Macromolecules **1994**, *27*, 7713−7717

Modification of Poly(methylphenylphosphazene) To Increase Hydrophobicity

Patty Wisian-Neilson,* Laurie Bailey, and Maneesh Bahadur

Department of Chemistry, Southern Methodist University, Dallas, Texas 75275-0314

Received July 19, 1994; Revised Manuscript Received September 26, 1994[⊗]

ABSTRACT: A series of alkyl- and fluoroalkyl-substituted polyphosphazenes, $\{[Me(Ph)PN]_x[(RMe_2SiCH_2)(Ph)PN]_y\}$, were prepared by deprotonation of the methyl groups on $[Me(Ph)PN]_n$ with *n*-BuLi, followed by treatment of the intermediate anion with the corresponding chlorosilanes, RMe_2SiCl [where R = $(CH)_2CH_3$, $(CH_2)_3CH_3$, $(CH_2)_7CH_3$, $(CH_2)_9CH_3$, $(CH_2)_{17}CH_3$, $(CH_2)_2CF_3$, $(CH_2)_2(CF_2)_5CF_3$, and $(CH_2)_2(CF_2)_7CF_3$]. The new polymers were characterized by elemental analysis, gel permeation chromatography, and ^1H and ^{31}P NMR spectroscopy. The range of substitution [i.e., $y/(x + y) \times 100\%$] was between 40 and 70% as determined by elemental analysis. The glass transition temperatures, which were determined by differential scanning calorimetry, decreased as the length of the side chain increased and ranged from −20 to +39 °C. Onsets of decomposition, which were measured in air using TGA, were between 290 and 350 °C. Contact angle measurements made with water showed that the new polymers became more hydrophobic as the length of the alkyl side group increased and values ranged from 90 to 97°. Those polymers with fluoroalkyl side groups were less wettable with contact angles between 97 and 101°. All these values were significantly larger than the contact angle of 73° for the parent polymer.

Introduction

While bulk properties such as elasticity, strength, and flexibility have long been recognized as important features of functional polymers, surface properties are also a significant aspect of the ultimate utility of a polymer system. This is especially important in biomedical devices, surface coatings, and composite materials.[1] The most notable variations of the surface properties of organic polymers occur when fluorine is incorporated into the system. This confers resistance to solvents, fuels, and oils as a result of the thermal, chemical, and oxidative stability of these systems. Low intermolecular forces at the air/solid interface give the surfaces very low free energy and, as a result, low surface tension. Hence, fluorinated polymers are extremely hydrophobic, are often insoluble in aqueous and organic liquids, and have surfaces that tend to be nonadhesive with low coefficients of friction.[2] The oxygen permeability of some fluorine-containing polymers is also high.[3]

Although most fluoropolymers have a carbon-based backbone with long perfluoroalkyl side chains, fluorinated silicone polymers are also known. Doeff and Lindner[4] reported recently that a series of fluorosilicon polymers $\{[(C_xF_{2x+1})CH_2CH_2](Me)SiO\}_n$ with side chains of aliphatic fluorocarbon groups had a surface energy that was lower than those of most fluorinated polymers with carbon-based backbones. This is explained by the presence of the very low surface energy side chains (CF_3 and CF_2 groups as the pendent groups) set on the very flexible siloxane backbone. The side chains determine the primary surface-active sites and the backbone decides the orientation of the side chains. It should be noted, however, that if the fluorinated side groups are too close to the Si−C bond (on the first or second carbon atom), the Si−C bond may weaken and Si−F bonds may form. Therefore, 1- and 2-fluoroalkyl silicone compounds have low thermal stability, partly due to the high affinity of fluorine for silicon.[5] Another feature of fluorinated silicones is their high permeability to certain gases, which makes them useful as membranes for separation of gases and liquids. For example, poly[(3,3,3-trifluoropropyl)methylsiloxane], $\{(CH_3)[CF_3(CH_2)_2]SiO\}_x$, is especially permeable to CO_2 relative to most other gases, since the solubility of CO_2 in this polymer is unusually high.[6]

Since polyphosphazenes also have very flexible skeletons, the attachment of fluoroalkyl or fluoroaryl substituents to a phosphazene backbone is of importance. The simplest example of such polymers is bis(trifluoroethoxy)phosphazene, $[(CF_3CH_2O)_2PN]_n$, which is formed by reacting sodium trifluoroethoxide with poly(dichlorophosphazene) in a THF−benzene medium.[7] This semicrystalline polymer forms excellent films and fibers, is soluble in common organic solvents, and has hydrophobic and nonadhesive surfaces. In fact, it is more water repellent than poly(tetrafluoroethylene). A more useful, commercial material is the mixed-substituent poly(fluoroalkoxyphosphazene) $\{(CF_3CH_2O)[HCF_2(CF_2)_xCH_2O]PN\}_n$.[8] This amorphous, low-temperature elastomer has been developed for use as O-rings, gaskets, hydrocarbon fuel hoses, and fire-resistant foam rubber devices based on its superior oil, chemical, and fuel resistance, low-temperature flexibility, high-temperature stability, tear and flex fatigue resistance, and damping ability.[9] This material has also shown remarkable biocompatibility in animal implant studies.[10]

The useful properties of both the poly(fluoroalkylsiloxanes) and poly(fluoroalkoxyphosphazenes) suggest that the properties of fully P−C bonded polyphosphazenes should also be significantly enhanced by incorporation of fluoroalkyl groups. The attachment of fluoroalkyl groups directly to the polyphosphazene backbone through P−C linkages by the reactions of various organometallic reagents with $[Cl_2PN]_n$ is precluded by the fact that these substitution reactions are generally accompanied by incomplete substitution and chain degradation.[11] The alternate synthesis of fluoroalkyl-substituted polyphosphazenes via condensation polymerization of silicon−nitrogen phosphorus compounds is also not completely straightforward because precursors such as $Me_3SiN{=}P(OCH_2CF_3)(CF_3)R$ do not readily undergo thermolytic condensation polymerization reactions.[12]

[⊗] Abstract published in *Advance ACS Abstracts,* November 1, 1994.

0024-9297/94/2227-7713$04.50/0

The modification of preformed poly(alkyl/arylphosphazenes) has provided access to new polyphosphazenes with certain reactive functional groups that cannot be attached by the condensation polymerization approach. Of particular relevance to this work are the deprotonation–substitution reactions of $[Me(Ph)PN]_n$[13] which have been used to attach silyl,[14] alcohol,[15] carboxylic acid,[16] and ferrocenyl[17] groups. In this study, we have extended this method to substitution reactions of a series of chlorosilanes, RMe_2SiCl with varying lengths of alkyl and fluoroalkyl moieties. The goals of this project were threefold: (1) to prepare a series of derivatized polyphosphazenes with long chain alkyl groups and fluoroalkyl groups, (2) to optimize the substitution of these hydrophobic groups, and (3) to ascertain the effect of such side groups on the bulk and surface properties of the new materials.

Results and Discussion

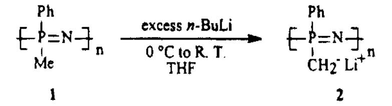
The best studied method for derivatizing preformed poly(alkyl/arylphosphazenes) is by deprotonation–substitution reactions of poly(methylphenylphosphazene), $[Me(Ph)PN]_n$.[14–17] This typically involved treatment of a THF solution of $[Me(Ph)PN]_n$ with 0.5 equiv of *n*-BuLi at −78 °C and subsequent stirring of the mixture for 2–3 h. The resulting polymer anion was then allowed to react with 0.5 equiv of electrophiles such as Me_3SiCl at −78 °C, yielding, for example, the silylated polymer $\{[Me(Ph)PN][(Me_3SiCH_2)(Ph)PN]\}_n$.[14] GPC analysis and intrinsic viscosity measurements demonstrated that no cleavage of the P–N backbone occurred in these transformations. Lower degrees of deprotonation were also obtained by decreasing the amount of *n*-BuLi used (e.g., 20%). Although this earlier work suggested that it was difficult to achieve degrees of substitution above 50%, we have recently found that anion formation at higher temperatures affords complete deprotonation of the methyl groups, and quenching with small electrophiles such as MeI gives as high as 95% substitution.[18] Even when treated with bulky electophiles such as Me_3SiCl, substitutions between 60 and 80% have been obtained.[19]

The simplicity of the deprotonation–substitution reactions, the high reactivity and high degrees of substitution with chlorosilanes, the ease of characterization of the new polymers from silyl substitution (e.g., by ^1H NMR spectroscopy), and the availability of a wide selection of chlorosilanes, RMe_2SiCl, make this one of the most desirable methods for modifying poly(alkyl/arylphosphazenes). Hence, this approach provided a feasible method for attaching a variety of long chain alkyl and fluoroalkyl groups that were capable of significantly altering the hydrophobicity of these polyphosphazenes.

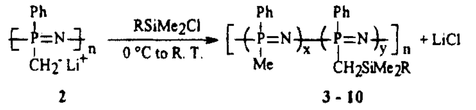
Table 1. Representative NMR Spectroscopic Data[a] for Polymers 3–10

polymer	^1H signal	^1H δ	^{31}P δ
3b	Ph	6.56–8.46	−1.2, 4.4
	PCH_2, PCH_3, PCH, CH_2, CH_3	0.55–2.05	
	Me_2SiCH_2	−0.20	
	$(Me_2Si)_2CH$	0.15	
4a	Ph	6.46–8.25	−1.6, 4.1
	PCH_2, PCH_3, PCH, CH_2, CH_3	0.52–1.90	
	Me_2SiCH_2	−0.41	
	$(Me_2Si)_2CH$	0.18	
5a	Ph	6.05–7.77	−1.5, 4.1
	PCH_2, PCH_3, PCH, CH_2, CH_3	−0.22 to +1.29	
	Me_2SiCH_2	−0.87	
	$(Me_2Si)_2CH$	−0.53	
6b	Ph	6.81–8.16	−1.5, 3.8
	PCH_2, PCH_3, PCH, CH_2, CH_3	0.80–1.85	
	Me_2SiCH_2	−0.23	
	$(Me_2Si)_2CH$	0.15	
7a	Ph	6.93–8.14	0.2, 1.7, 4.7
	PCH_2, PCH_3, PCH, CH_2, CH_3	0.48–1.78	
	Me_2SiCH_2	−0.26	
	$(Me_2Si)_2CH$	0.07	
8a	Ph	6.58–8.44	−0.5, 2.5
	PCH_2, PCH_3, PCH, CH_2, CH_3	0.66–2.22	
	Me_2SiCH_2	−0.28	
	$(Me_2Si)_2CH$	0.34	
9a	Ph	6.69–8.22	−0.8, 2.9
	PCH_2, PCH_3, PCH, CH_2, CH_3	0.25–2.10	
	Me_2SiCH_2	−0.31	
	$(Me_2Si)_2CH$	0.12	
10a	Ph	6.54–8.08	−0.6, 3.2
	PCH_2, PCH_3, PCH, CH_2, CH_3	0.42–1.84	
	Me_2SiCH_2	−0.35	
	$(Me_2Si)_2CH$	0.13	

[a] Chemical shifts relative to Me_4Si for ^1H NMR spectra and H_3PO_4 for ^{31}P NMR spectra.



(1)



(2)

3, R = $(CH_2)_2CH_3$
4, R = $(CH_2)_3CH_3$
5, R = $(CH_2)_7CH_3$
6, R = $(CH_2)_9CH_3$
7, R = $(CH_2)_{17}CH_3$
8, R = $(CH_2)_2CF_3$
9, R = $(CH_2)_2(CF_2)_5CF_3$
10, R = $(CH_2)_2(CF_2)_7CF_3$

The deprotonation of $[Me(Ph)PN]_n$ in this study was accomplished by slow addition of slightly more than 1 equiv of *n*-BuLi to a ca. 0.7–1.0 M THF solution of the polymer at 0 °C. Five minutes after this addition, the ice bath was removed and the mixture was stirred for only 1 h at room temperature rather than the longer reaction times and cooler temperatures used previously. These conditions permit complete deprotonation of all methyl groups to give the polymer anion **2** (eq 1).[18] To obtain the highest possible degree of incorporation of the alkylsilyl and fluoroalkylsilyl side groups, slightly more than 1 equiv of the chlorosilanes was then added (eq 2). Although complete substitution was not observed, the degree of substitution, as determined by elemental analysis [i.e., $y/(x + y) \times 100\%$] ranged from 40 to 70%. Steric hindrance undoubtedly accounts for the incomplete substitution, with the long chain groups blocking some of the anionic sites, thus restricting attachment of additional silyl groups. Nonetheless, most of these new polymers have higher degrees of silyl substitution than those prepared in our laboratory by generating the anion sites at −78 °C.[14]

Once purified by several reprecipitations (see Experimental Section) to ensure removal of unreacted chlorosilanes and their siloxane hydrolysis products, the new polymers were characterized by ^1H and ^{31}P NMR

Table 2. Physical and Elemental Analysis Data for Polymers 3–10

			elem anal.[c]			thermal anal.		
polymer	yield[a] (%)	substitution[b] (%)	% C	% H	% N	T_g (°C)	T_{onset} (°C)	contact angle θ (deg)
3a	51	60	60.32	7.77	7.05	30/16		
3b	27		56.37	7.62	6.43	28	347	90
			(60.89)	(7.77)	(7.10)			
4a	48	60	58.77	7.72	6.75	19	353	91
4b	21		60.73	8.13	6.66	5	334	
			(61.90)	(8.04)	(6.81)			
5a	64	70	65.56	9.13	5.14			
5b	49		65.24	9.09	5.52	−19	322	94
5c	73		65.29	9.24	4.81			
			(65.41)	(9.45)	(5.45)			
6a	73	60	66.58	9.36	5.38	−20	348	95
6b	71		64.16	8.93	5.43	−18	348	
			(66.42)	(9.50)	(5.45)			
7a	91	70	69.81	10.30	4.25	13	330	97
7b	90		70.76	10.69	3.44			
			(72.31)	(10.32)	(3.76)			
8a	71	70	50.90	5.87	5.68	27	292	96
8b	56		49.43	6.37	5.34	39	320	
8c	66		50.42	5.80	5.15			
			(51.46)	(5.88)	(5.72)			
9a	52	50	40.67	3.58	3.42	−17		97
9b	57		41.65	3.82	3.76			
			(41.22)	(3.46)	(3.85)			
10a	47	40	39.89	3.22	3.51	−19	310	101
10b	22		40.87	3.32	3.67	−18		
10d	61		40.81	3.15	3.42			
			(40.03)	(3.30)	(3.67)			

[a] Based on theoretical yield calculated from the degree of substitution determined from elemental analysis. [b] Determined by best fit of elemental analysis data with different degrees of substitution; generally, these values were within 10–20% of those obtained by integration of ^1H NMR spectra. [c] Calculated values are in parentheses.

spectroscopy and elemental analysis (Tables 1 and 2). The ^{31}P NMR spectra of each new polymer contained two very broad signals demonstrating that substitution had occurred. The broadness and close proximity of these signals, however, precluded obtaining definitive integration data for estimating degrees of substitution. The ^1H NMR spectra contained the expected broad, overlapping signals in the aliphatic region as well as aromatic signals for the *P*-phenyl groups. The latter were often very small relative to the various alkyl peaks so integrations of these spectra, which have previously provided very useful data for determining degrees of substitution [i.e., $y/(x + y) \times 100\%$],[14,15] afforded only rough estimates in these polymers. These estimates were subsequently compared with elemental analysis data to confirm the composition of these new polymers. The degree of substitution across the two series of new polymers varied between 40 and 70%, but for each chlorosilane, the substitution was relatively consistent. Moreover, these x and y values are generally within ca. 10–20% of those obtained from elemental analyses. In several cases, the carbon analyses were 1–4% low. This can be attributed to incomplete combustion of the polymer samples as has been observed for polystyrene grafted derivatives reported from our laboratory.[20]

Molecular weight increases relative to the parent polymer $[Me(Ph)PN]_n$ were also observed by gel permeation chromatography (Table 3). The number-average molecular weights, M_n, were 1.2–3 times higher than those of the parent polymer, which approximates the theoretical increases. Polydispersities (M_w/M_n) ranged from 1.9 to 4.3 relative to the parent polymer (M_w/M_n = 1.9). The variations in molecular weight data can be attributed to a variety of factors that affect the actual size and shape of a polymer molecule in solution, including changes in side group–solvent interactions and polymer conformations that result from the incorporation of the large alkylsilyl and fluoroalkylsilyl groups. The data clearly show that molecular weights did not decrease during the successful derivatization process.

The thermal properties of the new alkyl-substituted polyphosphazenes and fluoroalkyl-substituted polyphosphazenes were also investigated by thermal gravimetric analysis and differential scanning calorimetry. From the TGA experiments, onsets of decomposition for the new polymers **3**–**10** (Table 2) are approximately the same as that of the parent polymer, $[Me(Ph)PN]_n$ (T_{onset}, ca. 350 in air). The glass transition temperatures (T_g) were, however, significantly affected by the attachment of the new alkyl and fluoroalkyl groups. For the alkyl-substituted derivatives **3**–**6**, as the length of the side chain increased from three carbons to ten carbons, T_g decreased. However, as shown in Figure 1, when the chain length was increased further to 18 carbons (polymer **7**), the trend was reversed and the T_g actually increased. The trend of decreasing T_g values with increasing chain lengths (ca. 3–10 carbons) is well established for many polymer systems[21] including poly(dialkoxyphosphazenes)[22] and ester derivatives of poly(methylphenylphosphazene).[23] It can be attributed to the generation of additional free volume as the polymer main chains are pushed further apart from each other by the longer side chains. Chain to chain interactions, however, become more important for extremely long chains. Physical tangling between the long chains may increase the glass transition temperature by lowering the backbone mobility and decreasing the free volume.[24] Although alkyl side groups with chains of lengths 12, 14, and 16 carbons were not part of this study, the similarities of the T_g's for polymers with R = $Si(Me)_2(CH_2)_xCH_3$ where $x = 7$ or 9 suggests that a plateau has been reached and that T_g values for polymers with side group chains of 12, 14, and 16 carbons should increase proportionately up to the T_g value measured for R = $Si(Me)_2(CH_2)_{17}CH_3$.

Table 3. GPC Data for Polymers 3–10

polymer	M_w[a]	M_n[b]	M_w/M_n[c]
3a	213 000 (64 000)[d]	49 000	4.3
3b	165 000 (66 000)	42 000	3.9
4a	157 000 (64 000)	39 000	4.0
4b	127 000 (68 000)	52 000	2.5
5a	64 000 (86 000)	28 000	2.3
5b	95 000 (80 000)	29 000	3.2
5c	125 000 (88 000)	42 000	2.9
6a	159 000 (86 000)	44 000	3.6
6b	126 000 (80 000)	40 000	3.1
7a	129 000 (104 000)	39 000	3.3
7b	86 000 (124 000)	35 000	2.5
8a	74 000 (78 000)	35 000	2.1
8b	169 000 (84 000)	64 000	2.6
8c	160 000 (86 000)	72 000	2.2
9a	75 000 (116 000)	39 000	1.9
9b	101 000 (108 000)	36 000	2.8
10a	not soluble in THF (108 000)		
10b	76 000 (108 000)	36 000	2.1
10d	76 000 (108 000)	37 000	2.0

[a] M_w of the parent polymer, $[Me(Ph)PN]_n$, is 44 000. [b] M_n of the parent polymer is 23 000. [c] M_w/M_n of the parent polymer is 1.9. [d] Theoretical molecular weights are in parentheses.

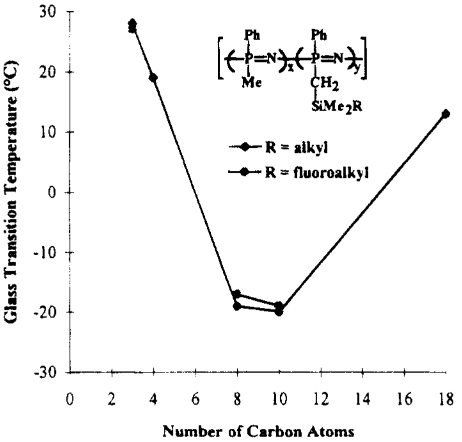


Figure 1. Plot of the length of the carbon side group versus glass transition temperature.

The T_g values of the fluoroalkyl-substituted polyphosphazenes, **8**–**10**, also decreased as the length of the side group increased (Figure 1), ranging from 39 °C for polymer **8b** to −19 °C for polymer **10a**. These numbers are virtually identical to those obtained for the alkyl-substituted polyphosphazenes of similar length (**3**, **5**, and **6**).

Contact angle measurements, which provide a simple evaluation of the nature of the surface of materials, were determined for the new silylated polymers **3**–**10**. The hydrophobicity of a polymer is directly related to the wettability of its surface and can be readily assessed by determining the angle of contact (θ) of a sessile drop of pure water on a smooth, solid surface. A lower contact angle indicates a more wettable surface and, therefore, indicates greater adhesional forces between the liquid and the solid surface. This, of course, is a function of the nature of the atoms that are located at the surface of the material and is generally independent of the interior bulk of the material.[25] Thus polymers with organic surfaces are less wettable than those with polar surfaces. Hydrophobicity is further enhanced by the presence of the C–F bond groups. The contact angles of a drop of water on polyethylene, poly(tetrafluoroethylene), and poly[bis(trifluoroethoxy)phosphazene], $[(CF_3CH_2O)_2PN]_n$ (94,[26] 108,[26] and 108°,[27] respectively), demonstrate this trend. For polymers **3**–**7** with increasingly long alkyl side groups, the contact angles increased from 90° to 96° (Table 1). The contact angles for the fluoroalkyl-substituted polyphosphazenes, **8**–**10** were slightly higher and ranged from 96° to 101°. Both sets of the new derivatives were considerably more hydrophobic than the parent polymer, $[Me(Ph)PN]_n$ ($\theta = 73°$) where coordination of H_2O to the basic lone pair on the backbone nitrogen is favorable.[28] The incorporation of the alkyl and (fluoroalkyl)silyl groups inhibits such interactions. Indeed, as the length of the R groups increased, so did the contact angles. The films of the fluoroalkyl-substituted polyphosphazenes were less wettable than those of the alkyl-substituted polyphosphazenes due to the hydrophobic nature of the fluorine atoms.

In summary, the deprotonation–substitution approach is a useful method for attaching long chain alkyl and fluoroalkyl groups to the polyphosphazene backbone by P–C linkages and is, therefore, an additional means for controlling the properties of this class of polymers. In terms of bulk properties, the glass transition temperatures of the new polymers varied systematically with the length of chain incorporated. The surface properties, as assessed by contact angle measurements, showed significantly decreased wettability of the new polymers relative to the parent polymer, $[Me(Ph)PN]_n$. Those with longer alkyl and fluoroalkyl groups were the most hydrophobic.

Experimental Section

Materials and General Comments. All reactions were performed under an atmosphere of dry nitrogen or under a vacuum. The following reagents were obtained from commercial sources and used without further purification: *n*-BuLi (hexane solution, 2.5 M), 2,2,2-trifluoroethanol, *n*-propyldimethylchlorosilane, *n*-butyldimethylchlorosilane, *n*-octyldimethylchlorosilane, *n*-decyldimethylchlorosilane, dimethyloctadecylchlorosilane, (3,3,3-trifluoropropyl)dimethylchlorosilane, (1*H*,1*H*,2*H*,2*H*-perfluorooctyl)-1-dimethylchlorosilane, and (1*H*,1*H*,2*H*,2*H*-perfluorodecyl)dimethylchlorosilane. Tetrahydrofuran (THF) was distilled from Na/benzophenone under a N_2 atmosphere the same day of use. A two-necked flask equipped with a stopcock adapter and a rubber septum was used to store the THF between collection and use. Hexane was distilled from calcium hydride. Poly(methylphenylphosphazene) was prepared according to published procedures[13a,b] and dried under vacuum at 50 °C for at least 18 h before the reaction was started.

The ^1H and ^{31}P NMR spectra were performed on an IBM/Bruker WP 200 SY FT NMR spectrometer. Elemental analyses were obtained on a Carbo Erba Strumentazione 1106 CHN elemental analyzer. The sample size was between 0.8 and 1.3 mg. Gel permeation chromatography measurements were performed on a Waters Associates GPC II instrument using 10^4, 10^5, and 10^6 Å μ-Styragel columns. The operating conditions consisted of a flow rate of 1.5 mL/min of unstabilized HPLC-grade THF containing 0.1% tetra-*n*-butylammonium bromide [$(n\text{-Bu})_4NBr$]. The temperature of the columns was 30 °C. The samples were dissolved in the mobile phase and filtered through 0.5 μm Teflon filters prior to injection. The injection volume was typically 0.05 mL of a 0.1% solution. The system was calibrated with a series of narrow molecular weight polystyrene standards in the molecular weight range of ca. 10^3-10^6. The glass transition temperatures were determined using a DuPont DSC Model 910 instrument equipped with a TA operating software module and data analysis data station. The samples weighed between 5 and 10 mg and were crimped in a small aluminum boat. Measurements were made against an aluminum reference at a heating rate of 10 °C/min. The temperature range used varied depending on the polymer, but the range was somewhere between -100 and $+100$ °C. Each sample was heated through the range at least twice. Thermal gravimetric analyses were performed using a DuPont TGA Model 951 module with the TA operating software and data analysis system. The polymer samples (ca. 50 mg) were heated at a rate of 10 °C/min under air from ambient temperature to 800 °C. Contact angle measurements were obtained on a Rame-Hart NRL Model 100 contact angle goniometer. Films of selected polymers were prepared on glass slides and allowed to dry for 2 days in a dust-free environment. Sessile drop measurements were performed on each film with drops of size 0.10 mL. To minimize the effects of surface roughness, at least 20 measurements were made on each film and the average of these readings is reported. Standard deviations were between 2.4 and 3.2°.

Preparation of Polymers 3–6 and 8–10. Typically, a 100 mL, two-necked flask was charged with approximately 7.3 mmol of $[Me(Ph)PN]_n$ and dried at 50 °C in a vacuum overnight. After cooling and removal from the oven, the flask was equipped with a magnetic stir bar, rubber septum, and stopcock inlet adapter. Then 10 mL of THF was added to dissolve the polymer. The flask was cooled to 0 °C and 1.2 equiv of 2.5 M *n*-BuLi was added via syringe to form the polymer anion. After 5 min, the ice bath was removed and the solution was stirred at room temperature for 1 h. The ice bath was reapplied and 1.2 equiv of the chlorosilane was added by syringe. After 5 min, the solution was allowed to warm to room temperature and the rubber septum was replaced with a glass stopper. The solution was allowed to stir for 4 days.

Preparation of Polymer 7. Basically, the preparation of polymer **7** was the same as that described above for the other polymers. However, since the appropriate chlorosilane is a solid, 1.2 equiv of the compound was dissolved in 10 mL of THF under N_2, and this solution was injected into the flask by syringe.

Purification of Polymers 3a, 4, 5a, 5c, 6b, 8b, and 8c. After 4 days of stirring, the polymer solutions were concentrated by rotary evaporator and the polymers were precipitated by dropwise addition to water. The water was removed by decantation; the polymers were redissolved in THF and reprecipitated into water. A third precipitation from THF into hexane for polymers **3a**, **4**, **8b**, and **8c** and from THF into methanol for polymers **5a**, **5c**, and **6b** was performed. The polymers were then dried at 50 °C in a vacuum oven for 5 days.

Purification of Polymers 3b, 5b, 6a, and 8a. After 4 days of stirring, the polymers were brought to dryness on the rotary evaporator. The materials were dissolved in benzene and then filtered through a glass-fritted filter to remove LiCl. The benzene solutions were concentrated on the rotary evaporator. Polymers **3b** and **8a** were collected by precipitation into hexane while polymers **5b** and **6a** were collected by precipitation into methanol. The products were dried under vacuum at 50 °C for 5 days.

Purification of Polymers 7a and 7b. THF was removed from the reaction mixture on a rotary evaporator to isolate polymer **7a**. This was then dissolved in benzene, the solution was filtered, and **7a** was collected by precipitation into methanol. Polymer **7b** was purified by two precipitations into water and one into methanol. Later, it was found to be necessary to precipitate this polymer into water once more and into methanol twice more in order to obtain satisfactory elemental analyses and NMR spectra. Products were dried under vacuum at 50 °C for 5 days.

Purification of Polymers 9 and 10. These polymers were dried on the rotary evaporator to remove the THF, dissolved in trifluoroethanol (CF_3CH_2OH), and collected by precipitation into water twice and into methanol once. The polymers were dried in the vacuum oven at 50 °C for 5 days.

Acknowledgment. We thank the Robert A. Welch Foundation, the U.S. Army Research Office, the Texas Higher Education Coordinating Board (Advanced Technology Program), and the Department of Chemistry at Southern Methodist University for support of this project.

References and Notes

(1) Cherry, B. W. *Polymer Surfaces*; Cambridge University: Cambridge, 1981.

(2) Antonuci, J. M.; Stanabury, J. W.; Cheng, G. W. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1990**, *31*, 320.

(3) Burke, A. J. In *Fluoropolymers*; Wall, L. A., Ed.; Wiley: New York, 1972; Chapter 15.

(4) Doeff, M. M.; Lindner, E. *Macromolecules* **1989**, *22*, 2951.

(5) Owen, M. J. *J. Appl. Polym. Sci.* **1988**, *35*, 895.

(6) Zhao, Q.; Mark, J. E. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1990**, *31*, 303.

(7) Allcock, H. R.; Kugel, R. L. *J. Am. Chem. Soc.* **1965**, *87*, 4216.

(8) Connelly, T. M.; Gillham, J. K. *J. Appl. Polym. Sci.* **1976**, *20*, 473.

(9) Penton, H. R. *ACS Symp. Ser.* **1988**, *360*, 277.

(10) (a) Wade, C. W. R.; Gourlay, S.; Rice, R.; Hegyeli, A.; Singler, T.; White, J. Biocompatibility of Eight Poly(organophosphazenes). *Organometallic Polymers*; Carraher, C. E., Sheats, J. E., Pittman, C. U., Eds.; Academic Press: New York, 1978. (b) Reichert, W. M.; Rilisko, F. E.; Barenberg, S. A. *J. Biomed. Mater. Res.* **1982**, *16*, 301. (c) Owen, D. R.; Zone, R.; Armer, T.; Kilpatric, G. Analytical Methods for the Determination of Biologically Derived Absorbed Species in Biomedical Elastomers. *Biomaterials: Interfacial Phenomena and Application*; American Chemical Society: Washington, DC, 1982.

(11) Allcock, H. R.; Harris, P. J.; Connolly, M. S. *Inorg. Chem.* **1981**, *20*, 11.

(12) Karthikeyan, S.; Neilson, R. H. *Inorg. Chem.*, submitted.

(13) (a) Wisian-Neilson, P.; Neilson, R. H. *Inorg. Synth.* **1989**, *25*, 69. (b) Neilson, R. H.; Hani, R.; Wisian-Neilson, P.; Meister, J. J.; Roy, A. K. *Macromolecules* **1987**, *20*, 910. (c) Neilson, R. H.; Wisian-Neilson, P. *Chem. Rev.* **1988**, *88*, 541.

(14) Wisian-Neilson, P.; Ford, R. R.; Neilson, R. H.; Roy, A. K. *Macromolecules* **1986**, *19*, 2089.

(15) Wisian-Neilson, P.; Ford, R. R. *Macromolecules* **1989**, *22*, 72.

(16) Wisian-Neilson, P.; Islam, M. S.; Ganapathiappan, S.; Scott, D. L.; Raghuveer, K. S.; Ford, R. R. *Macromolecules* **1989**, *22*, 4382.

(17) Wisian-Neilson, P.; Ford, R. R. *Organometallics* **1987**, *6*, 2258.

(18) Wisian-Neilson, P.; Claypool, C. L.; Bahadur, M. *Macromolecules*, in press.

(19) Wisian-Neilson, P.; Islam, M. Q.; Bailey, L., unpublished results.

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

(21) Sperling, L. H. *Physical Polymer Science*; Wiley-Interscience: Toronto, 1986.

(22) Allcock, H. R.; Connolly, M. S.; Sisko, J. T.; Al-Shali, S. *Macromolecules* **1988**, *21*, 323.

(23) Wisian-Neilson, P.; Huang, L.; Islam, M. Q.; Crane, R. A. *Polymer*, in press.

(24) (a) Foucher, D. A.; Ziembinski, R.; Ben-Zhung, T.; Macdonald, D. M.; Massey, J.; Jaeger, C. R.; Vansco, G. J.; Manners, I. *Macromolecules* **1993**, *26*, 2878. (b) Billmeyer, F. W., Jr. *Textbook of Polymer Science*, 3rd. ed.; Wiley: New York, 1984; p 340.

(25) Shafrin, E. G.; Zisman, W. A. *J. Phys. Chem.* **1960**, *64*, 519.

(26) Wall, L. A. *Fluoropolymers*; Wiley: New York, 1972.

(27) Allcock, H. R.; Rutt, J. S.; Fitzpatrick, R. J. *Chem. Mater.* **1991**, *3*, 442.

(28) Wisian-Neilson, P.; Garcia-Alonso, F. J. *Macromolecules* **1993**, *26*, 7156.