn, B. S. *Macromolecules* **1989**, *22*, 1534.
(16) Allcock, H. R.; Kuharcik, S. E.; Nelson, C. J. *Macromolecules* **1996**, *29*, 3686.
(17) Allcock, H. R.; Smith, D. E. *Report* **1995**, *95*, 20.
(18) Speier, J. L.; Webster, J. A.; Barnes, G. H. *J. Am. Chem. Soc.* **1957**, *79*, 974.
(19) Karsted, B. D. Platinum Catal. for Hydrosilylation: U.S. Patent 3 775 452, 1973.
(20) Ojima, I. *The Hydrosilylation Reaction*; J. Wiley & Sons: New York, 1989.

(21) (a) Morikawa, A.; Kakimoto, M.; Imai, Y. *Macromolecules* **1991**, *24*, 3469. (b) Saam, J. C.; Macosko, C. W. *Polym. Bull.* **1987**, *18*, 463.

(22) (a) Clarson, S. J.; Mark, J. E.; Dodgson, K. *Polym. Commun.* **1988**, *29*, 208. (b) Clarson, S. J.; Dodgson, K.; Semlyen, J. A. *Polymer* **1985**, *26*, 930.

(23) DeSimone, J. M.; York, G. A.; McGrath, J. E. *Macromolecules* **1991**, *24*, 5330.

(24) Patel, N. M.; Dwight, D. W.; Hedrick, J. L.; Webster, D. C.; McGrath, J. E. *Macromolecules* **1988**, *21*, 2698.

(25) Owens, M. J. *Ind. Eng. Chem. Prod. Res. Dev.* **1980**, *19*, 97.

(26) She, H.; Chaudhury, M. K.; Owens, M. J. In *ACS Symposium Series*; Clarson, S. J. et al., Eds.; Oxford University Press: New York, 2000; Vol. 729, p 322.

(27) Jukarainen, H.; Clarson, S. J.; Seppala, J. V. In *ACS Symposium Series*; Clarson, S. J. et al., Eds.; Oxford University Press: New York, 2000; Vol. 729, p 353.

(28) Pike, J. K.; Tai, H. Wynne, K. J. *Macromolecules* **1996**, *8*, 856.

(29) Tai, H.; Wynne, K. J. *Macromolecules* **1996**, *29*, 3991.

MA010088G