7446 *Macromolecules* **2010**, *43*, 7446–7452
DOI: 10.1021/ma100876z

Macromolecules
ARTICLE

Synthesis of Poly(alkyl/arylphosphazenes) via the Ambient Temperature Phosphite-Mediated Chain-Growth Polycondensation of (*N*-Silyl)bromophosphoranimines

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Received April 20, 2010; Revised Manuscript Received July 15, 2010

ABSTRACT: The room temperature addition of stoichiometric amounts of trimethyl phosphite, $P(OMe)_3$, to *N*-silyl(halogeno)organophosphoranimines $BrRR'P{=}NSiMe_3$ in chlorinated solvents led to the direct formation of high molecular weight polyphosphazenes $[RR'P{=}N]_n$. The majority of polymerizations were complete within 18 h. The polymers prepared include poly(dialkylphosphazenes) (e.g., $[nBu_2P{=}N]_n$ **1b**), poly(alkylarylphosphazenes) (e.g., $[PhMeP{=}N]_n$ **1d**), new materials featuring unsaturated substituents (e.g., $[nHex\{H_2C{=}C(H)CH_2\}P{=}N]_n$ **1n**), and random copolymers (e.g., $\{[PhMeP{=}N]_x{-}[PhnBuP{=}N]_y\}$ where $x{:}y = 2{:}1$, **7a**). The precursor silylaminophosphines $RR'P{-}N(SiMe_3)_2$ (**5a−q**) and bromo(silylamino)phosphoranimines $BrRR'P{=}NSiMe_3$ (**4a−q**) were synthesized and fully characterized prior to polymerization studies. The presence of alkoxy, carboranyl, and/or phenyl substituents on the *N*-silylbromophosphoranimines, as found in $BrEt[CF_3CH_2O]P{=}NSiMe_3$ (**4g**), $Br(2\text{-}[Me]\text{-}o\text{-}C_2B_{10}H_{10})EtP{=}NSiMe_3$ (**4h**), or $BrPh_2P{=}NSiMe_3$ (**4i**), respectively, was found either to severely retard or to preclude polymerization altogether. The mild reaction conditions enabled the preparation of polyphosphazenes that are substituted with reactive alkyne groups (e.g., R = Et, $R' = -CH_2C{\equiv}CSiMe_3$ **1p**), materials that have not been accessible using high-temperature thermal routes. These moieties undergo further convenient chemical transformations as illustrated by deprotection of **1p** by $TBAF\cdot 3H_2O$ (TBAF = tetra(*n*-butyl)ammonium fluoride) as well as chemical cross-linking with the disiloxane $HMe_2SiOSiMe_2H$ in the presence of Karstedt's catalyst. The polyphosphazene materials were characterized by a variety of techniques including ^1H, ^{13}C, and ^{31}P NMR spectroscopy and GPC and, in selected cases, by IR, DLS, TGA, DSC, and WAXS.

Introduction

In the field of inorganic polymers, polyphosphazenes are regarded as promising candidates for a wide variety of different applications.[1−3] The most well-established route to these interesting materials involves thermal ring-opening polymerization (ROP) of $[NPCl_2]_3$ at 200−250 °C. This leads to the formation of polydichlorophosphazene $[Cl_2P{=}N]_n$ which, following subsequent macromolecular halogen replacement reactions with oxygen- or nitrogen-based nucleophiles, provides access to polyphosphazenes with alkoxy, aryloxy, and amino substitutents.[1] Poly(alkyl/arylphosphazenes) (**1**, $[RR'P{=}N]_n$) with pendant organic groups directly attached through phosphorus−carbon bonds to the backbone are structural analogues of the isoelectronic silicones such as $[Me_2Si{-}O]_n$ and are also an attractive target.[3] However, the formation of polyphosphazenes with side groups bound by P−C bonds via substitution chemistry on poly(dichlorophosphazene) is generally not feasible with Grignard and organolithium reagents as they degrade the polyphosphazene backbone, especially under the forcing conditions often required to ensure complete substitution.[3] The key breakthrough in the preparation of poly(alkyl/arylphosphazenes) involved the discovery of the high-temperature (180−200 °C) chain growth polycondensation of phosphoranimines of type $(CF_3CH_2O)RR'P{=}NSiMe_3$ (**2**), which was reported in 1980 by Neilson and Wisian-Neilson (Scheme 1).[3] Materials formed by this route and by subsequent postpolymerization modification involving deprotonation and electrophilic strategies possess attractive properties that complement those of polyphosphazenes accessed via the ROP route.[3,4]

Recently, two examples of the preparation of poly(dichlorophosphazene) via an ambient temperature route have been described. These methods involve ROP of $[NPCl_2]_3$ in the presence of silylcarborane initiators[5] and chain growth polycondensation[6] of the phosphoranimine $Cl_3P{=}NSiMe_3$ in the presence of PCl_5. The latter route can also be adapted to organo-substituted phosphoranimines $RCl_2P{=}NSiMe_3$ and $RR'ClP{=}NSiMe_3$ to yield polyphosphazenes with substituents bound by direct P−C bonds, although the molecular weights are generally low (Scheme 2).[7]

In a preliminary communication we reported that the chain growth polycondensation of *N*-silyl-(bromo)organophosphoranimines can be performed at room temperature in the presence of stoichiometric or catalytic amounts of phosphites $P(OR)_3$ (e.g., $P(OMe)_3$) to give high molecular weight poly(alkyl/arylphosphazenes) (Scheme 3).[8] This mild new procedure offers opportunities to prepare poly(alkyl/arylphosphazenes) with unsaturated side groups such as vinyl, allyl, and acetylide which are difficult or impossible to introduce via the elevated temperature procedure.[9] In this paper we examine the scope and limitations of this new and promising ambient temperature approach.

Results and Discussion

1. Synthesis and Characterization of the Phosphoranimine Monomers (4).

*a. Synthesis and Characterization of N-Bis(dimethylsilyl)phosphines (**5a−q**).* The precursors to the phosphoranimine monomers **4**, the *N*-bis(trimethylsilyl)phosphines

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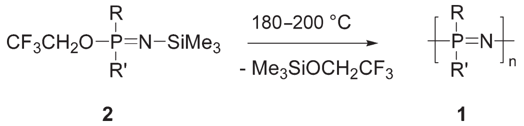
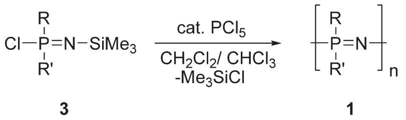
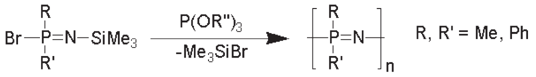
Scheme 1



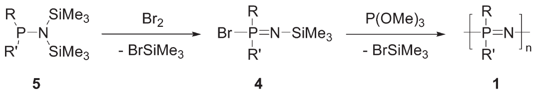
Scheme 2



Scheme 3

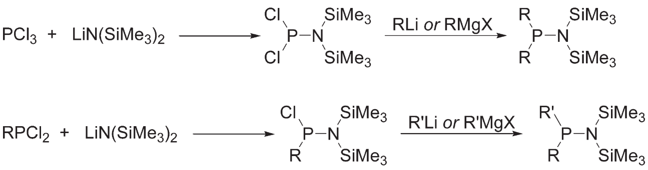


Scheme 4



a	R = R′ = Me	**j**	R = -C≡C-Me, R′ = Ph
b	R = R′ = *n*Bu	**k**	R = -C≡C-Ph, R′ = Ph
c	R = R′ = *n*Hex	**l**	R = R′ = -CH$_2$C(H)=CH$_2$
d	R = Me, R‘ = Ph	**m**	R = -CH$_2$C(H)=CH$_2$, R′ = Et
e	R = *n*Bu, R‘ = Ph	**n**	R = -CH$_2$C(H)=CH$_2$, R′ = *n*Hex
f	R = R′ = -OCH$_2$CF$_3$	**o**	R = (Me)C=C=CH$_2$, R′ = Ph
g	R = -OCH$_2$CF$_3$, R′ = Et	**p**	R = -CH$_2$C≡C-SiMe$_3$, R′ = Et
h	R = -*ortho*-(Me)-dodecacarborane, R′ = Et	**q**	R = -CH$_2$C≡C-SiMe$_3$, R′ = Ph
i	R = R‘ = Ph	**r**	R = -CH$_2$C≡C-H, R′ = Et

Scheme 5



(**5**, Scheme 4), were prepared by reacting the chlorophosphines (Cl_3P, ClRR′P or Cl_2RP) with lithium bis(trimethylsilyl)amide followed by the appropriate nucleophile(s) in Et_2O, THF, or a combination thereof (Scheme 5).

It was found that the route favored in published syntheses,[10] which involves the direct reaction of Grignard reagents with the chlorophosphine, in our hands generally led to lower yields. Whenever feasible, the corresponding lithium reagent was chosen for the synthesis of new phosphines from chlorinated species in the nucleophilic substitution step. The *n*-hexyl/allyl variant **5n** required the protection and deprotection of the allylphosphine via the diisopropylamine phosphine (Scheme 6).[11] For the allenic/phenyl species **5o**, the phosphine was synthesized by lithiating but-2-yne[12] and reacting with $ClPhPN(SiMe_3)_2$. Using the protected 1-trimethylsilylpropyne gave the alkyne-containing product **5q** exclusively (Scheme 7). The distilled phosphines **5** were in most cases quite sensitive to oxidation and were characterized by multinuclear NMR spectroscopy prior to conversion to the phosphoranimine (vide infra).

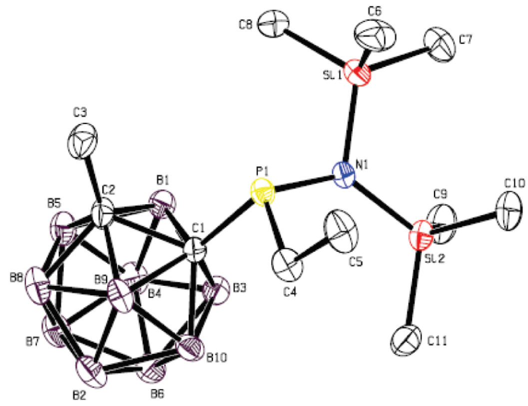
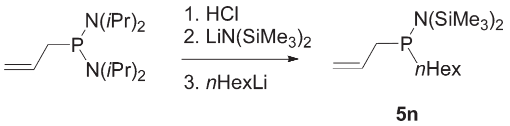
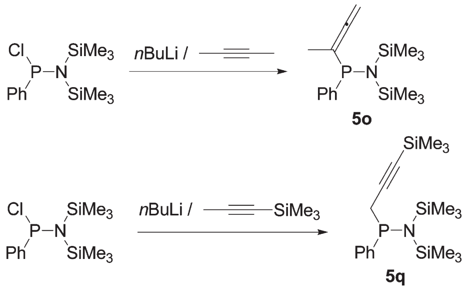


Figure 1. Molecular structure of *N*-bistrimethylsilylamino-([Me]-*o*-dodecacarborane)ethylphosphine (**5h**) using 50% probability thermal ellipsoids. All hydrogen atoms have been removed for clarity.

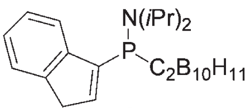
Scheme 6



Scheme 7



The carborane/ethylphosphine species **5h** was made in a straightforward manner by lithiating Me-*o*-dodecacarborane and reacting the product with $ClEtPN(SiMe_3)_2$ to give an air-stable phosphine that could be recrystallized from ethanol. This species was notably resistant to oxidation to the phosphine oxide compared to the other phosphines prepared. The structure of **5h** was also confirmed by single crystal X-ray diffraction (Figure 1).[13] Even with two sterically demanding pendant groups, access to the P atom does not appear to be significantly blocked from potential oxidants ($\sum \angle P = 315.1°$). The ^{31}P NMR resonance at 72.6 ppm is removed from those of the other silylaminophosphines in this study (40−55 ppm). This is in good agreement with analysis of a similar neutral dodecarborane disopropylamino indenyl phosphine ligand (**6**) synthesized by Xie et al. which possesses a ^{31}P NMR resonance at 74.1 ppm, and the respective P−C/P−N distances all fall within 0.03 Å of those in the structure of **5h**.[14]



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b. Synthesis and Characterization of N-Silylbromophosphoranimines (***4a−q***). The *N*-silylhalogenophosphoranimine monomers for the polymerizations were synthesized from the respective phosphines by direct bromination

Table 1. Synthesis of Poly(alkyl/arylphosphazene) Homopolymers $[\mathrm{RR'P{=}N}]_n$ (1) via the Phosphite-Mediated Condensation of the Respective Monomers (4) (in $\mathrm{CDCl_3}$, 1 equiv of $\mathrm{P(OMe)_3}$, 25 °C)

monomer	R	R′	polymer product	yield, % (time, h)	M_w ($\times 10^{-5}$),[b] g mol^{-1}	PDI
4a	Me	Me	**1a**	90 (3)	[a]	
4b	*n*Bu	*n*Bu	**1b**	85 (12)	(insoluble)	
4c	*n*Hex	*n*Hex	**1c**	80 (12)	(insoluble)	
4d	Me	Ph	**1d**	87 (3)	4.80	1.70
4e	*n*Bu	Ph	**1e**	87 (12)	1.28	3.40
4f	$-\mathrm{OCH_2CF_3}$	$-\mathrm{OCH_2CF_3}$		no reaction		
4g	$-\mathrm{OCH_2CF_3}$	Et	**1g**	60 (240)	5.34	1.41
4h	*o*-$\mathrm{(Me)C_2B_{10}H_{11}}$	Et		no reaction		
4i	Ph	Ph	**1i**	80 (60)	(insoluble)	
4j	$-\mathrm{C{\equiv}C{-}Me}$	Ph		no reaction		
4k	$-\mathrm{C{\equiv}C{-}Ph}$	Ph		no reaction		
4l	$-\mathrm{CH_2C(H){=}CH_2}$	$-\mathrm{CH_2C(H){=}CH_2}$	**1l**	90 (36)	3.07	1.81
4m	$-\mathrm{CH_2C(H){=}CH_2}$	Et	**1m**	90 (6)	4.85	1.23
4n	$-\mathrm{CH_2C(H){=}CH_2}$	*n*Hex	**1n**	95 (4)	2.24	3.32
4o	$\mathrm{(Me)C{=}C{=}CH_2}$	Ph		no reaction		
4p	$-\mathrm{CH_2C{\equiv}C{-}SiMe_3}$	Et	**1p**	95 (4)	1.06	5.20
4q	$-\mathrm{CH_2C{\equiv}C{-}SiMe_3}$	Ph	**1q**	17 (50)	2.33	4.01

[a] Could not be analyzed by our GPC instrument due to insolubility in THF. [b] GPC data were collected in THF containing 0.1 wt % $[n\mathrm{Bu_4N}]\mathrm{Br}$ using polystryene standards for column calibration.

(Scheme 4) which proceeded at −78 °C in dichloromethane. This reaction modification was found to increase the yield over the published method using benzene at 0 °C for brominations.[3b] Even when unsaturated groups were present, no significant bromination of the alkene or alkyne moieties was observed. For example, the allenic species **5o** was cleanly oxidized to phosphoranimine **4o**, readily identified in particular by the diagnostic ^{13}C NMR resonance for the internal allenic carbon at 210 ppm.

The more volatile (bp < 100 °C, ca. 10^{-2} mbar) or robust phosphoranimines were purified by distillation as clear colorless liquids; many of the less volatile phosphoranimines, particularly those with trimethylsilyl-capped alkyne moieties (**4q** and **4p**), decomposed under the same conditions. The brown residues that remained gave broad signals in their ^{31}P NMR spectra, and a series of low molecular weight species were indicated by MALDI-TOF measurements. The partial purification for these phosphoranimines was achieved by removal of the volatile side products (e.g., solvent, $\mathrm{BrSiMe_3}$), leaving the product in 95−99% purity (by ^{1}H and ^{31}P NMR spectroscopy). This level of purification was found to be sufficient for the following polymerizations.

2. $\mathrm{P(OMe)_3}$-Mediated Polycondensation of Phosphoranimines 4a−e, 4g, 4i, 4l−n, 4p, and 4q. *a. Homopolymerizations.* To examine the polymerization behavior of the bromophosphoranimines, these species were treated with a stoichiometric amount of $\mathrm{P(OMe)_3}$ in chloroform, and the resulting solution was allowed to stir at room temperature under an inert atmosphere. The reaction was monitored by ^{31}P NMR spectroscopy. Substoichiometric amounts of $\mathrm{P(OMe)_3}$ also initiate the polymerization effectively, but the reaction is significantly slower.[8] Completion of the successful reactions was suggested by the increased viscosity of the solutions and confirmed by the consumption of the starting phosphoranimine monomer and the growth of broad signals significantly shifted upfield by ^{31}P NMR spectroscopy which were assigned to the resulting polymer. Workup was carried out by concentration of the reaction solution followed by multiple precipitations into *n*-pentane and/or hexanes. Molecular weights of the resulting polyphosphazenes were estimated by GPC using polystyrene standards, and for soluble materials M_w values were around or larger than 10^5 g mol^{-1}. The results are tabulated in Table 1.

All of the poly(alkyl/arylphosphazenes) **1a**−**e**, **1g**, **1i**, **1l**−**n**, **1p**, and **1q** were isolated as white/off-white fibrous materials or powders. The previously reported and well-known polymers $[\mathrm{Me_2P{=}N}]_n$ (**1a**)[3] and $[\mathrm{MePhP{=}N}]_n$ (**1d**)[3] were synthesized and identified by comparison to literature by ^{1}H and ^{31}P NMR. The poly(dialkylphosphazenes) $[n\mathrm{Bu_2P{=}N}]_n$ (**1b**) and $[n\mathrm{Hex_2P{=}N}]_n$ (**1c**) were prepared in a similar manner. These polymers remained soluble in the reaction media, and their solution ^{31}P NMR spectra showed signals at 20.5 and 21.0 ppm, respectively.[3] Further analysis was hindered on the purified materials as they became increasingly insoluble in common solvents after multiple precipitations. The unsymmetrical polyphosphazene $[\mathrm{Ph}n\mathrm{BuP{=}N}]_n$ (**1e**) was also synthesized. This mixed-substituent material was much more soluble in a variety of solvents and was fully characterized.

The chloro-substituted phosphoranimine $\mathrm{ClPhMeP{=}NSiMe_3}$[15] (**3**, R = Me, R′ = Ph, Scheme 2) was also shown to undergo polymerization to afford $[\mathrm{PhMeP{=}N}]_n$ (**1d**) under similar conditions to the bromo analogue **4d**. Interestingly, the quantitative generation of **1d**[16] was observed after 18 h, substantially longer than the polymerization of $\mathrm{BrMePhP{=}NSiMe_3}$ (**4d**) (3 h). The shorter reaction time for the polymerization of **4d** may be the due to the weaker P−Br bond compared to the P−Cl bond present in $\mathrm{ClMePhP{=}NSiMe_3}$.

The presence of electron-withdrawing groups at phosphorus was found to significantly affect the propensity of *N*-silylhalogenophosphoranimines to polymerize in the presence of a phosphite. Fully halogenated species (i.e., $\mathrm{Cl_3PNSiMe_3}$) as well as those with two alkoxides directly bound to the phosphorus center such as $\mathrm{Br(CF_3CH_2O)_2P{=}NSiMe_3}$ (**4f**) were resistant to polymerization in the presence of $\mathrm{P(OMe)_3}$. Increasing the reaction temperature did not prove to be a viable alternative: heating **4f** with $\mathrm{P(OMe)_3}$ at 60 °C did not result in polymerization, and instead the formation of an unidentified mixture of products was indicated by ^{31}P NMR spectroscopy.

The mixed alkyl/alkoxy species, $\mathrm{Br(CF_3CH_2O)EtP{=}NSiMe_3}$ (**4g**), showed no noticeable polymerization after stirring for 2 days in $\mathrm{CDCl_3}$ with 1 equiv of $\mathrm{P(OMe)_3}$. However, after 10 days the solution was found to be slightly viscous, and ^{31}P NMR spectroscopy showed a broad peak centered at 20.2 ppm. A polymer (**1g**) was isolated in 60% yield as a white powder and possessed a M_w of 534 000 Da with a PDI value of 1.41. The presence of even a single alkoxy substituent group in **4g** appears to severely hinder the polymerization process.

The phosphoranimines $\mathrm{BrPh(MeC{\equiv}C)P{=}NSiMe_3}$ (**4j**) and $\mathrm{BrPh(PhC{\equiv}C)P{=}NSiMe_3}$ (**4k**) were also treated with equimolar amounts of $\mathrm{P(OMe)_3}$ in $\mathrm{CDCl_3}$ at room temperature, and no reaction was observed. The phosphoranimine $\mathrm{BrPh_2P{=}NSiMe_3}$ (**4i**) was surveyed as well, and while the insoluble polymer $[\mathrm{Ph_2P{=}N}]_n$ (**1i**) precipitated out of solution as it formed, the

3 days required to fully consume the monomer indicated that this was one of the slower reactions surveyed in this study.

Other phosphoranimines with electron-withdrawing and sterically demanding groups were synthesized, and their propensity for polymerization was investigated. One such example was the (*o*-methyldodecacarboranyl)phosphoranimine (**4h**), for which no conversion to the polymer was detected after 2 days on exposure to stoichiometric amounts of $P(OMe)_3$ in $CDCl_3$. Further attempts to polymerize the material with PCl_5[6] led only to the salt $[Br(Et)(o\text{-}MeC_2B_{10}H_{10})P{=}N{=}PCl_3][PCl_6]$ which was characterized by ^1H and ^{31}P NMR spectroscopy.

These results suggest that unsaturated and/or bulky organic substituents directly attached to the phosphorus center in the bromophosphoranimines either hinders or prevents polymerization. The reason for this change in reactivity is not known at present but may be clarified in the future upon the elucidation of the mechanism of the polymerization. Nevertheless, the successful synthesis of polyphosphazenes with alkyne and alkene groups (**1l**−**n**, **1p**,**q**) was accomplished by the introduction of a methylene spacer between the unsaturated moiety and the backbone (see below). Presumably the presence of the spacer reduces the influence of the unfavorable electronic and/or steric factors that otherwise hinder the polymerization.

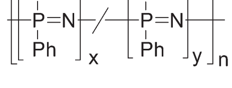
The polymers $[\{H_2C{=}C(H)CH_2\}_2P{=}N]_n$ (**1l**) and $[Et\{H_2C{=}C(H)CH_2\}P{=}N]_n$ (**1m**) were both readily synthesized, although the polymerization was much slower in the former case. After two precipitations into hexanes these materials were found to be insoluble in hydrocarbons, sparingly soluble in THF, and only slightly soluble in halogenated solvents. Freshly sonicated samples of **1m** in CH_2Cl_2 showed a major peak by dynamic light scattering (DLS) assigned to be unimers with a hydrodynamic radius, R_h, of 4.7 nm. The material then began to form aggregates of size greater than 250 nm within a period of minutes, giving a visible precipitate within hours. Addition of aqueous strong acids to suspensions of **1l** and **1m** actually decreased their solubility, and introducing anhydrous HCl to THF suspensions of the materials did not solubilize the polymers to any degree. While the lowered solubility of **1l** may be rationalized by comparison of the material to the intractable poly(di-*n*-propylphosphazene) ($[nPr_2P{=}N]_n$),[17] the similar behavior in the mixed substituent material **1m** species was more surprising. The origin of this limited solubility may be the insufficient length of the side groups to promote solubility on organic solvents. Indeed, substantially changing the size of the aliphatic side group was found to lead to soluble materials. The $[nHex\{H_2C{=}C(H)CH_2\}P{=}N]_n$ variant (**1n**), made specifically due to the poor solubilities of the other species, was isolated as an off-white fibrous material and was soluble in a broad range of polar and nonpolar solvents.

Phosphoranimines with unsaturated carbon centers attached directly to phosphorus were found to either hinder polymerization or to be completely unreactive. The phenyl/allene phosphoranimine **4o** did not react after stirring 7 days at room temperature in the presence of $P(OMe)_3$. Increasing the temperature to 65 °C resulted in the formation of multiple products by ^{31}P NMR spectroscopy, none of which corresponded to the corresponding polymer.

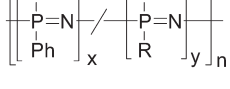
We also investigated whether phosphoranimines with the acetylenic group $-CH_2C{\equiv}CSiMe_3$ would polymerize efficiently. If successful, this would show that monomers with an internal alkyne functionality were compatible with this new polymerization route and that a saturated methylene group spacer circumvents the problems detected when unsaturated organic substituents are attached directly to phosphorus. A comparison of the reactivities of the ethyl and phenyl variants of the methylene-alkynated phosphoranimines (**4p** and **4q**, respectively) clearly indicated conversion to **1p** after 4 h in near quantative yield by ^{31}P NMR spectroscopy while after 2 days only a 17% yield of **1q** was attained. As noted previously, the bulky phenyl group seems to hinder the polymerization of the phosphoranimine. Polyphosphazene **1p** was stable under ambient conditions and was readily purified by standard precipitation techniques. The purified material formed a hard light-yellow glass upon standing but was very soluble in chlorinated solvents and moderately so in THF. The material was even moderately soluble in non-coordinating solvents such as toluene.

Two of the phosphoranimines featuring alkyne groups, **4q** and **4p**, were also reacted with small amounts of PCl_5 at room temperature in CH_2Cl_2 and monitored by ^{31}P and ^1H NMR spectroscopy to determine if the alternative cationic route (see Scheme 2), known to be compatible with the presence of saturated alkyl and phenyl groups,[7] was also viable with unsaturated alkyne moieties. However, a variety of partially chlorinated species, insoluble material, and starting material were recovered after 2 h of reaction time.

b. Synthesis and Characterization of Poly(alkyl/arylphosphazene) Random Copolymers. This room temperature phosphite-mediated polymerization route also allowed for the preparation of different poly(alkyl/arylphosphazene) random copolymers by using a mixture of two different monomers, as demonstrated previously[3] at elevated temperature (180−200 °C). For example, treatment of different molar ratios of $BrPhMeP{=}NSiMe_3$ (**4d**) [$\delta(^{31}P) = 4.0$ ppm] and $BrPhnBuP{=}NSiMe_3$ (**4e**) [$\delta(^{31}P) = 13.3$ ppm] in the presence of a stoichiometric amount of $P(OMe)_3$ in CH_2Cl_2 at 25 °C afforded random copolymers **7a** and **7b** in good yields as white fibrous materials. ^{31}P NMR spectroscopy confirmed the random nature of these polymers by showing a single and very broad signal centered at 10.3 ppm (**7a**) and 13.3 ppm (**7b**), respectively, unlike the two signals expected in case of polymerization of both monomers separately ($[PhMeP{=}N]_n$, $\delta(^{31}P) = 1.4$ ppm; $[Ph(n\text{-}Bu)P{=}N]_n$, $\delta(^{31}P) = 6.5$ ppm). The polymers were shown to possess high molecular weights by GPC with a M_w values of ca. 1.5×10^5 g/mol and a PDI of ca. 2.0. The presence of only one single peak by GPC is also consistent with the formation of a random copolymer rather than a mixture of the two respective homopolymers. Moreover, this result raised the question of whether a random copolymer with $[PhMeP{=}N]$ and $[R_2P{=}N]$ (R = Me, *n*Bu, and *n*Hex) repeat units would also be a soluble material. Thus, the random copolymers (**7c**−**h**) were prepared in an analogous manner to **7a**, **b** and were indeed found to be soluble materials with a ratio of 10−20% of $[R_2P{=}N]$ (R = Me, *n*Bu, and *n*Hex) units in the main chain. Analysis by ^{31}P NMR spectroscopy again confirmed a random copolymer structure for **7c**−**h**. The polyphosphazene copolymers **7c**,**d** showed a single very broad signal centered at 6.3 ppm. However, two sets of broad signals were found for the copolymers **7e**,**f** ($-[NPMePh]-$, $\delta(^{31}P) = 8.1$ ppm; $-[NP(n\text{-}Bu)_2]-$, $\delta(^{31}P) = 29.9$ ppm) and for **7g**,**h** ($[NPMePh]$, $\delta(^{31}P) =$ ca. 5.1 ppm; $[NP(n\text{-}Bu)_2]$, $\delta(^{31}P) =$ ca. 27.2 ppm). The relative integration of the two signals was consistent with the ratio of repeat units proposed for the copolymers **7e**−**h**. These organopolyphosphazenes with saturated alkyl substituents and aryl groups, possessed high molecular weights by GPC (Table 2).



7a x:y = 2:1
7b x:y = 1:2



7c R = Me x:y = 9:1
7d R = Me x:y = 4:1
7e R = *n*Bu x:y = 9:1
7f R = *n*Bu x:y = 4:1
7g R = *n*Hex x:y = 9:1
7h R = *n*Hex x:y = 4:1

3. Morphology of $[nBu_2P{=}N]_n$ (1b) and $[nHex_2P{=}N]_n$ (1c). The crystallinity of the insoluble *n*-alkyl-substituted polyphosphazenes **1b** and **1c** was probed by DSC and WAXS

Table 2. Synthesis of Poly(alkyl/arylphosphazene) Random Copolymers [(RR′P=N)−(RR′P=N)]$_n$ (7a−h) via the Phosphite-Mediated Condensation of the Respective Phosphoranimine Monomers 4 (in CDCl$_3$, 1 equiv of P(OMe)$_3$, 25 °C)

monomer A	RR′ groups from monomer A (equiv)	monomer B	RR′ groups from monomer B (equiv)	polymer product	yield, % (time, h)	M_w ($\times10^{-5}$), g mol^{-1}	PDI
4d	PhMe (0.67)	**4e**	Ph*n*Bu (0.33)	**7a**	92 (12)	1.48	2.0
4d	PhMe (0.33)	**4e**	Ph*n*Bu (0.67)	**7b**	84 (12)	1.66	1.8
4d	PhMe (0.9)	**4a**	Me$_2$ (0.1)	**7c**	77 (12)	1.52	1.8
4d	PhMe (0.8)	**4a**	Me$_2$ (0.2)	**7d**	73 (12)	2.17	1.6
4d	PhMe (0.9)	**4b**	*n*Bu$_2$ (0.1)	**7e**	86 (12)	1.20	2.4
4d	PhMe (0.8)	**4b**	*n*Bu$_2$ (0.2)	**7f**	69 (12)	0.74	3.7
4d	PhMe (0.9)	**4c**	*n*Hex$_2$ (0.1)	**7g**	89 (12)	1.05	2.3
4d	PhMe (0.8)	**4c**	*n*Hex$_2$ (0.2)	**7h**	76 (12)	0.59	3.2

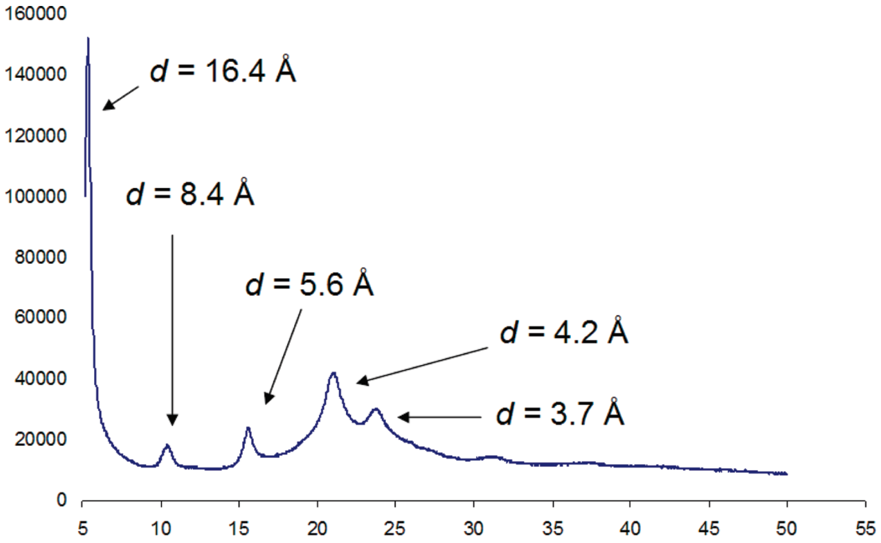


Figure 2. WAXS pattern (2θ vs counts [arbitrary]) for polymer **1c**.

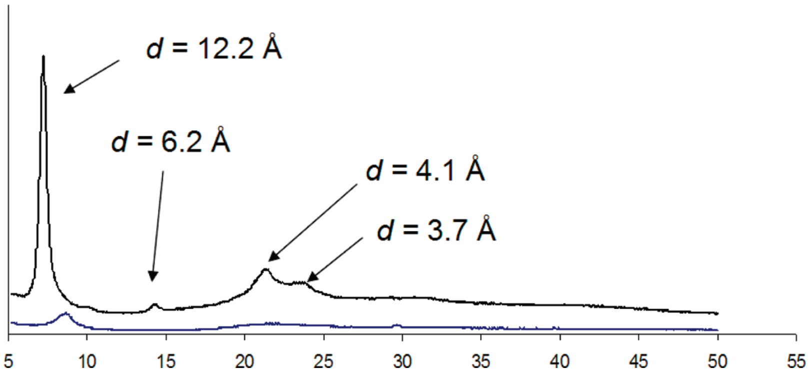


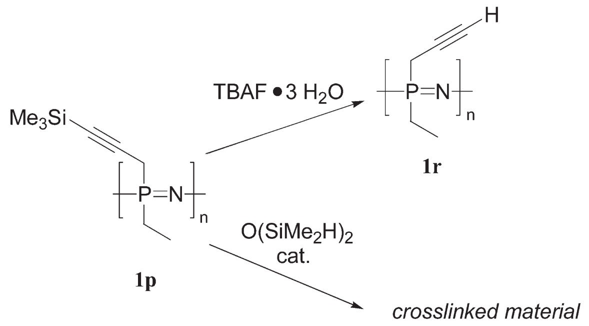
Figure 3. WAXS patterns (2θ vs counts [arbitrary]) for polymers **1b** (top) and **1e** (bottom) at 25 °C.

measurements, as reported previously for the known insoluble polyphosphazenes [Et$_2$P=N]$_n$[18] and [nPr$_2$P=N]$_n$.[17] In the latter two cases the insolubility of the material has been at least partially attributed to their crystallinity (T_m = 217 and 248 °C, respectively). Polymer **1c** displayed a clear T_m at 155 °C that was consistent over multiple heating/cooling cycles. In contrast, **1b** had no detectable T_m below 175 °C (the maximum temperature investigated).

For the WAXS measurements, the polymers were analyzed in their as prepared state and also after annealing at 145 °C for 12 h; no significant differences in the WAXS traces were detected. The WAXS patterns of **1b** and **1c** (Figure 2 and upper trace of Figure 3), showed several relatively sharp peaks characteristic of a semicrystalline material. Although beyond the scope of this work, the WAXS traces are of sufficient quality to suggest that further studies of highly oriented materials such as fibers are worthwhile and may allow successful indexing of the diffraction peaks and conformational information. For comparison, the WAXS pattern of the unsymmetically substituted material [PhnBuP=N]$_n$ (**1e**), which would be expected to be amorphous, was collected as well. The pattern for the latter polymer showed only a broad peak and an amorphous halo (Figure 3, lower trace). The results suggest that the insolubility of **1b** and **1c** may also be attributed to their crystallinity, which provides an additional enthalpic barrier to dissolution due to the lattice energy. However, the insolubility of other mixed-substituent materials such as **1m** suggests that short (C$_4$ or less) substituents also impart insufficient hydrophobicity to the polymer to counter the effect of the highly polar polymer backbone, and even such amorphous materials show very low solubility in common organic solvents.

4. Postpolymerization Reactions of Acetylide Polymer 1p. Proof-of-concept experiments to stimulate further work with these materials involved a brief study of the postpolymerization

Scheme 8



derivitatization of **1p**. The good solubility of the material allowed two selected reactions, a deprotection and cross-linking, to be attempted (Scheme 8).

The silyl group of **1p** can be readily cleaved with TBAF·3H$_2$O (TBAF = tetra(*n*-butyl)ammonium fluoride) in THF (carefully avoiding excess fluoride which is capable of cleaving the phosphazene backbone), and the process was monitored by the disappearance of the silyl peak and the growth of a broad acetylenic proton signal at 2.1 ppm by ^{1}H NMR spectroscopy. A fine white fibrous polymer (**1r**) was collected after precipitations into distilled water and *n*-pentane. Comparison of the parent polymer with the deprotected material in THF solution through DLS showed similar peaks for the two species (R_h values of 12.5 Å [**1p**] and 9.5 Å [**1r**]) with the expected contraction of the hydrodynamic radius for the deprotected material and with no suggestion of degradation of the polymer backbone.

For the cross-linking reaction, the protected polymer **1p** was found to undergo direct hydrosilylation with 5 mol % of the bifunctional siloxane O(SiMe$_2$H)$_2$ in the presence of Karstedt's catalyst in toluene. A white precipitate formed rapidly on the side of the reaction flask, and the cross-linked material was found to be insoluble in all standard solvents. Further analysis was carried out using IR spectroscopy; the relative intensity of alkyne C−C stretch (2171 cm^{-1}) to the starting material weakened while a strong band in the alkene C−C stretching region (1696−1670 cm^{-1}) appeared, as expected. Clearly many applications of the facile modification chemistry possible with materials such as **1p** can be envisaged.

Summary

We have explored and expanded the scope of the promising room-temperature polycondensation of *N*-silylbromophosphoranimines (**4**) in the presence of P(OMe)$_3$ by synthesizing a number of previously known and new polyphosphazenes, often in near-quantitative yields. Both poly(alkyl/arylphosphazene) homopolymers (**1**) and copolymers (**7**) are accessible with this methodology. Notably, the soluble polymers such as **1n** and **1p** containing side-group unsaturation were made efficiently as a result of the mild conditions. The latter species was shown to be capable of further reactivity, as illustrated by deprotection and cross-linking experiments. The potential for this new and mild polymerization route will to a large extent be dependent on the feasibility of preparing the *N*-silylbromophosphoranimines monomers, although some electron-withdrawing and/or bulky groups (alkoxy, phenyl) do appear to hinder the phosphite-mediated polycondensation. In addition, chlorophosphoranimines appear to polymerize more slowly than their bromo analogues.

We are currently investigating the mechanism of the phosphite-mediated phosphoranimine polycondensation reaction in detail. We have recently prepared P-donor-stabilized phosphoranimine cations that may be related to the proposed propagating site.[19] Detailed understanding of the mechanism may allow access to living systems with their associated molecular weight control and narrow polydispersities. Understanding the various steps in the polymerization may also allow us to expand the range of polymerizable monomers for this new, mild, and versatile method.

Experimental Section

Materials. Acetonitrile, diethyl ether, THF (for bulk reactions), and toluene were collected from Grubbs type solvent purification systems. For sensitive reactions, THF was dried over sodium benzophenyl ketyl and distilled prior to use. P(OMe)$_3$ (97%) was bought from Aldrich and used directly under glovebox conditions as well as being further purified by distillation from sodium wire. It was found that the polymerizations with freshly distilled phosphite proceeded similarly but were up to 1.5 times slower. The purchased chloro- and dichlorophosphines were distilled prior to use. All other reagents were used as purchased. Me$_2$PN(SiMe$_3$)$_2$ [**5a**],[20] BrMe$_2$P=NSiMe$_3$ [**4a**],[20] MePhPN(SiMe$_3$)$_2$ [**5d**],[20] BrMePhP=NSiMe$_3$ [**4d**],[20] (CF$_3$CH$_2$O)$_2$PN(SiMe$_3$)$_2$ [**5f**],[20] Br(CF$_3$CH$_2$O)$_2$P=NSiMe$_3$ [**4f**],[20] Ph$_2$PN(SiMe$_3$)$_2$ [**5i**],[20] BrPh$_2$P=NSiMe$_3$ [**4i**],[20] (CH$_2$=CHCH$_2$)$_2$PN(SiMe$_3$)$_2$ [**5l**],[21] and Br(CH$_2$=CHCH$_2$)$_2$P=NSiMe$_3$ [**4l**][22] were prepared according to the literature. Preliminary details of the phosphite-mediated synthesis of [Me$_2$P=N]$_n$ (**1a**) and [MePhP=N]$_n$ (**1d**) were previously reported.[8] All synthetic steps were carried out under an atmosphere of nitrogen or argon. Precipitation of polymers usually involved the formation of a viscous solution from a good solvent by careful solvent removal via rotary evaporation followed by the addition of the sample into the vortex of a stirred nonsolvent.

Equipment. NMR experiments were performed on a JEOL Lambda 300 and Eclipse 300 spectrometers in dry solvents. NMR chemical shifts were referenced to tetramethylsilane or residual protonated solvent peaks. Conventional gel permeation chromatography (GPC) was carried out on a Viscotek GPCmax chromatograph equipped with a refractometer. Two columns (with lower and upper exclusion limits 100−10 000 and 100−1 000 000) were packed with a porous styrene divinylbenzene copolymer packing material (5 μm particle size). A flow rate of 1 mL/min in THF with 0.1% w/w nBu$_4$NBr was used, and calibration was performed using polystyrene standards. Dynamic light scattering experiments were performed using a Malvern spectrometer in a quartz cuvette using THF at 20 °C. MALDI-TOF mass spectra were collected on a 4700 Proteomics Analyzer (Applied Biosystems). Samples were prepared in THF using 2,5-dihydroxybenzoic acid as a matrix (1:5, sample: matrix) and drop-cast by micropipet into sample wells. TGA measurements were run on a TGA Q500 apparatus at 10 °C/min. DSC was run on a DSC Q100 apparatus at 10 °C/min under a N$_2$ atmosphere. The instrument was calibrated using indium for heat flow and sapphire for heat capacity. T_g and T_m values were calculated from the inflection point and the endothermic maximum, respectively. IR spectra were measured using a Perkin-Elmer FT-IR spectrometer. Powder X-ray diffraction was measured on a Bruker D8 Advance diffractometer with Cu Kα radiation, and the samples were scanned at step widths of 0.02° with 1.0 s/step in the range of 5°−50° 2θ. Details of the single-crystal X-ray diffraction are in the Supporting Information.

Representative Syntheses. Full experimental details and characterization data can be found in the Supporting Information. The following are representative syntheses.

a. Polyphosphazene Homopolymer: [nHex(H$_2$C=CHCH$_2$)P=N]$_n$ (***1n***). A 1 mL CDCl$_3$ solution containing 1.24 g (10 mmol) of P(OMe)$_3$ was added to a rapidly stirring 15 mL CHCl$_3$ solution of **4n** (3.2 g, 10 mmol). The resulting solution became very viscous after 18 h. All volatiles were removed from the polymer syrup that yielded a white solid. The polymer was redissolved in CHCl$_3$ and then added dropwise into 200 mL of *n*-pentane. The resultant white polymer was filtered and dried under vacuum for 24 h (yield: 1.63 g, 95%). ^{31}P{^{1}H} NMR

($CDCl_3$): $\delta = 19.8$ ppm. ^1H NMR (CD_2Cl_2): $\delta = 0.80$ (t, $^3J_{HH} = 6.2$ Hz, CH_3); 1.20−1.27 (other CH_2s); 1.48 (br, PCH_2CH_2); 1.79 (m, PCH_2CH_2); 2.75 (br, $CH_2CH{=}CH_2$); 5.10 (br, $CH_2CH{=}CH_2$); and 5.81 ppm (br, $CH_2CH{=}CH_2$). $M_w = 224\,000$ (PDI = 3.32).

b. Polyphosphazene Random Copolymer: $\{[PhMeP{=}N]_{0.67}\text{-}[PhnBuP{=}N]_{0.33}\}_n$ (***7a***). In the glovebox, 0.30 g (1.0 mmol) of **4d** and 0.10 g (0.3 mmol) of **4e** were dissolved in 3 mL of CH_2Cl_2, and 0.15 mL (1.3 mmol) of $P(OMe)_3$ was added. The reaction was stirred at room temperature overnight. The viscous solution was precipitated into hexanes, and the white solid obtained was purified by two more precipitations (CH_2Cl_2/hexanes) to afford a white fibrous material. The polymer was dried at 40 °C for 2 days (yield: 0.185 g, 92%). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): $\delta = 10.3$ ppm (br, 7−17 ppm). ^1H NMR (CD_2Cl_2): $\delta = 0.6$ (br, CH_3), 1.1 (br, CH_2), 1.3−1.5 (PCH_3), 1.6−2.1 (PCH_2CH_2), and 7.1−7.7 ppm (PC_6H_5). $M_n = 147\,600$ (PDI = 2.0).

Acknowledgment. We thank AWE for financial support. A.P.S. thanks the EU for a Marie Curie postdoctoral fellowship, and I.M. thanks the EU for a Marie Curie Chair.

Supporting Information Available: Full Experimental details and TGA, DSC, WAXS, and single crystal X-ray diffraction data. This material is available free of charge via the Internet at http://pubs.acs.org.

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