Deprotonation−Substitution Reactions of Poly(Methylalkylphosphazenes) and Their *N*-Silylphosphoranimine Precursors

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ABSTRACT: Diethyl ether solutions of the phosphoranimines, $Me_3SiN{=}P(OPh)(CH_3)(R)$ {R = *n*-Bu, *n*-Hex} and tetrahydrofuran (THF) solutions of the polymers $[Et(Ph)P{=}N]_n$, $[Me(n\text{-}Bu)P{=}N]_n$, and $[Me(n\text{-}Hex)P{=}N]_n$ were sequentially treated with *n*-BuLi and appropriate electrophiles to afford new phosphoranimines, $Me_3SiN{=}P(OPh)(CH_2SiMe_3)(R)$ {R = *n*-Bu, *n*-Hex} and $Me_3SiN{=}P(OPh)(CH_2PPh_2)(n\text{-}Bu)$, and new copolymers, $[Et(Ph)P{=}N]_x\{[(CH_3)(Me_3Si)CH](Ph)P{=}N\}_y$, $[Me(R)P{=}N]_x\{[(Me_3Si)CH_2](R)P{=}N\}_y$, and $[Me(R)P{=}N]_x\{[(\eta^5{-}C_5H_5)Fe(\eta^5{-}C_5H_4)CH(OH)CH_2](R)P{=}N\}_y$. The new phosphoranimines were characterized by elemental analysis and ^1H, DEPT ^{13}C, and ^{31}P NMR spectroscopy. The new polymers were characterized by elemental analysis, gel permeation chromatography (GPC), differential scanning calorimetry (DSC), ^1H and ^{31}P NMR spectroscopy, contact angle measurements, and density measurements. The range of substitution of the polymers {i.e., $[y/(x + y)] \times 100$} was 30−70% as determined by elemental analysis. Glass transition temperatures and molecular weights of the derivatives were both higher than the parent polymers. Measurements of Young's contact angles (θ_Y) indicated that the incorporation of Me_3Si and ferrocene groups into the polymers increased the hydrophobicity relative to unsubstituted poly(dialkylphosphazenes).

Introduction

Chemical modification of poly(phosphazenes) has provided access to a large number of polymers with a diverse range of properties. It is clearly established that the nature of the side groups R in poly(phosphazenes), $[R_2P{=}N]_n$, determines the properties of the polymer and that control of properties is readily achieved by the proper choice of the side groups.[1] Our studies of the structure−property relationships in poly(phosphazenes) with alkyl and aryl groups attached to the P−N backbone by direct P−C bonds have focused on modifications of poly(methylphenylphosphazene), $[Me(Ph)P{=}N]_n$.[2] The tetrahydrofuran (THF) solubility of amorphous $[Me(Ph)P{=}N]_n$ facilitates the formation of a synthetically useful anionic intermediate via deprotonation of the methyl substituent. This polymeric "organolithium reagent" has provided access to polymers with a diverse set of functional groups and with a variety of chemical and physical properties. Such "functionalized" polymers cannot be obtained by condensation polymerization of *N*-silylphosphoranimines which contain reactive or bulky groups[3] or by ring-opening polymerization of cyclic phosphazenes with these substituents.[4]

With the exception of poly(dimethylphosphazene), $[Me_2P{=}N]_n$,[5] the semicrystalline dialkyl-substituted homopolymers (e.g., $[Et_2P{=}N]_n$,[5] $[Pr_2P{=}N]_n$) are insoluble in common organic solvents, and all are insoluble in coordinating solvents such as THF or ether,[6,7] thus limiting the scope of their derivative chemistry to surface reactions. The *methylalkyl*-substituted phosphazene homopolymers, $[Me(R)P{=}N]_n$ where R = Et, Pr, Bu, or Hex, on the other hand, are amorphous and are soluble in solvents such as THF, CH_2Cl_2, hexane, ether, benzene, ethyl acetate, and methanol.[6,7] In addition to enhanced solubility, the poly(methylalkylphosphazenes) generally have glass transition temperatures well below 0 °C.[6,7] Thus, deprotonation−substitution reactions of these systems offer ample opportunity to further vary and control the properties of poly(phosphazenes). In the work reported here, we examined the deprotonation−substitution reactions of both the methylbutyl- and methylhexyl-substituted poly(phosphazenes) and their phosphoranimine precursors. The wettability, glass transition temperature, and free volume of the new polymer derivatives were determined and are compared to the properties of similarly substituted derivatives of poly(methylphenylphosphazene), $[Me(Ph)PN]_n$.

Results and Discussion

Because the dialkyl polymers $[Me(Bu)PN]_n$ and $[Me(Hex)PN]_n$ have two potential sites for deprotonation, the first part of this study involved the deprotonation−substitution reaction of a related polymer, $[Et(Ph)PN]_n$ [5] (**1**). This readily available polymer, which has a single ethyl side group, was used to demonstrate that alkyl groups other than methyl groups could be deprotonated. Of particular interest were the NMR spectra of **1** and its deprotonation substitution product, **3**, which were useful for later studies of the dialkyl-substituted poly(phosphazenes).

The deprotonation of polymer **1**, dissolved in THF, with *n*-BuLi was straightforward at room temperature. Quenching of the intermediate polymer anion, **2**, with $ClSiMe_3$ yielded polymer **3** (eq 1), which was characterized by NMR spectroscopy. The ^{31}P NMR spectrum contained two phosphorus signals: one for the unsubstituted phosphorus and one for the Me_3SiCH-substituted phosphorus. This is similar to the spectrum previously reported for $[Me(Ph)PN]_x[Me_3SiCH_2(Ph)PN]_y$, the product of the same reaction of $[Me(Ph)PN]_n$.[8]

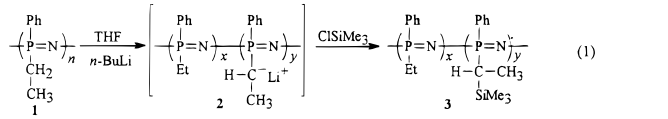

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Table 1. Characterization Data for Phosphoranimines

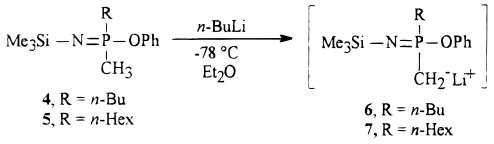
compd	% yield	bp (°C) (pressure (mmHg))	elem anal[a] % C	elem anal[a] % H	signal	^{1}H δ	^{1}H J_{PH}[b]	^{13}C δ	^{13}C J_{PC}	^{31}P δ
8	71	100 (0.03)	57.34 (57.42)	9.64 (9.64)	*Me*$_3$SiN	−0.16		3.8		29.2
					$CH_2Si\mathit{Me}_3$	0.2		0.4		
					CH_2SiMe_3	1.4−1.6[c]		18.9	89.8	
					$P\mathit{CH}_2CH_2$	1.7−1.9[c]		33.0	87.0	
					$PCH_2\mathit{CH}_2$	1.2−1.6[c]		25.8		
					CH_2CH_3	1.2−1.6[c]		24.0	16.9	
					$CH_2\mathit{CH}_3$	0.83	(7.3)[b]	13.9		
					Ph	7.2−7.4[c]		124−152		
9	39	120 (0.01)	59.89 (59.48)	10.00 (9.98)	*Me*$_3$*Si*N	−0.1		3.4		29.2
					$CH_2\mathit{SiMe}_3$	0.2		0.3		
					PCH_2SiMe_3	1.5−1.7[c]		18.7	90.2	
					$P\mathit{CH}_2CH_2$	1.7−1.9[c]		33.1	88.1	
					$PCH_2\mathit{CH}_2$	1.1−1.5[c]		31.5		
					$P(CH_2)_2\mathit{CH}_2$	1.1−1.5[c]		23.6		
					$\mathit{CH}_2CH_2CH_3$	1.1−1.5[c]		30.5	17.2	
					$CH_2\mathit{CH}_2CH_3$	1.1−1.5[c]		22.6		
					$CH_2CH_2\mathit{CH}_3$	0.92	(6.7)[b]	14.1		
					Ph	7.2−7.4[c]		121−151		
10	64	183 (0.01)	66.15 (66.78)	7.75 (7.54)	Me_3Si	−0.2		3.6	3.4	26.6, 26.9,
					PCH_2P	2.5[c]	14.9	31.0	88.0, 31.2	−26.8
					$P\mathit{CH}_2CH_2$	1.6[c]		31.8	94.1	(53.0)[d]
					$PCH_2\mathit{CH}_2$	1.3[c]		25.0	3.7	
					CH_2CH_3	1.1[c]		24.0	17.7	
					$CH_2\mathit{CH}_3$	0.7	(7.3)	13.8		
					Ph	7.2−7.4[c]		121−152		

[a] Calculated values are in parentheses. [b] J_{HH} are in parentheses. [c] Complex multiplet. [d] J_{PP} is in parentheses.

Relative to the parent polymer **1**, the ^{1}H NMR spectrum of polymer **3** showed two new signals, one for a $SiMe_3$ group and another in the range of a CH group, as well as the signals from the unsubstituted ethyl group. This indicates that deprotonation−substitution occurred on the PCH_2 group of the ethyl side group. The integration of the ^{1}H NMR spectrum indicated that ca. 25% of the ethyl groups were substituted with $SiMe_3$ groups.

The substitution of the PCH_2 carbon of the Et group implies that there could be competition between the PCH_2 and PCH_3 groups in the deprotonation−substitution reactions of poly(dialkylphosphazenes) such as [Me(*n*-Bu)PN]$_n$. To better study this, the reactions of the *P*-dialkyl-*N*-silylphosphoranimine precursors (**4** and **5**)[6,7] to the polymers were investigated. The phosphoranimines serve as models for the reactions of the dialkyl polymers and generally provide better, sharper NMR spectra, thus facilitating the distinction between substitution sites.

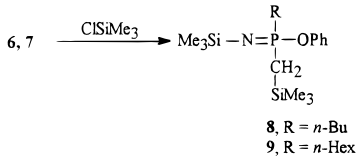
Phosphoranimines **4** and **5** were dissolved in ether and then sequentially treated with *n*-BuLi (eq 2) and Me_3SiCl (eq 3) or Ph_2PCl (eq 4) at −78 °C. On the basis of previous studies of the anion intermediate produced by deprotonation of $Me_3SiN{=}PMe_2OCH_2CF_3$, anions **6** and **7** were not allowed to warm above −78 °C due to the possibility of decomposition.[3,9] The new phosphoranimines **8**−**10** were purified by distillation at reduced pressure.



4, R = *n*-Bu
5, R = *n*-Hex

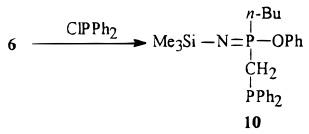
6, R = *n*-Bu
7, R = *n*-Hex

(2)



8, R = *n*-Bu
9, R = *n*-Hex

(3)



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The ^{1}H and ^{13}C NMR spectra of the phosphoranimines (Table 1) clearly demonstrated that *deprotonation−substitution occurred only on the methyl groups*. This is expected on the basis of the well-established order of stability of carbanions.[10] By comparison to the starting phosphoranimines **4** and **5**, the ^{1}H NMR spectrum of the new phosphoranimines **8**−**10** contained no PCH_3 signals (δ = 1.6 ppm). In the case of the silyl-substituted phosphoranimines **8** and **9**, a new Me_3Si signal at δ = 0.2 ppm was observed for the Me_3SiCH_2 group along with the Me_3SiN signal. The PPh_2-substituted phosphoranimine **10** had new signals in the phenyl range. Unfortunately, the new signal for the substituted PCH_2 group was obscured by the signals of the long alkyl groups for each phosphoranimine. DEPT ^{13}C NMR spectra were also obtained for the starting materials and the products. Phosphoranimines **4** and **5** showed signals (upward) for the PCH_3 (doublet) and terminal CH_3 on the butyl and hexyl groups. By contrast the phosphoranimine derivatives **8**−**10** showed only the terminal CH_3 signal of the butyl and hexyl groups, while the PCH_3 doublet disappeared and was replaced by the PCH_2 (downward) signal. Generally, the ^{31}P NMR spectra were less informative since the signals of both parents and derivatives were in the same general regions (δ 29). As expected the ^{31}P NMR spectrum of **10** showed a doublet for each phosphorus (δ = +26.5 and −26.8) in the molecule, with a J_{PP} coupling constant of 32.6 Hz. This compares favorably to a related phosphoranimine, $Me_3SiN{=}P(OCH_2CF_3)(CH_2PPh_2)Me$.[9]

Elemental analysis (Table 1) of the substituted phosphoranimines **8**−**10** agreed with the theoretical values of the substituted phosphoranimines, and their yields

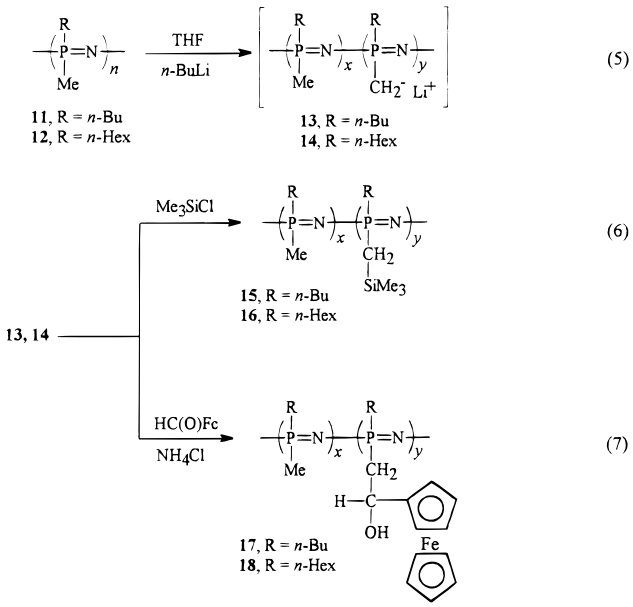
Table 2. Characterization Data for Polymers

			elem anal[a]			NMR spectrosc data			GPC data			contact angles (deg)		
polym	% yield	T_g (°C)	% C	% H	% N	signal	^{1}H (δ)[b]	^{31}P (δ)[b]	M_w	M_n	M_w/M_n	θ_Y	θ_A	θ_R
11		−51[4]	51.15 (51.27)	10.34 (10.33)	11.48 (11.96)	CH_3	0.5−0.7	9.0	40 000	30 000	1.36			
						$(CH_2)_3$	0.9−1.7							
						PCH_2	0.9−1.7							
						PMe	1.5−1.7							
12		−69[4]	57.32 (57.91)	11.40 (11.11)	9.35 (9.65)	CH_3	0.8	10.3[4]	18 000	9 300	1.52	22	31	41
						$(CH_2)_4$	1.1−1.6							
						PCH_2	1.1−1.6							
						PMe	1.3							
15	71	−35	50.94 (50.95)	10.41 (10.53)	8.77 (9.14)	$SiMe_3$	0.0−0.3	7.3	41 000	30 000	1.41	86	91	34
						PMe	0.8−1.0	9.0						
						PBu	1.2−1.8							
						PCH_2	1.6−1.8							
16	76	−23	56.85 (56.87)	11.32 (11.12)	8.68 (8.40)	$SiMe_3$	−0.0	10.1	23 000	10 000	2.1	92	105	49
						PMe	0.7	13.5						
						PHex	1.1							
						PCH_2	1.3							
17	97	24	55.34 (56.26)	7.87 (7.64)	6.38 (6.25)	PBu	0.5−2.3	9.0	118 000	64 000	1.86	88	94	50
						PCH_2	1.8−2.3	14.2						
						CH	4.5−4.8							
						OH	5.5−6.2							
						Cp	3.8−4.5							
18	86	23	59.71 (59.85)	7.80 (7.86)	4.38 (4.75)	PHex	0.6−1.6	10.2	30 000	20 000	1.5	88	97	52
						PCH_2	1.1−2.2	15.9						
						CH	4.7							
						OH	7.0							
						Cp	3.9							

[a] Calculated values in parentheses; percentage substitutions (x and y) are given in the text. [b] Broad signals.

ranged from 39 to 71%. The boiling points (Table 1) of the silylated phosphoranimines **8** and **9** were 20−30 °C higher than the underivatized phosphoranimines **4** and **5**. The boiling point of diphenylphosphine derivative **10**, however, was ca. 100 °C higher than its precursor, **4**. Thus, the diphenylphosphine derivative of **5** was not prepared since decomposition during purification by vacuum distillation appeared likely. In fact, upon distillation of the PPh_2 derivative **10**, some decomposition (elimination of Me_3SiOPh) was observed.

The formation of the $SiMe_3$ and Ph_2P derivatives (phosphoranimines **8**−**10**) clearly demonstrated that deprotonation occurs at the PCH_3 group and not at the PCH_2 group. These straightforward reactions thus indicated that the deprotonation−substitution reactions of the analogous poly(phosphazenes) should proceed in a similar manner. Using procedures similar to those used to deprotonate $[Me(Ph)PN]_n$,[8,11] the dialkyl polymers **11** and **12** were deprotonated by treatment of THF solutions of the polymers with *n*-BuLi at 0 °C (eq 5). After the solutions were stirred for 1 h at room temperature, the anion intermediates (**13** and **14**) were quenched either with Me_3SiCl (eq 6) or with ferrocenecarboxaldehyde followed by saturated ammonium chloride (eq 7) to obtain polymers **15**−**18**. The new polymers were purified by precipitation from THF into water followed by drying under vacuum. The ferrocene-substituted polymers were also subjected to Soxhlet extraction with acetone prior to drying.



The new polymers were characterized by NMR spectroscopy, elemental analysis, and gel permeation chromatography. The ^{31}P NMR spectra for each polymer exhibited two signals, one for unsubstituted PMe(alkyl) segments and a second signal for the substituted portions (Table 2). Integration of the ^{1}H NMR spectra was used to determine the percentage substitution (i.e., $\{[y/(x + y)] \times 100\%\}$). For polymers **15** and **16**, the integration of the $SiMe_3$ versus the CH_3 and CH_2 regions showed 50 and 30% substitution, respectively. Integration of the CH_2 and CH_3 regions versus the CH, Cp, and OH regions for polymers **17** and **18** indicated 50 and 70% substitution, respectively. We have previously observed that the substitution of the ferrocenyl group on $[Me(Ph)PN]_n$ was higher than for substitution of silyl groups under similar reaction conditions.[12] Elemental analyses confirmed these degrees of substitution and established the purity of the isolated polymers. The molecular weights of the new polymers were generally no smaller than the parent polymers, thus indicating that no chain degradation occurred during the deprotonation−substitution process.

The influence of the structural variation of the side groups was clearly evident in the solubility, glass transition temperatures, and surface wettability of these polymers. All were soluble in THF and chlorinated hydrocarbons but insoluble in diethyl ether and acetone. However, unlike $[Me(Ph)PN]_n$ and most of its derivatives, these polymers showed an enhanced solubility in

Table 3. Correlation of T_g and V_F for Selected Poly(phosphazenes)

polym	dens	V_F	T_g
$[Me(Hex)PN]_n$ (**12**)	0.9074	0.3430	−69[6,7]
$[Me(Hex)PN]_x\{[(Me_3Si)CH_2](Hex)PN\}_y$ (**16**)	0.9725	0.2806	−23
$[Me(Hex)PN]_x\{[(\eta^5-C_5H_5)Fe(\eta^5-C_5H_4)CH(OH)CH_2](Hex)PN\}_y$ (**18**)	1.1643	0.2707	23
$[Me(Bu)PN]_n$ (**11**)	0.9497	0.3351	−51[6,7]
$[Me(Bu)PN]_x\{[(Me_3Si)CH_2](Bu)PN\}_y$ (**15**)	0.9500	0.3059	−35
$[Me(Bu)PN]_x\{[(\eta^5-C_5H_5)Fe(\eta^5-C_5H_4)CH(OH)CH_2](Bu)PN\}_y$ (**17**)	1.1859	0.2784	24

hydrocarbons. Although the butyl-substituted polymers **15** and **17** do not fully dissolve in hexane, they did not readily precipitate when concentrated THF solutions were added to hexane. The hexyl polymers were even less likely to precipitate under similar conditions.

The glass transition temperatures were also affected by the substitution of the silyl and ferrocenyl groups. In general, the T_gs (Table 2) of the derivatives were higher than the parent polymers **11** (T_g = −51 °C [6,7]) and **12** (T_g = −69 °C [6,7]) as expected for the increased steric bulk of the silyl and ferrocene substituents which tend to lower the ease of torsional movement of the polymer backbone. Hydrogen bonding of the OH groups in the ferrocene-substituted polymers **17** and **18** further limits the flexibility of these systems as shown by T_gs that are over 50 °C higher than the parent polymers. The T_gs of the polymers reported here also correlate with differences in free volume (V_F) or openness of the polymers[13] (see Table 3). In the butyl series **11**, **15**, and **17**, the T_gs are −51, −35, and +24 °C, respectively, with a corresponding V_F change from 0.3351 to 0.2784. The same trend (Table 3) is observed with the hexyl series **12**, **16**, and **18**. It is noteworthy that these new polymers have significantly different T_gs than the $[Me(Ph)PN]_n$ derivatives, thus demonstrating that the incorporation of long alkyl groups adds an additional dimension in the design and synthesis of polymers with preselected properties. For example, the ferrocene-substituted butyl and hexyl polymers have T_gs near room temperature, while the corresponding ferrocene derivative of $[Me(Ph)PN]_n$ has a T_g of 92 °C[12] {versus a T_g of 37 °C for the parent $[Me(Ph)PN]_n$[5]}. Similarly the silylated derivative of the phenyl polymer has a T_g of 50 °C[14] as compared to T_gs well below 0 °C for the butyl and hexyl analogues. Clearly, the long alkyl groups pack less efficiently than the phenyl groups and generate more free volume in these systems. The observation of only one T_g is also evidence of random rather than block substitution.

The contact angles of water on films of these polymers were also measured to assess the hydrophobicity or wettability of the new systems (Table 2). The parent polymers **11** and **12** are very hygroscopic and appear to almost absorb the water droplet. Although no contact angle measurements could be made for **11**, a quick and approximate measurements of Young's angle (θ_Y), the advancing angle (θ_A), and the receding angle (θ_R) for **14** were 22, 31, and 41°, respectively. This behavior is signicantly different from that of the poly(phenylalkylphosphazenes), $[Me(Ph)PN]_n$ and $[Et(Ph)PN]_n$, where θ_Ys are 73 and 92°, respectively. This affinity for water is so great that, after a week in a saturated water atmosphere, a dry sample of $[Me(Bu)PN]_n$ (**11**) had absorbed 15 mol % water. Presumably, the basicity of the backbone nitrogen is enhanced by the presence of two electron releasing alkyl groups, thus facilitating better hydrogen bonding to water.[15] The simple incorporation of $SiMe_3$ and ferrocene groups, however, significantly increased the hydrophobicity of the poly(methylalkylphosphazenes). The θ_Ys of polymers **15**−**18** were ca. 90°, which is similar to previous measurements on derivatives of $[Me(Ph)PN]_n$ that had fluorocarbon and silicon side groups.[16]

In summary this study demonstrates that the deprotonation−substitution reactions of poly(dialkylphosphazenes) may be used to extend the range of properties of poly(phosphazenes) with P−C bonded substitutents. Although deprotonation of the $P-CH_2$ group in $[Et(Ph)PN]_n$ occurs, the preferred site of deprotonation in methylalkyl systems is at the $P-CH_3$ group as demonstrated by reactions on both phosphoranimine precursors and $[Me(alkyl)PN]_n$. The new polymer systems displayed the expected structure−property relationships as shown by solubilities, glass transition temperatures, and surface wettability.

Experimental Section

Materials and General Comments. All reactions were performed under an atmosphere of dry nitrogen. The following reagents were obtained from commercial sources and used without further purification: *n*-BuLi (hexane solution, 2.5 M), methylmagnesium bromide (diethyl ether solution, 3.0 M), ethylmagnesium bromide (diethyl ether solution, 2.0 M), *n*-butylmagnesium chloride (diethyl ether solution, 2.0 M), *n*-hexylmagnesium bromide (diethyl ether solution, 2.0 M), ammonium chloride, dichlorophenylphosphine, diphenylchlorophosphine, ferrocenecarboxaldehyde, hexachloroethane, 1,1,1,3,3,3-hexamethyldisilazane, phenol, and phosphorus trichloride. Diethyl ether and hexane were distilled from calcium hydride, and THF was distilled on the day of use from benzophenone and sodium. Sodium phenoxide was prepared from sodium and phenol in ether and dried under vacuum at room temperature.

The ^1H, ^{31}P, and ^{13}C NMR spectra were obtained on either a Bruker WP 200 SY FT NMR spectrometer equipped with a Techmag computer interface or a SGI/Bruker DRX-400 sb spectrometer. Elemental analyses were obtained on a Carlo Erba Strumentazione CHN elemental analyzer 1106 or by E+R Microanalytical Laboratory, Inc.

Gel permeation chromatography measurements were performed on a Waters Associates GPC II instrument using 500, 10^4, 10^5, and 10^6 Å μ-Styragel columns and UV or refractive index detectors. 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 [$(n\text{-}Bu)_4NBr$], a column temperature of 30 °C, and a sample injection volume of 0.05−0.1 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 g/mol.

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 varied, depending on the polymer, but was typically between −100 and +200 °C. Each sample was heated through the range at least twice.

Contact angle measurements were taken on films cast on glass slides from CH_2Cl_2 solutions of the polymers. Measurements were performed by adding a drop (0.10 mL) of doubly distilled water to each film. A Rame-Hart NRL Model 100

contact angle goniometer was used to obtain θ_Y, θ_R, and θ_A. Sessile drop measurements were performed to obtain θ_Y. Advancing angles were obtained by increasing the volume of the drop across the surface, and receding angles were obtained by decreasing the volume of the drop on the surface of the polymer. Measurements were taken at least 10 times to minimize the effect of surface roughness.

The density of the polymers was measured at 25 °C by suspending a piece of polymer in a solution of water, calcium nitrate, and ethanol. The density of the solution was varied by addition of calcium nitrate or ethanol until the polymer neither floated nor sank. Then the polymer was removed and part of the solution was transferred into a preweighed volumetric flask. The volumetric flask was then weighed again to obtain the mass of the solution. The densities were used to calculate free volume: $(V_F) = (V_T - V_0)/V_T$, where V_T is the specific molar volume at temperature T [$V_T = M_w$/density] and V_0 is 1.3 times[17] the van der Waals volume calculated by the group contribution method of Bondi.[18]

Preparation of Phosphoranimines 4 and 5, $Me_3SiN{=}P(OPh)(CH_3)(R)$. The following preparation is an adaptation of two published methods.[6,19] A 5 L, three-neck flask, equipped with an N_2 inlet, a mechanical stirrer, and a pressure equalizing addition funnel with a rubber septum, was charged with hexamethyldisilazane (typically, 0.8 mol) and diethyl ether (500 mL). The solution was cooled to 0 °C, and an equal molar portion of *n*-BuLi was added. After warming to room temperature, the solution was cooled to −78 °C and an equimolar amount of PCl_3 was added. This mixture was allowed to warm to room temperature and stirred for 2 h. A 1 equiv amount of (*n*-alkyl)MgX was transferred to the addition funnel by a cannula and added dropwise to the reaction mixture that was now cooled with an ice bath. This mixture was allowed to stir while being warmed to room temperature over 2 h. The ice bath was reapplied, and 1 equiv of MeMgBr was added dropwise. After standing overnight, the mixture was filtered under nitrogen through a fritted filter. The salts were washed with hexane three times. The filtrate and washings were combined and placed into a clean 5 L, three-neck flask with an N_2 inlet, magnetic stirrer, stopper, and rubber septum. Hexachloroethane (0.95 mol) dissolved in diethyl ether (600 mL) was then added via cannula to the phosphine solution at 0 °C, and this solution of *P*-chlorophosphoranimine was allowed to stir for 3 h.

In a separate reaction, LiOPh was prepared in a 3 L, three neck flask equipped with a stopper, a magnetic stirrer, a pressure equalizing addition funnel with a rubber septum, and an N_2 inlet. The flask was charged with 0.96 equiv (relative to PCl_3) of phenol and 500 mL of diethyl ether. The solution was cooled to −78 °C and 1 equiv (relative to phenol) of *n*-BuLi was added dropwise over 1.5 h. After the reaction was complete, the solution was allowed to warm to room temperature for 20 min and was then added to the phosphoranimine solution (which was at 0 °C) via cannula. After the solution was stirred overnight, the *P*-phenoxyphosphoranimine was isolated by decanting the liquid from the salts, washing the salts with hexane three times, and removing the solvent under reduced pressure from the combined decantate and hexane washings. The phosphoranimine was further purified by distillation under vacuum on a 5 cm column. An NMR spectrum of the distilled phosphoranimine showed a mixture of dimethyl-substituted, dialkyl-substituted, and the desired methyl/alkyl-substituted phosphoranimines. Pure methyl-/alkylphosphoranimines were separated by several additional distillations of the phosphoranimines at a higher pressure on a 20 cm column (Table 1).

Preparation of 8−10, $Me_3SiN{=}P(OPh)(CH_2E)(R)$. In a typical procedure, a 500 mL, two-necked flask, equipped with an N_2 inlet, a magnetic stirrer, and a rubber septum, was charged with phosphoranimine **4** (6.6 g, 23.3 mmol) and ether (45 mL). The solution was cooled to −78 °C, and an equal molar quantity of *n*-BuLi (9.4 mL) was added by syringe. After the mixture was stirred for ca. 30 min, Me_3SiCl was added by syringe, and the mixture was warmed to room temperature and stirred overnight. Then hexane was added (ca. 45 mL) to the reaction flask, and the mixture was filtered under N_2. Following solvent removal, the new phosphoranimines were purified by distillation at reduced pressure (Table 1).

Preparation and Derivatization of $[Ph(Et)PN]_n$ (1). The phosphoranimine, $Me_3SiN{=}P(OPh)(Ph)(Et)$, was prepared by a procedure analogous to that described for **4** and **5**. It was distilled into an ampule and degassed. The ampule was sealed under vacuum and heated at 190 °C for 2 weeks. The polymer was purified by precipitation from CH_2Cl_2 or THF into hexane with subsequent drying in a vacuum oven at 75 °C for 2 days. Yield: 88%.

Then 5 mmol of **1** was placed in a 100 mL, two-necked flask and dried at 125 °C in a vacuum oven for 2 days. The flask was equipped with an N_2 stopcock inlet adapter, a magnetic stirrer, and a rubber septum, and ca. 10 mL of THF was added to dissolve the polymer. After the solution cooled to 0 °C, 3.3 mL of 2.5 M *n*-BuLi was added and the solution was stirred for 1 h. The reaction mixture was then recooled to 0 °C and quenched with an equivalent of Me_3SiCl (1.0 mL). After the solution was stirred overnight, the polymer was collected and purified by precipitation into water two times and then into hexane, followed by drying under vacuum at 90 °C for ca. 24 h. ^{1}H NMR: δ −0.4 to +0.2 ($SiMe_3$), 0.6−1.1 (CH_3), 1.1−1.6 (CH_2), 1.6−2.1 (PCH), 6.7−8.3 (Ph). ^{31}P NMR: δ 7.0 (PCH_2CH_3) and 11.5 ($PCHSiMe_3$).

Preparation of $[Me(n\text{-}Bu)PN]_n$ (11) and $[Me(n\text{-}Hex)PN]_n$ (12). A magnetic stir bar was placed in a round-bottom flask with a condenser sealed to it and was preweighed. Then NaOPh (0.1 mol %) was transferred into this reaction apparatus in a glovebag. After the system was heated under a vacuum to increase the surface area of this catalyst, $Me_3SiN{=}P(OPh)(R)(Me)$ that was deemed pure by ^{31}P NMR spectroscopy was distilled directly onto the catalyst. The polymerization flask was removed from the distillation apparatus and equipped with an N_2 stopcock inlet adapter and then evacuated and filled with N_2 three times. After being heated at 180 °C in an oil bath for 5 days, the system was cooled to room temperature. The resulting polymer was purified by vigorous stirring with acetone and with water with subsequent removal of these solvents by decantation. The polymer was dried under vacuum for at least 2 days.

Preparation of $[Me(R)PN]_x[(Me_3SiCH_2)(R)PN]_y$ (15 and 16). Typically, a 100 mL, two-necked flask was charged with approximately 5 mmol of polymer **11** or **12** and heated at 125 °C in a vacuum oven for 2 days. After cooling, the flask was equipped with an N_2 stopcock inlet adapter, a magnetic stirrer, and a rubber septum. Then 10 mL of THF was added to dissolve the polymer. After the solution was cooled to 0 °C, 3.3 mL of 2.5 M *n*-BuLi was added and the solution was stirred at room temperature for 1 h. The reaction mixture was then recooled to 0 °C and quenched with excess Me_3SiCl (ca. 1.0 mL). After this mixture was stirred overnight at room temperature, the polymer was collected, purified by precipitation into water two times, and dried under vacuum at 90 °C (Table 2).

Preparation of $[Me(R)PN]_x[\{(\eta^5{-}C_5H_5)Fe(\eta^5{-}C_5H_4)CH(OH)CH_2\}(R)PN]_y$ (17 and 18). A 100 mL, two-necked flask was charged with approximately 5 mmol of polymer **11** or **12** and was placed in a vacuum oven at 125 °C for 2 days. After cooling, the flask was equipped with an N_2 stopcock inlet adapter, a magnetic stirrer, and a rubber septum. Then THF (10 mL) was added to dissolve the polymer. The solution was cooled to 0 °C, 3.3 mL of 2.5 M *n*-BuLi was added, and the solution was stirred at room temperature for 1 h. The mixture was then recooled to 0 °C, and 1 equiv of ferrocenecarboxaldehyde (0.9 g in 25 mL of THF for **11**; 1.1 g for **12**) was added to the reaction mixture. After the mixture was stirred overnight, the reaction was quenched with 1 mL of saturated NH_4Cl and stirred for 1 h. The polymer was purified by precipitating into water from THF twice, followed by Soxhlet extraction with acetone overnight (Table 2).

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