separated from **2** was isolated. The yield and M_n of these poly(St)'s were found to increase with reaction time, as shown in Figure 2, indicating that these graft copolymerizations also proceeded via a living radical mechanism similar to the case of BDA.

Moreover, the graft polymer **2** was observed to act as a photoiniferter of radical polymerization of methyl methacrylate (MMA, M_2), as shown in Table I. After extraction of homopoly(MMA) and hydrolysis of the resulting graft–block copolymer attached to PSG (**3**), a block copolymer of poly(St) with poly(MMA) (**4**) was isolated by extraction of benzene. Yield and molecular weight increased with reaction time.

From GPC measurement, however, the block copolymer **4** thus obtained was observed to contain ca. 10% homopoly(St), even after a prolonged reaction time (20 h). These results were in agreement with those observed for the block copolymer synthesis using DC photoiniferters.[4,6] The formation of the homopoly(St) might be due to part of the DC iniferter groups at the grafted poly(St) chain end in **2** being destroyed during polymerization, as a result of the previously reported[2] deviations from ideal living radical polymerization.

To avoid homopoly(St) formation, TD (0.03 mol/L), which can dissociate into *N,N*-diethyldithiocarbamate radicals,[1] was added to the photopolymerization system of St with **1** (see Figure 2 for conditions). When **2** thus obtained was used as a PSG photoiniferter for the polymerization of MMA, followed by extraction and hydrolysis of the resulting graft–block copolymers (**3**), a block copolymer of poly(St) with poly(MMA) which contained only a trace of homopoly(St) was isolated. The block copolymer **4** thus obtained was confirmed by GPC to be pure and free from homopolymer.

The graft–block copolymer consisting of St–MMA blocks attached to PSG (**3**), obtained by the polymerization of MMA in the presence of **2** and TD, was confirmed to induce further photopolymerization, leading to pure PSt-*b*-PMMA-*b*-PSt triblock copolymers. Moreover, tricomponent triblock copolymer, PSt-*b*-poly(*p*-chlorostyrene)-*b*-PMMA and PSt-*b*-PMMA-*b*-poly(methyl acrylate), were synthesized by a similar technique.

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Registry No. PSt, 9003-53-6; BDA, 3052-61-7; (St)·(MMA) (copolymer), 25034-86-0; KDC, 686-07-7.

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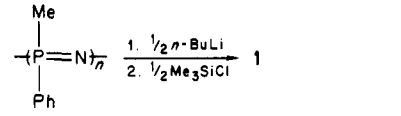
Silylated Derivatives of Poly[methylphenylphosphazene][1]

The preparation of polyphosphazenes with alkyl and aryl substituents directly attached to phosphorus by carbon–phosphorus bonds has been accomplished by thermolysis of *N*-silylphosphoranimines, $Me_3SiN{=}P(OCH_2CF_3)RR'$, where R, R′ = Me, Et, Ph[3]. With the availability of these simple polymers, we have now begun to investigate synthetic approaches to other polyphosphazenes with more diverse substituents attached to the backbone via P–C bonds. These new systems could possess such useful properties as higher thermal stability, unusual solubility characteristics, and enhanced mechanical and surface properties and might also contain reactive sites for cross-linking, binding of transition metal catalysts, or interaction with biological systems.

We are investigating three methods of altering the substitutents at phosphorus. These are (1) synthesis of new primary phosphine precursors, $(Me_3Si)_2NPRR'$, where R and R′ are more complex alkyl and aryl moieties, (2) alteration of R and R′ in the immediate *N*-silylphosphoranimine precursors, $Me_3SiN{=}P(OCH_2CF_3)RR'$, and (3) alteration of R and R′ in preformed poly(alkyl/arylphosphazenes) such as $[Ph(Me)P{=}N]_n$. We report here our first results related to the latter approach. In these cases, a methyl group attached to the P–N backbone is the site of derivatization.

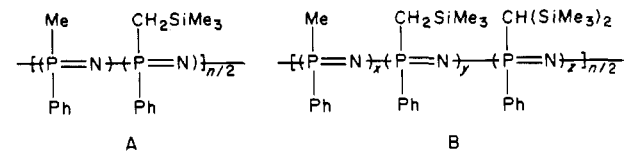
Methyl groups attached to phosphorus in both cyclic phosphazenes[4] and in *P*-methyl-*N*-silylphosphoranimines[5,6] have been deprotonated with alkyllithium reagents. In this study we found that a portion of the methyl groups in poly[methylphenylphosphazene][3b] can be deprotonated by *n*-BuLi. When a 0.6–1.0 M solution of $[Ph(Me)PN]_n$ in THF at −78 °C was treated with 0.5 equiv of *n*-BuLi, stirred for 1.5 h, and quenched with 0.5 equiv of Me_3SiCl (eq 1), a new polymer[7] **1** was obtained. Elemental analysis



(1)

(Table I) of **1** indicated that complete reaction had taken place, i.e., that 0.5 equiv of Me_3Si groups were incorporated into the polymer. More importantly, GPC analysis of **1** showed that no cleavage of the P–N backbone occurred. Due to the incorporation of the Me_3Si group, the $\bar{M}_w$ of **1** (73 000) was, as expected, 26% higher than $\bar{M}_w$ of the parent polymer, $[Ph(Me)PN]_n$ (58 000) (Table II). Furthermore, the molecular weight distributions (Figure 1) of the parent and derivative were virtually identical. Intrinsic viscosity measurements (Table II) also verified the lack of chain degradation. Although cleavage of the P–N backbone occurs when poly(halophosphazenes) are treated with organolithium reagents,[8] the milder conditions of this reaction presumably prevented a similar problem.

The simplest representation of **1** is formula A, the logical product if the reaction proceeds by initial CH_2^- anion formation followed by quenching with Me_3SiCl. The ^{31}P



A B

NMR spectrum of **1**, which consisted of two broad singlets (δ ($CDCl_3$) 4.8, 0.5) of approximately equal intensity, supports formula A. The ^1H and ^{13}C NMR spectra,[9] however, suggested that deprotonation and substitution

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Table I
Analytical Data[a]

polymer	% C	% H	% N
1	58.62 (58.94)	6.85 (6.98)	8.02 (8.09)
3a	59.77 (60.32)	6.92 (6.75)	7.82 (7.82)
3b	59.48 (60.13)	6.75 (6.81)	10.25 (10.52)
3c	56.44 (57.81)	6.82 (6.67)	8.23 (8.43)
4a	59.06 (60.23)	6.29 (6.38)	9.33 (9.24)
4b	59.03 (60.85)	6.25 (6.29)	8.99 (9.10)

[a] Calculated values in parenthesis; analysis performed by Galbraith Laboratories, Inc., Knoxville, TN.

Table II
Viscosity and Molecular Weight Data[a]

polymer	intrinsic viscosity $[\eta]$,[b] cm^3/g	GPC analysis[c] $\bar{M}_w$	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$
1	22.1	73 000	35 000	2.09
	(20.9)	(58 000)	(27 000)	(2.15)
3a	24.5	107 000	38 000	2.82
	(22.2)	(61 000)	(26 000)	(2.35)
3b	27.9	110 000	49 000	2.24
	(22.2)	(61 000)	(26 000)	(2.35)
3c	26.7	88 000	41 000	2.15
	(22.2)	(61 000)	(26 000)	(2.35)
4a	22.8	66 000	30 000	2.20
	(22.2)	(61 000)	(26 000)	(2.35)
4b	23.0	94 000	33 000	2.85
	(22.2)	(61 000)	(26 000)	(2.35)

[a] Values for parent polymer $[Ph(Me)PN]_n$ from which new polymer derivative was prepared are given in parentheses. [b] Measured in THF at 30 °C. [c] Solvent, THF containing 0.1% $(n\text{-Bu})_4NBr$; flow rate, 1.5 mL/min at 30 °C; columns, 10^5, 10^4, 500Å μStyragel; sample size, 40–60 μL, 0.1% concentration; molecular weights based on polystyrene standards and supported by membrane osmometry and light scattering data of simple poly(alkyl/arylphosphazenes).[3c]

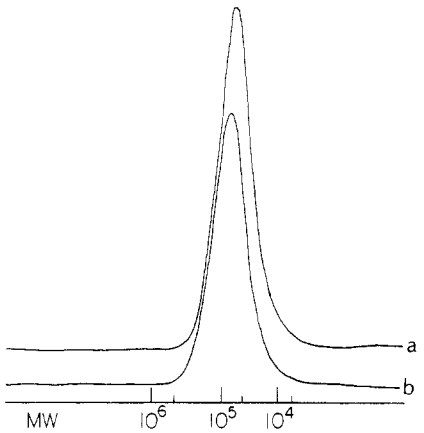
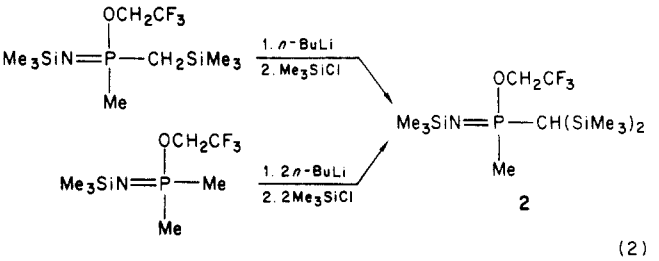


Figure 1. GPC molecular weight distribution for (a) parent polymer $[Ph(Me)P{=}N]_n$ and (b) silylated derivative 1.

occurred more than once on some of the methyl groups, resulting in a polymer with structure B. In addition to the large expected singlet for Me_3SiCH_2 (δ −0.3) observed in the ^1H NMR of 1, additional smaller signals (δ 0.0, 0.1) (ca. 16% as intense) were also present. These signals and a corresponding signal (δ 3.1) in the ^{13}C NMR spectrum, were assigned to the methyl group of a $(Me_3Si)_2CH$ substituent. The intensity of these extra ^1H NMR signals increased significantly when the reaction (eq 1) was carried out under more dilute conditions or by two separate sequential additions (0.25 equiv each) of n-BuLi/Me_3SiCl. In these cases the ^{31}P NMR spectra of the polymers contained three signals (δ 4.5, 2.0, −0.5) and the ^1H and ^{29}Si NMR spectra had signals that were assigned to the $(Me_3Si)_2CH$ group.[10] These assignments correspond to those of a model compound $Me_3SiN{=}PMe[CH(SiMe_3)_2](OCH_2CF_3)$ (2)[6b] and are consistent with a polymer having structure B where z/y is significantly larger than in polymer 1.

The preparation of 2 (eq 2)[6b] confirms that the CH_2 protons in the Me_3SiCH_2 group are more acidic than those on a simple methyl group. These reactions (eq 2) also

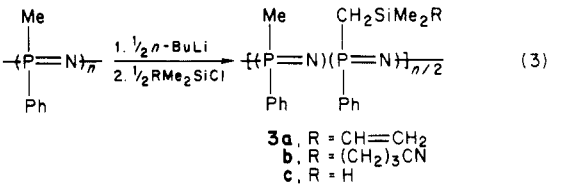


(2)

suggest that a possible reaction sequence for the formation of 1 involves partial reaction of n-BuLi, quenching of the resulting ion with Me_3SiCl to form Me_3SiCH_2 substituents, subsequent reaction of the remaining n-BuLi with the more acidic protons to form $PC(SiMe_3)H^-$ anions, and finally reaction with the chlorosilane to form $(Me_3Si)_2CH$ groups. This pathway should be favored by dilute conditions which would slow the initial anion formation. Alternatively, a proton migration might occur such that a PCH_2^- anion rearranges to the more stable $PC(SiMe_3)H^-$ anion. This is supported by the fact that treatment of $[Ph(Me)PN]_n$ with 0.5 equiv of n-BuLi and then two 0.25-equiv portions of Me_3SiCl at a 1-h interval resulted in a more highly disubstituted $[(Me_3Si)_2CH]$ polymer.

The thermal stability of 1 is promising in that TGA indicated that the onset of decomposition (391 °C) was 32 °C higher than that of the parent compound. Similar enhancement of thermal stability has been observed with P-silylmethylphosphoranimines such as $Me_3SiN{=}PMe(OCH_2CF_3)(CH_2SiMe_3)$.[6b]

We have also prepared related polymers that contain reactive functional groups separated from the backbone by Me_2SiCH_2 spacer groups. A reaction sequence analogous to eq 1 was used with substituted chlorosilanes acting as the quenching reagents (eq 3). As discussed above,

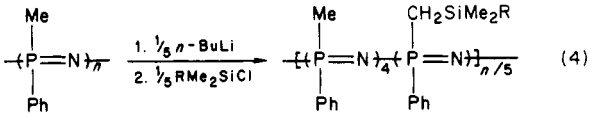


(3)

3a, R = CH=CH2
b, R = (CH2)3CN
c, R = H

GPC and intrinsic viscosity data showed the expected increases in molecular weight (Table II), confirming that the polymer backbone remained intact throughout the deprotonation/quenching process. While the elemental analyses of **3a–c** indicated that approximately 0.5 equiv of silyl groups (i.e., all that were added) were incorporated into the polymer, the ^1H NMR data[11] again suggested that a small degree of disubstitution (i.e., formation of $(RMe_2Si)_2CH$) took place. For polymers **3b** and **3c**, where R is $(CH_2)_3CN$ and H, the polymers appear to be somewhat chemically unstable since repeated reprecipitation, handling in air, and/or exposure to water gave materials that were no longer soluble. This observation lends support to the proposal of using the active sites for further derivatization reactions.

The parent polymer was also treated with 0.2 equiv of n-BuLi (eq 4) and chlorosilanes. Again the molecular weight distribution was essentially the same as that of the



(4)

4a, R = Me
b, R = CH=CH$_2$

parent polymer (Table II). In these cases, very little disubstitution was observed, as evidenced by one very large singlet and only a small second singlet in the Me_2Si region of the ^1H NMR spectrum.[12] The elemental analyses of **4a,b** were less satisfactory than for **1** and **3a–c**, but this can be attributed to the more noticeable effect of even minor deviations in the stoichiometric measurements.

In summary, these reactions demonstrate that *under mild conditions, the poly(alkyl/arylphosphazenes) can be derivatized without chain degradation via sequential treatment with n-BuLi and chlorosilanes.* In this manner a series of silylated polymers that contain predominantly Ph, Me, and RMe_2SiCH_2 with minor portions of $(RMe_2Si)_2CH$ substituents attached to the polymer backbone were prepared. The potential for enhanced thermal stability and for further derivatization of these new materials via the reactive functional groups R are under investigation.

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Registry No. **2**, 102537-44-0.

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(9) ^1H NMR ($CDCl_3$) δ 7.2, 7.3 (s, Ph), 1.4 (m, Me, CH_2, CH), 0.0, 0.1, –0.3 (m, Me_3Si); ^{13}C NMR ($CDCl_3$) δ 125.0–143.9 (m, Ph), 19.3–26.6 (m, Me, CH_2), 0.4, 3.1 (m, Me_3Si); ^{29}Si NMR ($CDCl_3$) δ –2.1.
(10) ^1H NMR ($CDCl_3$) δ 7.2, 7.8 (s, Ph), 1.4 (m, Me, CH_2), 0.8 (m, Si_2CH), 0.1, –0.1, –0.2 (m, Me_3Si); ^{29}Si NMR ($CDCl_3$) δ –2.1, –1.5.
(11) **3a**: ^{31}P NMR ($CDCl_3$) δ 4.0, –0.4(br s); ^1H NMR ($CDCl_3$) δ 7.8, 7.2 (s, Ph), 5.4–6.3 (m, CH=CH_2), 1.5 (m, Me, CH_2Si), 0.1, –0.2 (m, Me_2Si); ^{29}Si NMR ($CDCl_3$) δ –9.7. **3b**: ^{31}P NMR ($CDCl_3$) δ 4.3 (br sh), 3.5 (br s), 0.1 (br s); ^1H NMR ($CDCl_3$) δ 7.8, 7.2 (s, Ph), 0.8–2.3 (m, Me, CH_2Si), 0.3, 0.1, –0.3 (s, Me_2Si); ^{29}Si-($CDCl_3$) δ 6.3 (weak s, Si_2CH), –1.1 (s, $SiCH_2$). **3c**: ^{31}P NMR ($CDCl_3$) δ 3.9, 0.5 (br s); ^1H NMR ($CDCl_3$) δ 7.8, 7.1 (s, Ph), 4.7, 3.9 (s, SiH), 1.4 (br s, Me, CH_2), 0.1, –0.2 (m, Me_2Si); ^{29}Si NMR ($CDCl_3$) δ –18.5 (d, J_{H-Si} = 184.0 Hz).
(12) **4a**: ^{31}P NMR ($CDCl_3$) δ 7.3 (br sh), 3.8 (br s); ^1H NMR ($CDCl_3$) δ 7.6, 7.3, 7.1 (s, Ph), 1.2–1.7 (m, Me, CH_2), 0.0, –0.3 (m, Me_3Si); ^{29}Si NMR ($CDCl_3$) δ –1.4 (w s), –2.0 (str s). **4b**: ^{31}P NMR ($CDCl_3$) δ 2.0–10.3 (br, s); ^1H NMR ($CDCl3$) δ 7.7, 7.3, 7.1 (s, Ph), 5.2–6.0 (m, CH=CH_2), 0.8–1.6 (m, Me, CH_2Si), –0.3 (br s, Me_3Si); ^{29}Si NMR ($CDCl_3$) δ –9.8.

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Excimer Emission from Copolymers of Aromatic Monomers in Dilute Solution

In 1977 and 1978 Reid and Soutar[1,2] published a study in which they investigated the ratio of excimer and monomer fluorescence intensity, I_e/I_m, as a function of composition of copolymers containing aromatic and nonaromatic monomer residues. They assumed that only neighboring aromatic residues could form excimers and that energy migration along the polymer chain was limited to a contiguous sequence of such residues. This led them to conclude that $I_e/I_m = kf_{aa}\bar{l}_a$, where f_{aa} was the fraction of aromatic residues adjoining a similar residue, $\bar{l}_a$ was the mean sequence length of such residues, and k was a proportionality constant.

Reid and Soutar argued[1] that "the concentration of excimer sites must be modified to include only those traps which are within 'striking distance' of the migrating exciton" and justified in this way the proportionality of I_e/I_m on $\bar{l}_a$. They presented data on 1-vinylnaphthalene, 2-vinylnaphthalene, and styrene copolymers with methyl methacrylate[2] which were in agreement with this prediction. Later, a study of Anderson et al.[3] concerned with 1-vinylnaphthalene copolymers with methyl acrylate also behaved as predicted.

In spite of these reports, the relation of Reid and Soutar seems to be incompatible with a simple statistical argument. Let us assume that a sequence of aromatic monomer residues contains a fraction α of "traps", i.e., monomer residues whose configuration and/or conformation is required for excimer formation (presumably meso diads of such residues[4,5]). Then the probability that a sequence of n residues contains no such trap is $P(n) = (1 - \alpha)^{n-1}$. If we denote the I_e/I_m ratio in the aromatic homopolymer by $(I_e/I_m)_h$, then this ratio in a copolymer should be

$$I_e/I_m = (I_e/I_m)_h[1 - \sum_n W(n)(1 - \alpha)^{n-1}] \qquad (1)$$

where $W(n)$ is the weight fraction of sequences of n aromatic residues which will depend on the probability that an aromatic monomer is followed by a nonaromatic comonomer residue. It may be noted that the summation on the right of eq 1 vanishes for long-chain homopolymers, while the equation of Reid and Soutar has I_e/I_m increasing without limit as $\bar{l}_a$ is extended.[6]

There is another difficulty with the Reid–Soutar relation. Anderson et al.[3] found that the proportionality constant k was 6 times larger in 1-vinylnaphthalene copolymers with methyl acrylate than in the copolymers with methyl methacrylate. This was ascribed to the higher flexibility of the methyl acrylate copolymers. Yet the flexibility of a section of the chain consisting of a series of 1-vinylnaphthalene residues cannot depend on the na-

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