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Fluorinated Polyphosphazenes Derived from Poly(methylphenylphosphazene) and Fluorinated Aldehydes and Ketones

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ABSTRACT: A series of fluorinated polyphosphazenes $[Me(Ph)PN]_x\{[RR'C(OH)CH_2](Ph)PN]\}_y$ (**3**, R = C_6H_5, R′ = CF_3; **4**, R = R′ = CF_3; **5**, R = $C_6H_4CF_3$, R′ = H; **6**, R = C_6H_5, R′ = CF_2CF_3; **7**, R = C_6F_5, R′= CH_3; and **8**, R = C_6F_5, R′ = H) were prepared by deprotonation of a portion of the methyl groups in $[Me(Ph)PN]_n$ (**1**), with *n*-BuLi, followed by treatment with fluorinated aldehydes and ketones, RR′C(=O). The range of substitution {i.e., $[y/(x + y)](100\%)$} was between 5% and 50% as determined by elemental analysis. Partially fluorinated polymer **10** was prepared by replacing the OH group in the related, non-fluorinated polymer, $[Me(Ph)PN]_x\{[Me_2C(OH)CH_2](Ph)PN\}_y$ (**9**), with fluorine using (diethylamino)sulfur trifluoride. The new polymers were characterized by ^1H, ^{13}C, and ^{31}P NMR spectroscopy, IR spectroscopy, elemental analyses, and gel permeation chromatography. The glass transition temperatures as determined by differential scanning calorimetry ranged from 38 to 94 °C. Aqueous contact angle measurements (77–92°) indicated that the surfaces of the new polymers were more hydrophobic than that of the parent polymer, **1**.

Introduction

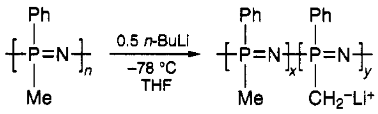
The incorporation of fluorine moieties into both organic and inorganic polymer systems may confer hydrophobicity, alter solubility, enhance thermal, chemical, and oxidative stability, reduce adhesion, improve biocompatibility, and increase gas permeability.[1] The fluoroalkoxy substituted polyphosphazenes such as $[(CF_3CH_2O)_2PN]_n$ and $\{(CF_3CH_2O)[HCF_2(CF_2)_xCH_2O]PN\}_n$[2] are notable examples of fluoropolymers with unique and useful properties. The analogous polyphosphazenes with fluoroalkyl groups attached directly to the polymer backbone by P–C linkages are, however, not readily accessible either by the substitution of $[Cl_2PN]_n$[3] or via condensation polymerization of silicon–nitrogen–phosphorus compounds.[4]

In a recent paper, we reported the preparation of polyphosphazenes with fluoroalkyl groups attached to the backbone phosphorus through CH_2Si spacer groups.[5] This approach involved the deprotonation of the methyl substituents in preformed $[Me(Ph)PN]_n$, followed by reaction with a series of chlorosilanes, RMe_2SiCl, where R = $(CH_2)_2CF_3$, $(CH_2)_2(CF_2)_5CF_3$, and $(CH_2)_2(CF_2)_7CF_3$. These polymers, $\{[Me(Ph)PN]_x[(RMe_2SiCH_2)(Ph)PN]_y\}_n$, are significantly less hydrophilic than the parent polymer $[Me(Ph)PN]_n$, (**1**), as demonstrated by contact angles of 97–101° relative to 73° for **1**. Moreover, recent studies of these fluorinated systems indicate enhanced gas permeabilities relative to the parent polymer **1**.[6] The glass transition temperatures are, however, relatively low (−20 to 39 °C), which often limits the structural integrity of films of these polymers.

In this study, we report the synthesis and characterization of a new series of fluorinated polyphosphazenes derived from $[Me(Ph)PN]_n$ and fluorinated aldehydes and ketones. This method is a simple, one-pot reaction that affords polymers with both fluoro and alcohol side groups. The utility of the method and the significantly altered thermal stabilities, glass transition temperatures, and hydrophobicities of these new fluorinated materials are discussed.

Results and Discussion

The intermediate polymer anion, **2**, that is formed by deprotonation of methyl groups in poly(methylphenylphosphazene), $[Me(Ph)PN]_n$ (**1**) (eq 1), has been used



$$\left[\overset{Ph}{\underset{Me}{P}}=N\right]_n \xrightarrow[-78\,^\circ C,\ THF]{0.5\ n\text{-}BuLi} \left[\overset{Ph}{\underset{Me}{P}}=N\right]_x\left[\overset{Ph}{\underset{CH_2^-Li^+}{P}}=N\right]_y \qquad (1)$$

1 **2**

to prepare new polyphosphazenes with a variety of functional groups attached to the phosphazene backbone. In addition to reactions with chlorosilanes[5,7] and other simple halides (e.g., MeI,[8] Ph_2PCl, Br_2[9]), the anion has provided routes to graft copolymers via anionic polymerization[10] and to carboxylic acid, salt, and ester derivatives by reaction with CO_2.[11] One of the most useful reactions of **2** is with simple aldehydes and ketones, RR′C(=O), which, upon quenching with NH_4Cl, yield alcohol functionalized polymers $[Me(Ph)PN]_x\{[RR'C(OH)CH_2](Ph)PN]\}_y$, where R and R′ are simple alkyl and aryl groups as well as ferrocenyl and thiophenyl groups.[12] The straightforward nature of this reaction and the commercial availability of a variety of fluorinated aldehydes and ketones suggested that this approach would be applicable to the synthesis of new fluorinated polyphosphazenes.

In this study, the anion intermediate **2** was prepared by addition of 0.5 equiv of *n*-BuLi to a ca. 1.0 M solution of $[Me(Ph)PN]_n$ in THF at −78 °C (eq 1). After stirring at −78 °C for ca. 1.5 h to assure complete reaction of the *n*-BuLi, the fluorinated aldehydes or ketones were added to the solution and the reaction was subsequently quenched with a saturated solution of ammonium chloride (eq 2). For polymers **3**, **4a**, **5**, **6**, **7**, and **8a**, 0.5

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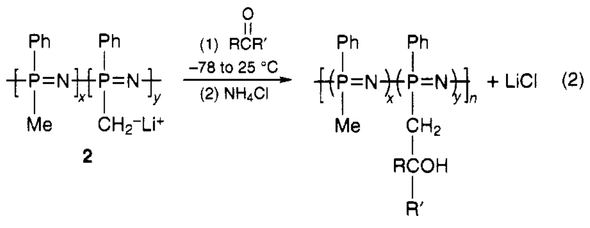


(2)

2

3–8

	3	4	5	6	7	8
R	C_6H_5	CF_3	$C_6H_4CF_3$	C_6H_5	C_6F_5	C_6F_5
R′	CF_3	CF_3	H	CF_2CF_3	CH_3	H

equiv of both n-BuLi and the carbonyl compounds were used to facilitate 50% substitution {i.e., $[y/(x+y)](100\%) = 50\%$}. For **4b**, **8b**, and **8c**, stoichiometries were aimed toward 20%, 25%, and 20% substitution, respectively. However, the actual degrees of substitution, as discussed below, were sometimes different.

The new polymers were purified by precipitations from THF into water and into hexane. Upon drying under vacuum, isolated yields were between 38% and 70%. With the exception of **8**, all of these fluorinated alcohol derivatives were soluble in common solvents such as THF, $CHCl_3$, and CH_2Cl_2. Polymers **8a** and **8b**, where theoretical substitution values were 50% and 25%, respectively, were insoluble in these solvents and in fluorinated THF. However, polymer **8c**, where the theoretical degree of substitution was 20%, was slightly soluble in THF and chlorinated hydrocarbons.

The composition of the new polymers was determined by both NMR and IR spectroscopy (Table 1) and by elemental analysis (Table 2). The ^1H NMR spectra generally contained broad signals in the aliphatic and aromatic regions, but integration was not particularly useful for determining degrees of substitution. The ^{19}F NMR spectra of polymers **3**–**6** contained characteristic signals for the CF_3 groups (δ −64.2 to −44.8). Two signals were observed in the ^{31}P NMR spectra of each of the fluorinated alcohol derivatives. The $^{13}C\{^1H\}$ NMR spectra, however, were the most informative. These spectra contained distinct signals for the PCH_2, PCH_3, and PPh carbons, as well as characteristic downfield resonances for the CF carbons. The presence of the PCH_2 signal clearly indicated that substitution of the polymer had occurred. In all but one case, resonances for the COH carbon were not observed, presumably because this signal is difficult to detect due to coupling to fluorine. The exception was polymer **5** (δ 66, COH) where the fluorine substituents were substantially distant from the COH carbon. The IR spectra of these polymers confirmed the incorporation of the fluorine-containing groups in that a new signal for the O–H stretch was observed between 3100 and 3400 cm^{-1} for each of these polymers. No residual C=O signals from unreacted aldehydes or ketones were found except in polymer **7**. In this case, a reasonably strong band was observed at 1800 cm^{-1}. This suggests that unreacted pentafluoroacetophenone remained in the sample and is consistent with the low degree of substitution (Table 2).

Elemental analyses (Table 2) were ultimately used to determine the degrees of substitution in these polymers. For polymers **3**, **4a**, **5**, and **6**, the substitution ranged from ca. 40% to 50%, which compares favorably with the theoretical value of 50% based on the reaction stoichiometry. Similarly, for **4b** the degree of substitution was ca. 15% (theoretical: 20%). For **7** and **8c**, however, the actual degrees of substitutions were considerably less than the 50% and 20% expected on the basis of reaction stoichiometries. This may be due, in part, to the decreased solubility imparted to the system by the C_6F_5 groups. Moreover, the low degree of substitution in polymer **7**, which was prepared from pentafluoroacetophenone, $(C_6F_5)C(=O)CH_3$, is consistent with other reactions of anion **2** and of organolithium reagents with methyl ketones. The protons of the methyl group are sufficiently acidic to react with such anions, thus competing with the reaction at the carbonyl carbon. This effect, which was previously observed to a lesser degree in the reactions of **2** with nonfluorinated acetophenone,[12] is enhanced for pentafluoroacetophenone because of the increased acidity of the methyl protons in this ketone.

Table 1. Representative NMR Spectroscopic Data[a]

		δ		
polymer	signal	^1H	$^{13}C^b$	^{31}P
3	PCH_3	0.8–2.0	20.9[c]	4.1, 5.6
	PCH_2	2.0–3.1	33.7[c]	
	CF_3		122.0	
	COH	4.8		
	C_6H_5	6.5–8.5	127.6–130.2, 137.0	
4	PCH_3	0.8–1.9	20.6[c]	1.4, 5.9
	PCH_2	2.1–2.5	31.2[c]	
	CF_3		120.9	
	COH	3.7		
	C_6H_5	6.9–8.1	125.9–137.2	
5	PCH_3	0.9–2.5	21.3 (85.5)	−4.2, 4.1
	PCH_2	0.9–2.5	43.6 (56.4)	
	C(H)OH	4.7	66.5	
	CF_3		125.0	
	C_6H_4, C_6H_5	6.3–8.5	126.5–139.7, 149.0	
6	PCH_3	0.8–3.0	20.6[c]	4.1, 12.8
	PCH_2	0.8–3.0	38.7[c]	
	COH			
	CF_2CF_3		110.3–125.0	
	C_6H_5	6.1–8.6	128.1–132.1, 138.1	
7	PCH_3	0.8–2.0	22.0 (85.6)	−5.3, 1.5
	PCH_2	0.8–2.0	52.6 (69.5)	
	CH_3	0.8–2.0	32.5	
	COH	3.2		
	C_6F_5		130.3–140.7	
	C_6H_5	7.1–8.0	130.3–140.7	
	C=O		202.9	
8	PCH_3	0.9–1.9		1.6, 0.5
	PCH_2	2.1–3.0		
	C(H)OH			
	C_6F_5			
	C_6H_5	7.1–8.0		
10	PCH_3	1.3–2.5	19.6[c]	1.4
	PCH_2	1.3–2.5	44.1[c]	
	$C(CH_3)_2$	1.3–2.5	34.6	
	CF		110.9	
	C_6H_5	7.1–7.2	124.5–135.4	

[a] Chemical shifts relative to Me_4Si for ^1H and ^{13}C NMR spectra, H_3PO_4 for ^{31}P NMR spectra, and $C_6H_5CF_3$ (corrected to $CFCl_3$) for ^{19}F NMR spectra. [b] J_{PC} in parentheses (Hz). [c] Broad signal.

The molecular weights of the soluble fluorinated polymers were measured by gel permeation chromatography (Table 3). In general, these were somewhat higher than the molecular weight of the parent polymer, **1**, as might be expected for the incorporation of the fluorinated groups.

Differential scanning calorimetry was used to determine the glass transition temperatures (T_g) of the new polymers. For all of these systems, the T_g's were higher than that of the parent polymer **1** (T_g = 37 °C). They ranged from 38 to 100 °C and are comparable to the T_g's of the nonfluorinated polyphosphazene alcohol

Table 2. Physical, Elemental Analysis, Thermal Analysis, and Contact Angle Data

			elemental anal.[c]			thermal anal.		contact angle[h]
polymer	yield[a] (%)	substitution[b] (%)	% C	% H	% N	T_g[d] (°C)	T_{onset}[e,f] (°C)	θ[i] (deg)
3	60	45	58.47 (59.09)	4.89 (4.79)	6.78 (6.50)	94	210 (227)	
4a	70	42	47.96 (47.96)	4.21 (3.90)	6.67 (6.77)	54	217 (226)	92 (92) [68]
4b	47	15	55.05 (55.23)	5.01 (4.98)	8.44 (8.64)			90 (91) [77]
5	66	50	58.67 (58.93)	4.69 (4.72)	6.15 (6.25)	81		77 (80) [56]
6	63	50	54.13 (55.43)	4.16 4.25)	5.53 (5.62)	45		92 (97) [66]
7	44	10	59.91 (59.25)	5.79 (5.29)	9.40 (8.86)	38		81 (82) [65]
8c	38	5	60.74 (60.09)	5.92 (5.52)	9.80 (9.53)			
10	63	30	60.94 (61.16)	5.99 6.17)	9.38 (9.03)	41	337[g] (369)	

[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. [c] Calculated values are in parentheses. [d] T_g for parent polymer **1** is 37 °C. [e] T_{onset} for parent polymer **1** is 390 °C. [f] T_{50} is in parentheses. [g] T_{onset} for **9** is 305 °C. [h] Young's angle for parent polymer **1** is 73°. [i] Young's angle, θ_Y, with advancing angle (θ_A) in parentheses and receding angle [θ_R] in brackets.

Table 3. Molecular Weight Data

polymer	M_w[a]	M_n[b]	M_w/M_n[c]
3	400 000	130 000	3.20
4a	245 000	102 000	2.40
4b	177 000	103 000	1.73
5	448 000	265 000	1.70
6	230 000	163 000	1.40
7	400 000	130 000	3.23
8	250 000	120 000	2.10
10	94 000[d]	34 500	2.75

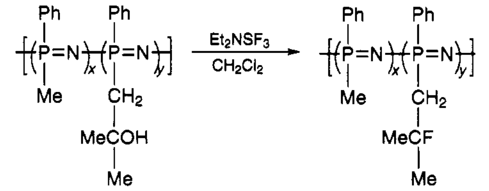
[a] M_w of the parent polymer, $[Me(Ph)PN]_n$ (**1**), is 140,000. [b] M_n of the parent polymer is 40 000. [c] M_w/M_n of the parent polymer is 3.4. [d] M_w for the alcohol-substituted polymer, **9**, from which **10** was made, was 180 000, and M_w for $[Me(Ph)PN]_n$ used to prepare **9** was 140 000.

derivatives reported earlier.[12] In both cases, these values are clearly influenced by the presence of the OH group, which reduces torsional backbone mobility via hydrogen bonding. For polymers **3** and **5**, the relatively high T_g's of 94 and 81 °C also reflect the presence of relatively large aromatic groups, as compared to **4**, where only CF_3 substituents are present and the T_g is 54 °C. The T_g of **6** (45 °C), however, is curiously low since this also contains an aromatic group. This lower value could be partially attributed to the increased length of the side group, which is essentially four atoms long [i.e., $PCH_2C(OH)(R)CF_2CF_3$]. The related silyl[5] and ester[13] systems with five and seven atom side groups have T_g values of slightly less than 40 °C. Generally, longer side groups increase the free volume of the system, thus facilitating the backbone mobility. The low degree of substitution in **7** and the presence of unreacted ketone detected in the IR spectrum account for the low T_g value for this polymer.

Thermogravimetric analysis indicated that the onsets of decomposition of these derivatives are significantly lower than that of the parent polymer **1**, despite the presence of the fluorinated substituents. In fact, with onsets of decomposition ranging from 210 to 250 °C in air, these polymers are also less thermally stable than nonfluorinated alcohol derivatives such as $[Me(Ph)PN]_x\{[RR'C(OH)CH_2](Ph)PN]\}_y$ (T_{onset} = 305 °C). This may be due to the relative ease of decomposition initiated by loss of water from the $PCH_2(OH)$ moieties.

Relative to the parent polymer $[Me(Ph)PN]_n$ (**1**), where Young's contact angle is ca. 73°, the new fluorinated polymers were somewhat more hydrophobic. Polymers **4** and **6** had the highest water contact angles with values of ca. 90°. The different degrees of substitution for **4a** and **4b** had little effect on this value. Polymer **7** had a relatively high contact angle of 81° in view of the fact that only 10% of the backbone units were substituted with the pentafluorophenyl group. This may reflect the high fluorine content of this substituent. Polymer **5**, on the other hand, was less hydrophobic (77°) than expected for incorporation of the (trifluoromethyl)phenyl group into half the backbone units.

A second part of this study involved the incorporation of fluorine into the polyphosphazenes by fluoride displacement of the OH groups. The reagent DAST ((diethylamino)sulfur trifluoride, Et_2NSF_3)) was chosen for both its ease of handling and generally mild reaction conditions.[14] Although attempts to fluorinate new polymers such as **3** and **4** were not successful, the OH group in the related non-fluorinated alcohol derivative, $[Me(Ph)PN]_x\{[Me_2C(OH)CH_2](Ph)PN]\}_y$ (**9**),[12] was readily replaced by fluorine (eq 3). Treatment of a CH_2Cl_2 solution of **9** with DAST at −78 °C, with subsequent warming to room temperature and appropriate workup, afforded the new polymer $[Me(Ph)PN]_x\{[Me_2C(F)CH_2](Ph)PN]\}_y$ (**10**). Although the ^1H NMR spectrum of **10** provided little information supporting fluorination, the $^{13}C\{^1H\}$ NMR spectrum showed a characteristic signal



9 **10**

(3)

at δ 110 for the CF carbon (Table 1). The ^{19}F NMR spectrum was not straightforward. Elemental analysis (Table 2) was also not particularly useful since the theoretical C, H, and N compositions of the OH-substituted precursor **9** and the F-substituted product **10** are not substantially different. Thus, the most conclusive spectral evidence supporting the replacement of the OH-group by fluorine was provided by IR spectroscopy. The strong O-H stretching frequency in the spectrum of **9** was not present in the IR spectrum of **10**. Furthermore, the T_g changed from 55 °C for **9** to 41 °C for the fluorinated polymer **10**. This decrease is expected since hydrogen bonding is no longer possible in the fluorinated derivative. TGA indicated a small increase in the onset of decomposition from 305 °C for **9** to 337 °C for the fluoro derivative **10**.

In summary, the fluorinated derivatives of poly(methylphenylphosphazene) are accessible via deprotonation–substitution reactions involving fluorinated aldehydes and ketone electrophiles. The fluorinated alcohol groups impart increased glass transition temperature, decreased thermal stability, and enhanced hydrophobicity relative to the simple parent polymer. In general, this approach to incorporation of fluorine-containing groups results in somewhat less hydrophobic surfaces than the attachment of fluoroalkyl silyl groups,[5] but it provides materials with significantly higher glass transition temperatures.

Experimental Section

Materials. Poly(methylphenylphosphazene), ($[Me(Ph)PN]_n$, **1**)[15] and $[Me(Ph)PN]_x\{[Me_2C(OH)CH_2](Ph)PN]\}_y$ (**9**)[12] were prepared by the published procedures and were dried under vacuum at 50 °C for at least 20 h. Tetrahydrofuran was freshly distilled from Na/benzophenone; hexanes, triethylamine, and dichloromethane were distilled from calcium hydride prior to use. The following reagents were purchased from commercial sources and were used without further purification: *n*-BuLi (2.5 M hexane solution), 2,2,2-trifluoroacetophenone, pentafluorobenzaldehyde, hexafluoroacetone, 2′,3′,4′,5′,6′-pentafluoroacetophenone, pentafluoroethyl phenyl ketone, 4-(trifluoromethyl)benzaldehyde, ammonium chloride, and (diethylamino)sulfur trifluoride (DAST).

Equipment. The ^{1}H, ^{13}C, ^{31}P, and ^{19}F NMR spectra were recorded on an IBM WP-200SY FT NMR spectrometer in $CDCl_3$. Positive ^{1}H NMR and ^{13}C NMR chemical shifts are downfield from the external reference Me_4Si, while positive ^{31}P NMR shifts are downfield from the external reference H_3PO_4. The ^{19}F chemical shifts are referenced to $C_6H_5CF_3$ and are corrected to $CFCl_3$. Elemental analyses were performed on a Carlo Erba Strumentazione CHN Elemental Analyzer 1106. The size-exclusion chromatography (SEC) measurements were performed on a Waters Associates GPC instrument with either a Maxima or Nelson Analytical data handling system using 500-, 10^4-, 10^5-, and 10^6-Å μStyragel columns. The SEC operating conditions consisted of a mobile phase of THF containing 0.1% $(n\text{-Bu})_4N^+Br^-$, a flow rate of 1.5 mL/min, a temperature of 30 °C, and a sample size of 0.05 mL of 0.1% solution. The system was calibrated with a series of narrow molecular weight polystyrene standards in the range of ca. 10^3–10^6. IR spectra were recorded on a Perkin-Elmer 710B infrared spectrometer. The samples were prepared as thin films by spreading a $CDCl_3$ solution between two KBr plates. Differential scanning calorimetry (DSC) measurements were made on a Du Pont Model 910 instrument equipped with a DuPont 1090 thermal analyzer data station or TA Operating Software Module and Data Analysis data station. Measurements were made under nitrogen against an aluminum reference from −40 to 150 °C using ca. 10 mg samples and heating at a rate of 10 °C/min. Each experiment was repeated at least 3 times on the same sample. Thermal gravimetric analyses (TGA) were performed on a DuPont TGA Model 951 instrument equipped with a DuPont 1090 thermal analyzer data station. The samples (ca. 10 mg), which were loaded on a platinum pan, were heated at rate of 10 °C/min from ambient temperature to 600 °C under a constant flow of air. 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 using doubly distilled water with drops of size 15 μL. In addition to the Young's contact angle (θ_Y), advancing (θ_A) and receding (θ_R) contact angles were also measured. The angles θ_A and θ_R are defined as contact angles when water is added to and withdrawn from the film surface, respectively. To minimize the effects of surface roughness, at least 10 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 and 5–7. Typically, a 250 mL, three-necked flask, equipped with a magnetic stirrer, N_2 inlet, and a septum, was flame-dried under vacuum and charged with 7.3 mmol (1.0 g) of $[Me(Ph)PN]_n$ that had been dried as above. Then 10 mL of THF was added to dissolve the parent polymer. The solution was cooled to −78 °C and stirred at this temperature for 30 min. Then *n*-BuLi (1.6 mL, 2.5 M) was added via syringe to initiate a polymer anion, and the solution was stirred for 1 h at −78 °C. 2,2,2-Trifluoroacetophenone (0.6 mL, 4.1 mmol) was added via syringe to the anion and the mixture was allowed to warm slowly to room temperature and stirred for at least 2 h before being quenched with 5 mL of a saturated solution of NH_4Cl. The mixture was then poured into H_2O (ca. 100 mL), and the crude polymer was precipitated. This crude polymer, **3**, was dissolved in ca. 10 mL of THF again and reprecipitated by slow addition of the solution to hexane. This process of dissolution and precipitation into hexane was repeated at least once. After precipitation, the polymer was dried under a vacuum at 60 °C. Polymers **5–7** were prepared according to the same procedure by using 4-(trifluoromethyl)benzaldehyde, pentafluorethyl phenyl ketone, and pentafluoroacetophenone, respectively. In the preparation of **7**, the reaction mixture gelled immediately when pentafluoroacetophenone was added to the anion. After the mixture was stirred for a couple of hours, the gel disappeared and a good solution formed. The IR spectrum of each of these polymers contained a broad signal for the OH group at 3300–3500 cm^{-1}. No signals for the carbonyl moiety were observed for polymers **3**, **5**, and **6**, but a C=O signal was observed for polymer **7**, indicating the presence of unreacted ketone. Other characterization data are given in Tables 1–3.

Preparation of Polymers 8a–c. Polymer **8a** was prepared by adding a solution of pentafluorobenzaldehyde (e.g., 0.8 g, 4.1 mmol for **8a**) in 10 mL of THF to the anion. An insoluble gel formed immediately, but unlike polymer **7**, polymers **8a** and **8b** remained insoluble even after quenching the reaction with aqueous NH_4Cl. Polymer **8c** was only slightly soluble in common solvents such as THF and CH_2Cl_2. Thus, no attempts at further purification were made.

Preparation of Polymer 4. The polymer anion was prepared as described above using 1.5 g (11.0 mmol) of $[Me(Ph)PN]_n$ and *n*-BuLi (2.2 mL, 2.5 M). After stirring for 1 h at −78 °C, the mixture was cooled to −196 °C and hexafluoroacetone (5.5 mmol, measured by expanding into a vacuum system of known volume using a pressure calculated by gas laws) was condensed into the mixture. When the transfer was complete, the mixture was allowed to warm to room temperature. Workup procedures were the same as for polymer **3**, including quenching with 5 mL of saturated aqueous solution of NH_4Cl, precipitation of the reaction mixture in H_2O, reprecipitation from THF into hexane, and drying under vacuum. IR spectroscopy data included a broad OH signal between 3100 and 3400 cm^{-1} as well as the typical broad signal for the P=N moiety at 1200–1300 cm^{-1}.

Preparation of Polymer 10. A 250 mL, three-necked flask, equipped with a magnetic stirrer, N_2 inlet, and septum, was flame-dried under vacuum. Then 5 mL of CH_2Cl_2 was added to the flask, and the solution was cooled to −78 °C.

DAST (0.96 g, 6.0 mmol) and then Et_3N (0.66 g, 7.0 mmol) were added to the solution via syringe. This mixture was stirred at −78 °C for ca. 10 min, and then a solution of $\{[Me(Ph)PN]_{0.7}\{[Me_2C(OH)CH_2](Ph)PN\}\}_{0.3}$ (**9**) (1.0 g, 6.0 mmol) in 10 mL of CH_2Cl_2 was added slowly via an addition funnel. When addition was complete, the mixture was allowed to warm to room temperature and stirred for 1 h. The color changed from orange to pink, and the flask became very warm, indicating an exothermic reaction. All volatile materials were removed under vacuum. The polymer was dissolved in THF and precipitated into H_2O. Subsequent purification involved dissolution in CH_2Cl_2 and precipitation into hexanes at least two times. The final product was dried overnight in a vacuum oven at 60 °C, yielding a pink-yellow solid (see Tables 1−3). IR: 1200 cm^{-1} (br, P=N).

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References and Notes

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