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Influence of Reaction Parameters on the Living Cationic Polymerization of Phosphoranimines to Polyphosphazenes

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ABSTRACT: A new approach to the synthesis of poly(dichlorophosphazene) and poly(organophosphazenes) has been developed via the cationic condensation polymerization of phosphoranimines. The effects of solvent, temperature, concentration, and initiator on the cationic condensation polymerization of $Cl_3P{=}NSiMe_3$ and $PhCl_2P{=}NSiMe_3$ are described. The ambient temperature polymerization of $PhCl_2P{=}NSiMe_3$ is faster in toluene, benzene, and dioxane than in methylene chloride or chloroform. The polymerizations of $Cl_3P{=}NSiMe_3$ and $PhCl_2P{=}NSiMe_3$ were monitored by both NMR (^{31}P and ^1H) and GPC methods. The initial polymerization rates are slow, presumably because of the precipitation of phosphazene short chain salts, $RCl_2P{=}N-[PR(Cl){=}N]_n-PCl_3{}^+PCl_6{}^-$ (where R = Cl or Ph; n = 0, 1, 2, ...). After the chains redissolve (∼15−60 min), polymerization proceeds, with the propagation rates following pseudo-first-order kinetics for both monomers. The reactions in toluene, benzene, or dioxane yielded polymers with controlled molecular weights in the range of 10^5, with narrow polydispersities (<1.3). The usefulness of this approach for the synthesis of a biomedically important polyphosphazene has also been demonstrated.

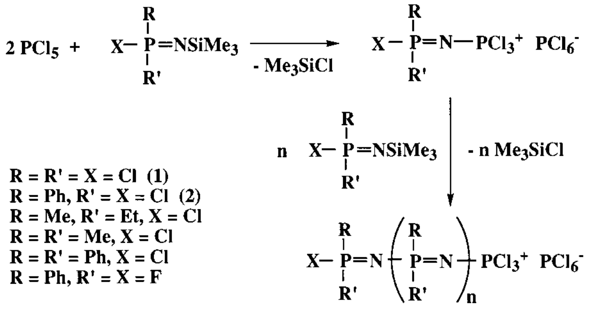
Introduction

The living cationic condensation polymerization of halophosphoranimines in solution at ambient temperatures is an advanced method for the synthesis of polyphosphazenes (Scheme 1).[1−3] This polymerization route provides poly(dichlorophosphazene) with controlled molecular weights and low polydispersities. In this respect, it is an improvement over the traditional thermal ring-opening polymerization of $(NPCl_2)_3$ that yields high polymers of poly(dichlorophosphazene) with broad polydispersities and bimodal molecular weight distributions with little or no control over the molecular weight.

We are currently exploring the possibilities and scope of the new methodology[4−6] and are attempting to overcome a number of existing problems. The polymers obtained by the initially developed techniques had controlled chain lengths but only modest molecular weights in the range of 10^4. These molecular weights are lower than the 10^6 values obtained by the thermal ring-opening method. However, we have recently synthesized higher molecular weight polymers ($M_w = 10^5-10^6$) from phosphoranimines through the use of two approaches. These are (1) by phosphoranimine polymerization in the absence of a solvent and (2) by the sequential addition of the monomer at prescribed stages during a solution polymerization. However, the polymers generated via both of these approaches have large polydispersities with little control over the molecular weight.[1,2]

Improvements to the solution cationic polymerization of *organo*phosphoranimines are also needed because the reactions in methylene chloride, for example, are often slow and do not proceed to completion.[3] The polymerization of organophosphoranimines is retarded by electron-donating, bulky side groups which are less favorable for polymerization than electron-withdrawing chlorine or fluorine atoms. Polyphosphazenes with phosphorus−carbon linkages to the side groups are of special interest because they can be modified by organometallic reactions without significant cleavage of the backbone.[7,8]

Scheme 1



High molecular weight polyphosphazenes usually yield solids with greater materials strength and elasticity than their shorter chain counterparts. Therefore, a major objective is to refine the cationic condensation to favor the formation of higher polymers. In this paper we describe how changes in solvent, concentration, and temperature can be used to produce higher molecular weight homopolymers and block copolymers from phosphoranimines. Attempts to synthesize phosphazene random copolymers through the copolymerization of two phosphoranimines were also attempted, but blocky copolymers were the favored products. The use of initiators other than PCl_5 has also been investigated.

Experimental Section

Materials. Lithium bis(trimethylsilyl)amide (97%), antimony pentachloride (99.99%), 2,2,2-trifluoroethanol (99+%), dichlorophenylphosphine (97%), propyl 4-hydroxy benzoate (99%), and sodium metal were obtained from Aldrich and used without further purification. Phosphorus pentachloride (95%) (Aldrich) was sublimed under vacuum. Sodium trifluoroethoxide and the sodium salt of propyl 4-hydroxy benzoate were prepared in THF by the addition of the alcohol or phenol to sodium metal. The monomers $Cl_3P{=}NSiMe_3$ (**1**) and $PhCl_2P{=}NSiMe_3$ (**2**) were synthesized and purified as reported pre-

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viously.$^{1-3}$ Toluene (99.5%), benzene (99.8%), 1,4-dioxane (99+%), and tetrahydrofuran (99+%) (Aldrich) were distilled into the reaction flask from sodium benzophenone ketyl in an atmosphere of dry argon. Dichloromethane (99.6%) and chloroform (99.8%) (Aldrich) were dried and distilled from CaH_2 into the reaction flask.

All glassware was dried overnight in an oven or flame-dried under vacuum before use. The reactions were performed using standard Schlenk techniques or in an inert atmosphere glovebox (Vacuum Atmospheres) under an atmosphere of dry argon or nitrogen.

Equipment. ^{31}P, ^{13}C, and ^{1}H spectra were recorded using a Bruker WM-360 NMR spectrometer operated at 146, 90.27, and 360 MHz or a Bruker DPX-300 spectrometer operated at 121.7, 75.2, and 300 MHz, respectively. ^{1}H and ^{13}C NMR spectra are referenced to $CDCl_3$ or an internal D_2O insert. ^{31}P NMR chemical shifts are relative to 85% phosphoric acid as an external reference, with positive shift values downfield from the reference. Molecular weights were estimated using a Hewlett-Packard HP 1090 gel permeation chromatograph equipped with an HP-1047A refractive index detector, American Polymer Standards AM gel 10 μm and AM gel 10 μm 10^4 Å columns, and calibrated vs polystyrene standards (Polysciences). The samples were eluted with a 0.1 wt % solution of tetra-*n*-butylammonium nitrate (97%) (Aldrich) in THF (OmniSolv) at 40 °C. Attempts to compare the GPC-derived molecular weights with values obtained from light scattering measurements were not informative because the molecular weights were too low to give reproducible light scattering data.

Phosphoranimine Polymerizations. All the polymerizations were carried out using the same procedures as given in the following specific example. Vacuum line, Schlenk line, and glovebox techniques were employed. The initiator (PCl_5, 0.013 g, 6.3×10^{-4} mol) was dissolved in dry toluene (~12 mL), and the solution was stirred for 1 h at 25 °C to produce a homogeneous solution. The monomer $Cl_3P{=}NSiMe_3$ (**1**) (5 g, 2.2×10^{-2} mol) was dissolved in toluene (~12 mL) and was added to the stirred initiator solution. This corresponded to a 350:1 molar ratio of monomer to initiator. The progress of the polymerization was followed by the removal of samples and analysis by ^{31}P and ^{1}H NMR spectroscopy. After complete conversion of the monomer to polymer had occurred, the solvent and condensation byproduct, chlorotrimethylsilane, were removed under vacuum. The polymer was then dissolved in dioxane, and the chlorine atoms were replaced by the addition of a solution of $NaOCH_2CF_3$ ($4. 4 \times 10^{-2}$ mol) in 28 mL of THF. The reaction mixture was stirred for at least 1 h and then concentrated under reduced pressure. The polymer was precipitated from the concentrated solution into deionized water and filtered off. Additional reprecipitations from THF into deionized water (2×) and hexane (1×) provided pure white materials. ^{31}P NMR for $(NPCl_2)_n$: ∂ −17 ($-PCl_2{=}N$), −16 ($-PCl_2{=}N-PCl_3^+$), −15 ppm ($-PCl_2{=}N-PCl_3^+$).

For the phosphoranimine polymerizations, peak integrations in both ^{31}P and ^{1}H NMR spectra were used to estimate $[M]_0/[M]$, the ratio of the initial monomer concentration to the monomer concentration, at different stages in the reaction. ^{1}H NMR spectroscopy indicated two peaks at 0.25 and 0 ppm for the polymerizations in toluene that were assigned respectively to the protons in the trimethylsilyl groups of the monomer and Me_3SiCl. Because both the monomer and Me_3SiCl remained soluble throughout the polymerizations, integration of the two peaks allowed $[M]_0/[M]$ to be determined. Integration of the ^{31}P NMR peaks to determine $[M]_0/[M]$ was somewhat less accurate than the ^{1}H NMR integration because the growing chain gives rise to a number of peaks. Furthermore, the initial $[M]_0/[M]$ ratios may not be accurate because of precipitation of the short chain species. Nevertheless, $[M]_0/[M]$ ratios estimated by peak integration from the ratio of monomer to polymer peaks were similar, within experimental error, to the results obtained from integration of the ^{1}H NMR peaks.

Variable Temperature Studies. The kinetic studies were conducted using a Bruker DPX-300 MHz NMR spectrometer. Monomer **1** (0.12 g, 0.71 mmol) was dissolved in toluene (0.5 mL), placed in a 5 mm NMR tube with an internal D_2O reference insert, and allowed to equilibrate with spinning at a selected desired temperature for 30 min in the spectrometer. The NMR tube was removed, and 0.5 mL of a solution of PCl_5 (5.25×10^{-2} g/mL, 0.0252 M) in toluene, prepared as a 10 mL solution, was added quickly via syringe. The sample was then reinserted into the spectrometer and spun at the desired temperature. For this study, ^{31}P NMR spectroscopy was used to monitor the reaction. The ^{31}P NMR spectrum of this monomer is a singlet at −56 ppm whereas the polymer gives a singlet at −17 ppm and may include a number of smaller peaks between 10 and −17 ppm. These smaller peaks have been assigned to the end groups, and the detection of them depends on the chain length. Integration of the peaks provided an indication of the percent monomer remaining after a given time. The percent monomer vs time was used to calculate reaction rates and Arrhenius parameters.

Attempted Random Copolymerization. Both monomers **1** and **2** were dissolved in the appropriate solvent, and a prepared solution of initiator was added to the monomer mixture. The polymerizations were conducted at ambient temperature (25 °C) following the general procedure described above. For example, monomers **1** (0.87 g, 0.0039 mol) and **2** (1.02 g, 0.0039 mol) were dissolved in CH_2Cl_2, and to this was added by syringe a solution of PCl_5 (0.08 g, 3.9 mmol) in CH_2Cl_2. Polymerization occurred at 25 °C and was monitored by ^{31}P NMR spectroscopy. The solvent and Me_3SiCl were removed under vacuum, the polymer was treated with $NaOCH_2CF_3$ (0.013 mol), and the final product was precipitated into water and was recovered by filtration.

Results and Discussion

In earlier work, the polymerization of $Cl_3P{=}NSiMe_3$ with PCl_5 as an initiator, in CH_2Cl_2, yielded polymers with controlled molecular weights in the range of 10^4 and low polydispersities.$^{1-6}$ However, the polymerization of *organo*phosphoranimines ($RCl_2P{=}NSiMe_3$ or $R_2ClP{=}NSiMe_3$) in CH_2Cl_2 was accomplished only with the use of high ratios of initiator to monomer or in concentrated solutions over an extended period of time (~7 days for a 100:1 $PhCl_2P{=}NSiMe_3/PCl_5$ polymerization). To improve the solution polymerizations, the influence of various conditions such as solvent, concentration, temperature, and initiator has been investigated. In earlier work, the solution polymerization of $Cl_3P{=}NSiMe_3$ (**1**) took place not only in CH_2Cl_2 but also in cyclohexane, tetrahydrofuran, acetonitrile, and nitromethane.^{2} However, only in CH_2Cl_2 and cyclohexane did the polymerizations proceed quantitatively, without unwanted side reactions.

Because monomer **1** polymerizes much faster in CH_2Cl_2 than in cyclohexane, earlier detailed polymerization studies were conducted solely with CH_2Cl_2 as a solvent at various temperatures.^{2} Solvent effects such as polarity, dielectric strength, and solvating ability were believed to be the main factors that control the polymerization rate. The polymerization of monomer **1** in CH_2Cl_2 appears to be living because (1) the polymerization rate follows pseudo-first-order kinetics with respect to monomer concentration, (2) the number-average degree of polymerization is proportional to the monomer conversion, (3) the molecular weight distribution corresponds to the Poisson distribution, and (4) the polymer system remains active for at least 24 h after complete conversion of monomer to polymer.^{2} The kinetics of polymerization in CH_2Cl_2 of the analogous organophosphoranimines, such as $PhCl_2P{=}NSiMe_3$, were difficult to examine because the polymerizations were slow and inconsistent.^{3}

Current Approach. We have now studied the polymerization of $Cl_3P{=}NSiMe_3$ (**1**) and $PhCl_2P{=}NSiMe_3$

Table 1. Higher Molecular Weight Polyphosphazenes Prepared in Toluene

[PCl$_5$]	**1**:PCl$_5$	reaction time (days)	$M_n \times 10^{-5}$ (g/mol) found	$M_n \times 10^{-5}$ (g/mol) calcd	PDI (M_w/M_n)
0.0050	350:1	28	0.49	1.7	1.72
0.0021	350:1	2	2.2	1.7	1.23
0.0012	350:1	21	0.94	1.7	1.96
0.0021	400:1	2	2.6	1.9	1.27
0.0021	400:1	3	2.5	1.9	1.29
0.0021	800:1	3	2.8	3.9	1.30

[a] Calculated molecular weights were based on the initial ratio of Cl$_3$P=NSiMe$_3$ ([**1**]$_0$:[PCl$_5$]$_0$) and by assuming that two initiator molecules, i.e., [PCl$_4$]$^+$[PCl$_6$]$^-$, are used to activate the chains.

(**2**) in chloroform, toluene, benzene, chlorobenzene, and dioxane. The polymerizations in toluene, benzene, and dioxane meet the above requirements for a living process and show some similarities to other ionic polymerizations. In addition, the reactions in chloroform and chlorobenzene were very similar to those carried out in CH$_2$Cl$_2$.

Solvents were originally chosen for their high polarity, high dielectric strength, and good solvating ability as the best choice for the most efficient cationic condensation polymerizations. However, these requirements are not crucial. Polymerization of monomer **1** with PCl$_5$ as the initiator (for ratios up to 100:1) in toluene or CH$_2$Cl$_2$ were complete within 12 h. However, the propagation rates for the polymerization of monomer **2** in toluene, dioxane, or benzene were dramatically faster than those in CH$_2$Cl$_2$ or CHCl$_3$. Solution polymerizations of monomer **2** with PCl$_5$ were conducted for ratios of up to 100:1. These reactions were reproducible and consistently went to completion. Moreover, previously inaccessible higher molecular weight polymers derived from monomer **1**, with controlled molecular weights and low polydispersities were synthesized in toluene, dioxane, or benzene with appropriately higher ratios of the monomer to PCl$_5$ initiator. It should be noted that trimethylchlorosilane can be used as the initial solvent for the polymerization, but polymer molecules precipitate from this medium before the reaction is complete. However, the presence of trimethylchlorosilane does not appear to affect the molecular weight distribution.

The best polymerization results were obtained with freshly prepared initiator solutions (PCl$_5$, SbCl$_5$, or PhPCl$_4$), because, as is well-known, the initiator may dissociate over time especially when the temperature is raised. Examination by ^{31}P NMR spectroscopy of PCl$_5$ dissolved in toluene revealed the presence of a sharp singlet at 220 ppm which is characteristic of PCl$_3$. In toluene, the chlorine released from PCl$_5$ can react with the solvent or be lost from solution. Small peaks between 4 and 5 ppm in the ^{1}H NMR spectra of the PCl$_5$ solution suggest that toluene is chlorinated to form benzyl chloride and other chlorinated products. Furthermore, heating of the solution resulted in the formation of larger amounts of PCl$_3$ and chlorinated toluene. Because this process reduces the amount of PCl$_5$ present, and because PCl$_3$ is apparently not an initiator, polymers with higher than the expected molecular weights were produced.

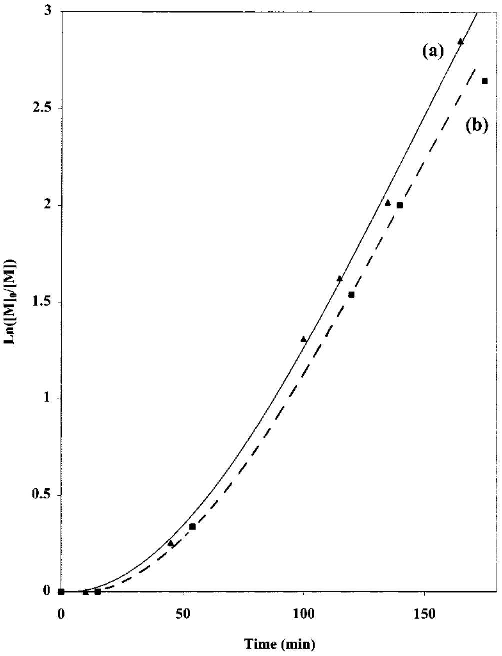

Figure 1. Kinetic study of a 50:1 Cl$_3$P=NSiMe$_3$ (**1**)/PCl$_5$ polymerization in toluene monitored by (a) ^{31}P and (b) ^{1}H NMR spectroscopy.

Higher MW Polymers. Polymers with controlled molecular weights, M_n, in the range of 10^5 with low polydispersities (<1.3) were synthesized via phosphoranimine polymerizations in toluene (Table 1). Products with molecular weights, M_n, up to 3×10^5 were formed by polymerization of 350:1 to 800:1 monomer **1**:PCl$_5$ systems in toluene (after replacement of the chlorine atoms by trifluoroethoxy groups). Similar results were obtained with benzene or dioxane as solvents. However, in CH$_2$Cl$_2$ these polymerizations either did not take place or yielded lower molecular weight polymers with broad molecular weight distributions. The polymerizations in toluene at these ratios were consistently complete within a few days at the appropriate PCl$_5$ concentration (0.0021 M), whereas polymerization times of 1 week or more were required for polymerizations in CH$_2$Cl$_2$.

NMR Characterization of the Polymers. For phosphoranimine polymerizations, the end groups of the growing polymer chain are detectable and distinct from the middle units in the ^{31}P NMR spectrum.[2] The polymerization of monomer **1** in the presence of PCl$_5$ yields a doublet in the spectrum at 9 ppm, attributed to the PCl$_3$$^+$ end groups. Also present are two triplet peaks at −15 and −16 ppm assigned respectively to the resonances for the first and second PCl$_2$ groups from the polymer chain end. Most notably, the interior PCl$_2$ groups yield a singlet at −17 ppm. By contrast, the polymerization of monomer **2** is characterized by a number of small sharp peaks between 40 and 0 ppm in the ^{31}P NMR spectrum. These peaks, attributed to the end groups, are difficult to assign because the random orientations of the phenyl and chloro groups result in different environments for the phosphorus atoms. Furthermore, short chains and/or cyclic phosphazenes are also produced in the polymerization process.

Kinetic Studies. Both ^{31}P and ^{1}H NMR spectroscopy were used to monitor the conversion of a phosphoranimine monomer to polymer over time to determine the propagation rates at room temperature. The following polymerization reactions were examined: (1) monomer **1** in toluene (Figure 1); (2) monomer **2** in toluene (Figure 2) or benzene (Figures 3 and 4); and (3) block copolymerization of monomers **1** and **2** in toluene (Figure 5). In all cases, the NMR integration data suggested that the propagation rates follow pseudo-first-order kinetics (ap-

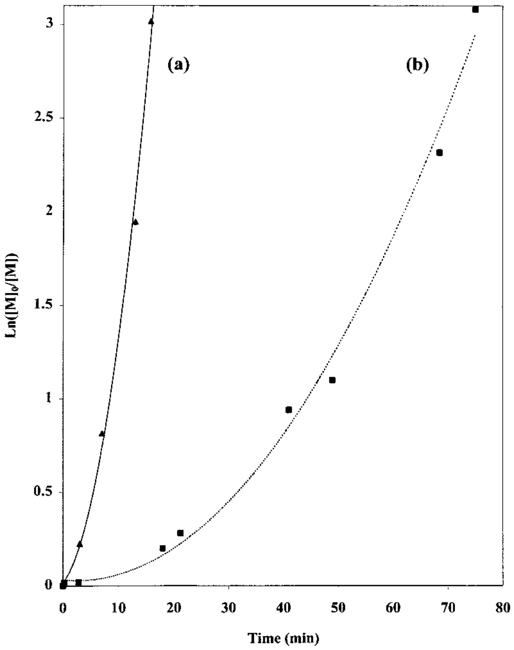

Figure 2. Kinetic study of $PhCl_2P{=}NSiMe_3$ (**2**): PCl_5 polymerizations in toluene monitored by ^1H NMR spectroscopy: (a) 10:1 and (b) 50:1 $PhCl_2P{=}NSiMe_3$ (**2**):PCl_5, showing the rate acceleration during the initial induction period.

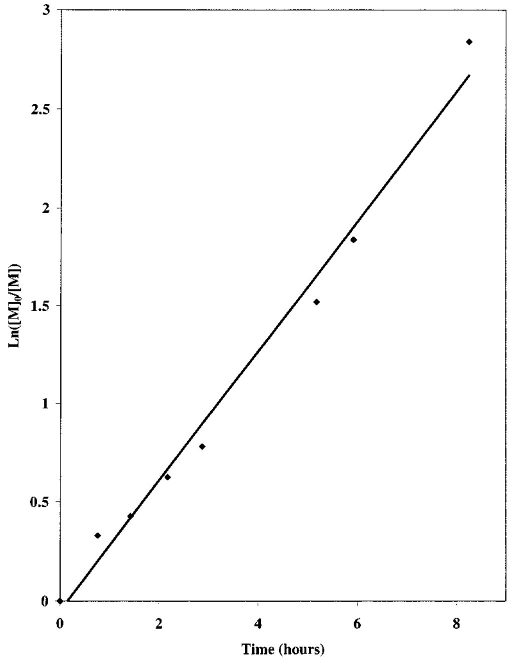

Figure 3. Kinetic study of a 50:1 $PhCl_2P{=}NSiMe_3$ (**2**): PCl_5 polymerization in benzene monitored by ^1H NMR spectroscopy.

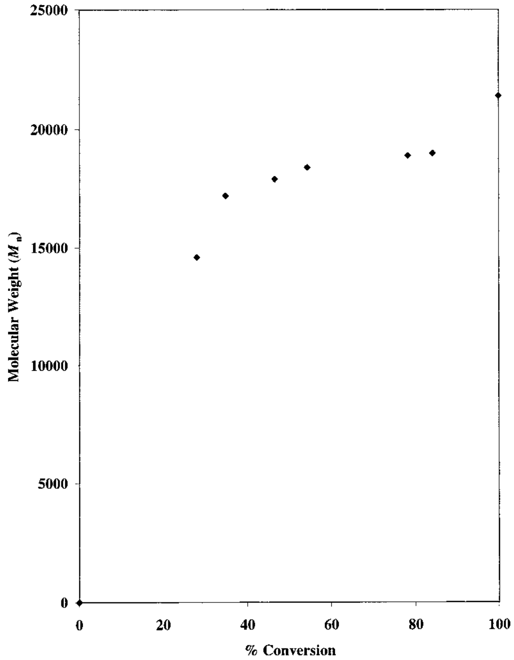

Figure 4. Molecular weight vs percent conversion for a 50:1 $PhCl_2P{=}NSiMe_3$ (**2**): PCl_5 polymerization in benzene.

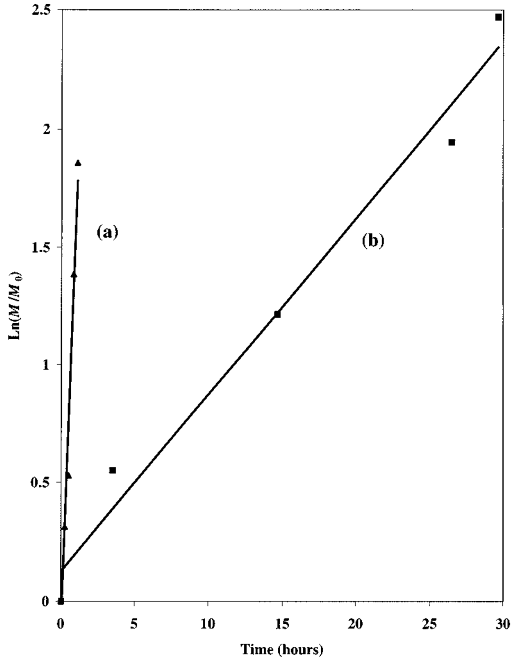

Figure 5. Block copolymerization of $Cl_3P{=}NSiMe_3$ (**1**) and $PhCl_2P{=}NSiMe_3$ (**2**). Curve a represents the polymerization of $Cl_3P{=}NSiMe_3$ with PCl_5 in the absence of the second monomer. Curve b represents the propagation of the monophenyl monomer from the active end of living poly(dichlorophosphazene) generated sequentially from $Cl_3P{=}NSiMe_3$ with PCl_5 and $PhCl_2P{=}NSiMe_3$ in a ratio of 20:1:50 respectively in toluene.

proximately linear ln $[M]_0/[M]$ vs time) after an initial induction period of 15 min to 1 h.

This slow induction period results from the initial precipitation of linear P−N−P short chain salts, $Cl_3P{=}N(PCl_2{=}N)_nPCl_3^+PCl_6^-$ (where $n = 0, 1, 2, ...$). However, initiation of the monomer with PCl_5 is quite rapid in the solvents studied, as indicated by the immediate formation of the precipitate. This cloudy or slightly hazy precipitate forms in highly concentrated polymerization solutions of all the solvents studied, including CH_2Cl_2. After the initial induction period, the precipitate dissolves to give a clear, colorless solution. The slow polymerization rate during the induction period resembles some typical cationic polymerizations[9] in the sense that acceleration of the polymerization occurs as the initiator is consumed. The eventual solubilization of the phosphazene short chain species in the phosphoranimine polymerizations results in an acceleration of the polymerization and the appearance of pseudo-first-order characteristics.

For monomer **1**, NMR spectroscopy was used to monitor reactions with 20:1 and 50:1 monomer **1**:PCl_5

Table 2. Effect of Different Polymerization Times on 50:1 $PhCl_2P{=}NSiMe_3$ (2): PCl_5 Reactions in Various Solvents

solvent	time (h)	% conv	$M_n \times 10^{-4}$ (g/mol) found	$M_n \times 10^{-4}$ (g/mol) calcd	PDI (M_w/M_n)
toluene	1.0	21	1.6	0.46	1.19
	5.1	66	1.7	1.5	1.19
	12	100	2.4	2.2	1.14
benzene	1.5	16	1.8	0.35	1.14
	6.1	65	2.1	1.4	1.14
	18.7	100	2.7	2.2	1.20
dioxane	1.0	15	1.4	0.33	1.12
	6.0	58	2.0	1.3	1.15
	18.5	100	2.3	2.2	1.11

[a] Molecular weights have been based on the initial ratio of monomer ($[\mathbf{1}]_0$:$[PCl_5]_0$) and assuming two initiator molecules, i.e., $[PCl_4]^+[PCl_6]^-$, are used to activate the chains.

ratios in toluene at room temperature. These polymerizations were conducted at approximately the same monomer concentration (0.9 M). The 50:1 ratio polymerization in toluene was complete in about 4 h, which is comparable to similar reaction times in CH_2Cl_2, but the 20:1 ratio reactions were slower (approximately 1.5 h vs 45 min in CH_2Cl_2). The kinetics indicate that the polymerization rates are initially faster in CH_2Cl_2, probably because the growing P−N−P chains are more soluble in CH_2Cl_2 than in toluene. Figure 1 illustrates that propagation rates in toluene follow pseudo-first-order kinetics for the 50:1 ratio reactions. After an initial induction period of about 20 min, the propagation rate is linear and faster than in CH_2Cl_2 for these specific polymerizations.

Solution polymerizations of monomer **2** in toluene were also reproducible. The propagation kinetics followed a similar trend to those of monomer **1**. For monomer **2**, 10:1 and 50:1 ratios of monomer to PCl_5 initiator were examined; NMR spectroscopy indicated that the propagation rates follow pseudo-first-order kinetics after an induction period of approximately 15 min. At the end of the induction period, the polymerization rate accelerates as the growing chain becomes more soluble (resulting in a steeper slope for $\ln([M]_0/[M])$ vs time) (Figure 2).

Comparable polymerizations of monomer **2** in 50:1 ratios of monomer to PCl_5 initiator (5×10^{-3} M) were carried out in dioxane and in benzene (Figure 3). These reactions were very similar to those in toluene. In *dioxane*, small amounts of small-molecule cyclic phosphazene species were formed as well as polymer, as indicated by ^{31}P NMR spectroscopy. Samples from the polymerization reaction mixture were treated with sodium trifluoroethoxide at various times to replace the chlorine atoms, and the resultant products were studied by both NMR and GPC methods (Table 2). A more detailed NMR/GPC study was conducted for the 50:1 monomer **2**:PCl_5 polymerization in *benzene* at a similar concentration (Figures 3 and 4). These reaction conditions result in a rapid molecular weight increase at low conversions. At 100% conversion of monomer to polymer, the theoretical molecular weights are reached. These reactions yield polymers with PDI < 1.3 and are consistent with results obtained for slow initiation cationic polymerizations.[9]

Finally, the propagation rates for the sequential block copolymerization of monomer **1** followed by monomer **2** were also examined by NMR spectroscopy. The propagation rates for both phosphoranimines follow pseudo-first-order kinetics. In the block copolymerization, some deviation from linearity was detected in the initiation and active site transformation (Figure 5).

Table 3. Polymerization of $Cl_3P{=}NSiMe_3$ (1) with PCl_5 Using Different Reaction Conditions

solvent	$[PCl_5]$	**1**:PCl_5	reaction time (min)	$M_n \times 10^{-4}$ (g/mol) found	$M_n \times 10^{-4}$ (g/mol) calcd	PDI (M_w/M_n)
toluene	0.055	20:1	140	1.38	0.97	1.18
toluene	0.011	20:1	180	1.53	0.97	1.05
toluene	0.007	20:1	185	1.62	0.97	1.09
CH_2Cl_2	0.055	20:1	60	1.85	0.97	1.09
CH_2Cl_2	0.011	20:1	100	1.59	0.97	1.14
CH_2Cl_2	0.007	20:1	130	1.04	0.97	1.34
toluene	0.022	50:1	70	2.11	2.4	1.08
toluene	0.009	50:1	80	2.29	2.4	1.09
toluene	0.004	50:1	90	2.48	2.4	1.09
toluene	0.003	50:1	90	2.83	2.4	1.05

[a] Molecular weights have been based on the initial ratio of monomer ($[\mathbf{1}]_0$:$[PCl_5]_0$) and assuming two initiator molecules, i.e., $[PCl_4]^+[PCl_6]^-$, are used to activate the chains.

Concentration Studies. The concentration of the reactants was an important factor when polymerizations were carried out in toluene as opposed to CH_2Cl_2. Reactions were monitored by NMR spectroscopy for both 20:1 and 50:1 ratios of monomer **1** to PCl_5 at various concentrations (ranging from 5.5×10^{-2} to 3.0×10^{-3} M PCl_5) (Table 3). For both polymerization ratios, the time of the reaction and the molecular weights of the polymers increased, while maintaining low polydispersities, as the initiator concentration was decreased. We believe that this molecular weight trend is due to the precipitation of short chain P−N−P species.

Identical experimental conditions were used with CH_2Cl_2 as a solvent to compare to the results in toluene. In this study, the reaction times were shorter in CH_2Cl_2 than in toluene. As in the toluene-based reactions, the overall reaction time increased as the initiator concentration was decreased. However, the molecular weights (after replacement of the chlorine atoms by trifluoroethoxy groups) actually decreased as the initiator concentration decreased. The enhanced reactivity and the decreased molecular weight can be attributed to the higher solubility of all the participating molecules in CH_2Cl_2.

Polymerizations were also carried out at higher monomer-to-initiator ratios. The production of well-defined polymers from **1** in toluene, with molecular weights in the range of 10^5, requires careful attention to the reagent concentration because the reactions are highly concentration dependent. Optimum polymerizations were achieved at initiator concentrations of approximately 0.002 M in toluene (Table 1). At this intermediate concentration, the polymerizations were complete within a few days at 25 °C for 350:1 monomer:initiator ratio reactions. However, in more concentrated or more dilute solutions, the polymerizations were slow, unpredictable, and gave lower molecular weight polymers with higher polydispersities.

Temperature Variation. ^{31}P NMR spectroscopy was used to monitor 20:1 monomer **1**:PCl_5 polymerizations in toluene at various temperatures (10, 25, and 50 °C). The rate of polymerization increased as the temperature increased. This result is similar to that found for reactions in CH_2Cl_2. However, the use of toluene allowed higher reaction temperatures to be used. Plots of the $\ln([M]_0/[M])$ vs time were linear after an initial induction period at the various temperatures (Figure 6).

The rates of propagation were determined from the slopes of the linear plots of $\ln([M]_0/[M])$ vs time by

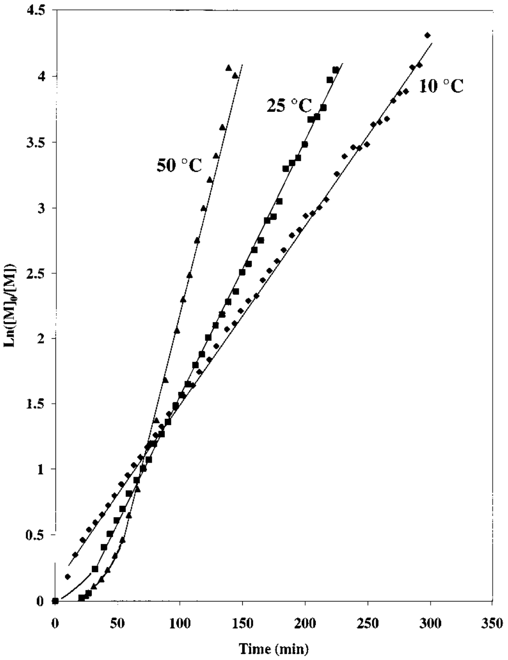

Figure 6. Variable temperature study of a 20:1 $Cl_3P{=}NSiMe_3$ (**1**)/PCl_5 polymerization in toluene.

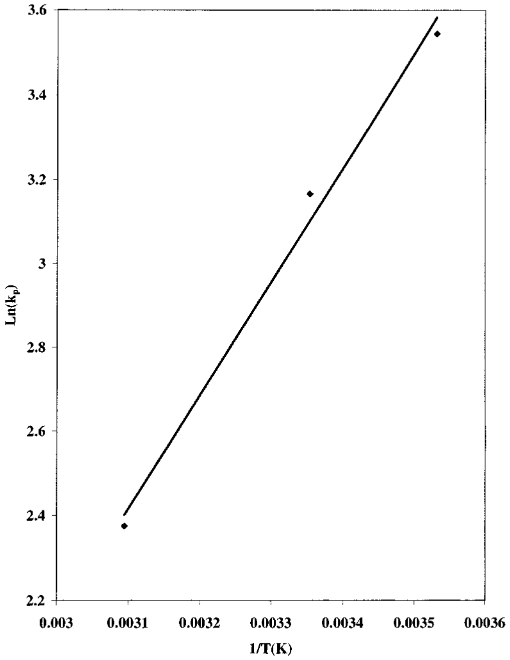

Figure 7. Arrhenius plot for a 20:1 $Cl_3P{=}NSiMe_3$ (**1**)/PCl_5 polymerization in toluene.

assuming $[M^*] = 0.5[I_0]$ and $k_p' = k_p[M^*]$ (steady-state approximation). The Arrhenius plot of ln k_p vs $1/T$ (Figure 7) was used to determine the energy of activation, $E_a = 22.5$ kJ/mol, and the preexponential factor, $A = 3.9 \times 10^2\ s^{-1}$. The values $E_a = 53.9$ kJ/mol and $A = 2.0 \times 10^9\ s^{-1}$ were obtained from a similar Arrhenius plot for 20:1 monomer **1**:PCl_5 polymerizations in CH_2Cl_2.[2] The polymerizations in toluene have lower energies of activation compared to those in CH_2Cl_2, but at the same time, the lower collision frequency factor in toluene, compared to CH_2Cl_2, predicts longer polymerization times at these ratios. This explains why polymerizations with higher ratios of monomer to initiator in toluene at certain concentrations are faster than in CH_2Cl_2 and thus go to completion.

Although the rate of propagation for the reaction in toluene can be maximized at a certain initiator concentration, two conflicting factors must be balanced. First, the reaction mixture must be sufficiently dilute for the polymer to form a homogeneous solution. The system also needs to be fairly concentrated to maximize the interactions between the monomer and the growing chain. The rate of propagation in toluene can be optimized by meeting both of these criteria. Multiple resonances were present in the ^{31}P NMR spectra for the 20:1 **1**:PCl_5 polymerizations in both methylene chloride and toluene. The end group peaks were much smaller for the higher temperature polymerization at 50 °C in toluene, which suggests that the higher temperature polymerization yields higher molecular weight polymers. Gel permeation chromatographs of the sodium trifluoroethoxide-treated sample also indicated higher molecular weights for the polymerizations at higher temperatures. The trifluoroethoxy-substituted polymer sample from the 50 °C polymerization had a higher molecular weight ($M_w = 2.6 \times 10^4$ with a PDI = 1.29) than the product formed at 25 °C ($M_w = 2.4 \times 10^4$ and PDI = 1.29) or 10 °C ($M_w = 2.2 \times 10^4$ and PDI = 1.16). The formation of a higher molecular weight polymer at higher temperatures may be due to the greater reactivity of PCl_5 initiator with toluene as discussed above.

Random Copolymerization Conditions. The random copolymerization of **1** and **2** was attempted in CH_2Cl_2 and toluene solvents in an attempt to synthesize copolymers with architectures that are different from the block systems that have already been described.[4,5] However, the polymerization did not proceed randomly. Monomer **2** polymerized first, and following its depletion, monomer **1** then polymerized from the active terminus to yield a blocky copolymer, identified by ^{31}P NMR techniques.[4,5] This suggests that the terminal species formed by the addition of monomer **2** is the most reactive of the two and that the further addition of monomer **2** to the growing chain is much faster than the addition of monomer **1**. Similar copolymerization kinetics exists for the anionic copolymerization of styrene and butadiene.[10] The homopolymerization of styrene is much faster than the homopolymerization of butadiene. However, in copolymerization reactions, the rate of butadiene addition remains very similar, but the polymerization rate of styrene is greatly decreased. Although reactivity ratios of the two phosphazene monomers were not established, it seems clear from the results that $r_{11} \gg r_{22}$ and that $r_{22} \sim r_{12} \gg r_{21}$, where r_{12} is the rate of monomer **2** addition to a chain end with monomer **1** end group and r_{21} is the rate of monomer **1** addition to a chain with monomer **2** end group.

Other Initiators. The alternative initiators, $SbCl_5$ and $PhPCl_4$, were reexamined. Previously, we reported that these polymerizations were similar to those when PCl_5 was employed as an initiator. Similar reaction times were reported, and GPC analyses indicated controlled molecular weights with low polydispersities. In the earlier study, the polymerizations were not monitored extensively by NMR spectroscopy. The present examination by ^{31}P NMR methods indicated that the polymerizations with $SbCl_5$ or $PhPCl_4$ as initiators generate multiple ^{31}P NMR resonances because of the different environments on the phosphorus atoms. The distinct environments on each end of the chain result in chains of the type $Cl_3P{=}N(PCl_2{=}N)_nSbCl_3^+X^-$ or $Cl_3P{=}N(PCl_2{=}N)_nPPhCl_2^+X^-$ (where X^- is the appro-

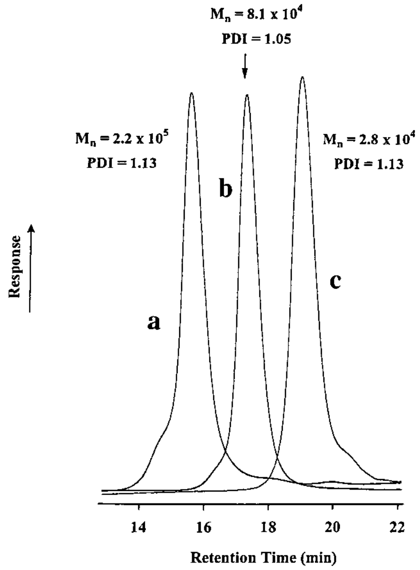

Figure 8. GPC profiles for poly[bis(4-propylcarboxylatophenoxy)phosphazene] produced from polymerizations of $Cl_3P{=}NSiMe_3$ (**1**) with PCl_5, with monomer-to-initiator ratios in toluene of (a) 357:1, (b) 178:1, and (c) 25:1.

priate counterion). These results further support a cationic polymerization mechanism.

Demonstration of These Principles To Prepare a Biomedical Polyphosphazene. Considerable interest exists in the synthesis of polyphosphazenes with controlled molecular weights for applications in medicine, such as in drug delivery, microencapsulation, and hydrogels. One polyphosphazene of interest is poly[bis(4-carboxylatophenoxy)phosphazene], $[N{=}P(OC_6H_4\text{-}COOH)_2]_n$,[11,12] the biological behavior of which depends on the polymer chain length. Obtaining controlled molecular weight polymer in the past has required fractionation of material with a very broad molecular weight distribution or other special techniques.[13] The cationic polymerization of monomer **1** in toluene, with monomer-to-initiator ratios of 357:1, 178:1, and 35:1, followed by substitution with the sodium salt of propyl 4-hydroxy benzoate, has yielded poly[bis(4-propylcarboxylatophenoxy)phosphazene], a precursor to poly[bis(4-carboxylatophenoxy)phosphazene]. The polymers produced have controlled molecular weights in the range $10^4{-}10^5$, with low polydispersities (Figure 8).

Summary

Polyphosphazenes with controlled molecular weights in the range of 10^5 have been synthesized in toluene, benzene, and dioxane. The solvating ability of these media appears to be lower than for chlorinated solvents such as CH_2Cl_2 or $CHCl_3$. However, this may allow the initiated species to be more reactive toward phosphoranimines than to impurities or to the solvent. The polymerization of the monomers, $Cl_3P{=}NSiMe_3$ (**1**) and $PhCl_2P{=}NSiMe_3$ (**2**), was reproducible in these solvents and resulted in more controlled reactions. The attempted simultaneous copolymerization of the two phosphoranimines did not yield a random copolymer. Instead, the propagation rate of **1** was greatly reduced in the presence of **2**, and this resulted in a blocky copolymer in which mainly monomer **2** polymerized first. Attempts to synthesize polyphosphazenes with controlled molecular weights in the range of 10^6 with low polydispersities are in progress.

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