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THE CONVERSION OF PHOSPHORANIMINES TO POLYPHOSPHAZENES IN THE PRESENCE OF ELECTROPHILES

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Key Words: Polyphosphazene; Phosphoranimine; Lewis acids; Brønsted acids; Phosphonitrilic compounds

ABSTRACT

The application of electrophilic compounds as initiators for the polymerization of *N*-silylated phosphoranimines represents a new and rapid method for the synthesis of low to moderate molecular weight polyphosphazenes. Several Brønsted and Lewis acids were studied, and antimony pentachloride was found to be particularly effective. Complete conversion of a phosphoranimine monomer was observed within 2 hours under mild conditions (ca. 100°C) in solution polymerization with $SbCl_5$. Poly[bis(trifluoroethoxy)phosphazenes] of molecular weight M_n = 10,000 to 50,000 were obtained with low to moderate polydispersities (M_w/M_n = 1.2 to 2.5) and were characterized by NMR, IR, GPC, and DSC techniques. Kinetic and mechanistic evidence support $SbCl_5$ as the true initiator, whereas the Brønsted haloacetic acids were found to initiate polymerization by the corresponding anions without the involvement of protons.

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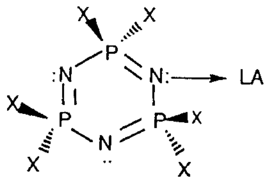
INTRODUCTION

The polymerization of *N*-silylated phosphoranimines to form polyphosphazenes in the presence of nucleophilic initiators and catalysts has been previously reported, and our investigation of this process has revealed a large number of anions and neutral bases that have a catalytic effect on the reaction [1-5]. The evidence to date supports an anionic chain-growth condensation polymerization in which the active chain ends are more reactive than the monomer [6].

Recently, we have been able to functionalize the polymer chain ends by reaction with new end-capping compounds to control molecular weight [7]. In addition, related efforts in our laboratory have produced the first phosphazene block copolymers via this anionic initiation route [8].

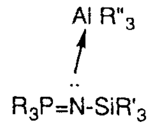
The success of the nucleophiles led us to consider the question of the effect of electrophilic compounds on the polymerization of these monomers.

The reaction of various phosphonitrilic compounds with acids has been documented in the previous reports of other workers. For example, certain Lewis acids have been found to form adducts with halocyclotriphosphazenes in which the phosphazene nitrogen coordinates with the acid as shown below [9, 10].



X = Cl, Br

In similar fashion, aluminum and gallium trialkyls have been found to form coordination complexes with *N*-trialkylsilyl phosphoranimines [11].



$$\begin{array}{c} AlR''_3 \\ \uparrow \\ R_3P{=}\ddot{N}{-}SiR'_3 \end{array}$$

The work of Horn and Kolkmann provided evidence for a BCl_3:hexakis(trifluoroethoxy)cyclotriphosphazene adduct [12]. They reported a mixture of polymeric phosphazenes in 50% yield after heating this cyclophosphazene trimer with equimolar boron trichloride for over 1000 hours at 150°C. The polymeric products contained both chloro- and trifluoroethoxy groups as determined by elemental analysis, thus indicating a ligand exchange reaction had occurred.

In related work, hexachlorocyclotriphosphazene was reacted with $SbCl_5$ or BCl_3 to produce long chain polymers, and $AlCl_3$ gave phosphazenyl cations [13]. $TiCl_4$ did not react with the chloro trimer, and boric acid esters produced a ligand exchange of one ester group for one chloro group.

Sennett and others have studied the kinetics of the boron trichloride catalyzed polymerization of hexachlorocyclotriphosphazene in trichlorobenzene solution [14]. In their mechanism, a BCl_3:phosphazene adduct was proposed as the initiation step.

Montoneri et al. reported the complex formed by SO_3 and $[NP(OC_6H_5)_2]_3$ cyclic trimer [15], and more recently, Wisian-Neilson and Garcia-Alonso have characterized the lithium and silver coordination complexes formed by the metal tetrafluoroborate salts and polyalkyl/aryl phosphazenes [16].

Brønsted acids react with phosphazenes as well. Protonated phosphazenes have been reported such as the hydrohalide adducts, in which the proton is associated with the backbone nitrogen atom [17]. Protonated polyalkyl/aryl phosphazenes are formed by the addition of hydrochloric acid [16]. In general, the ease of protonation follows the relative basicity of the phosphazene nitrogens, which depends on the availability of the nitrogen lone pair electrons [10]. The basicity of the nitrogens is reduced by electron-withdrawing substituents at the phosphorus centers, and is enhanced by electron-donating groups.

All of the earlier reports provide ample precedent for the reactivity of phosphazenes with acidic compounds and suggest that there should be many potential reactions to explore.

In this paper, we report the polymerization of an *N*-silylated phosphoranimine using various electrophiles. This method represents a new approach to the rapid conversion of these polyphosphazene precursors.

EXPERIMENTAL

Screening Study of Acids

Several 5 mm NMR tubes were dried overnight at 150°C, capped with natural rubber septa and Teflon tape, and cooled under an argon purge. Freshly distilled liquid monomer, $(CF_3CH_2O)_3P{=}N{-}Si(CH_3)_3$, was added by syringe (1.5 mmol) to a dry NMR tube. Approximately 1 to 2 mol% of the acid was added and mixed thoroughly. Solid acids were added to the tube in a nitrogen-filled glove box prior to monomer addition.

The sealed tubes were heated in an oil bath at the temperature and time shown in Table 1. Dry diglyme, distilled from CaH_2, was added to dissolve any polymer formed, and ^{31}P-NMR spectra were recorded. Yields of polymer shown in Table 1 were estimated from the spectral peak integration.

Bulk Polymerization of Phosphoranimine with $SbCl_5$ Initiator

The monomer, $(CF_3CH_2O)_3P{=}N{-}Si(CH_3)_3$, was prepared according to a previously published method [30]. Bulk polymerization was accomplished in a 25-mL 3-neck round flask equipped with magnetic stirbar, 25 mL addition funnel, thermometer, and a water-jacketed condenser with a cold Dean-Starke trap. The apparatus was sealed with rubber septa and Teflon tape and flame-dried under a dry argon purge.

Under a blanket of argon, 15 mmol distilled monomer was added by syringe and 0.15 mmol $SbCl_5$ (1.0 M in CH_2Cl_2, Aldrich Chemical Co. as received) was added by microsyringe under agitation. A hot mineral oil bath at 120–130°C was raised under the flask. Liquid condensate was collected in the cold trap during the reaction over a 3-hour period.

Upon removal of the oil bath, the melt solidified upon cooling, and was dissolved in 10 mL dry THF solvent. The THF solution was quickly added to excess cold chloroform (250 mL), and a white precipitate was obtained. The precipitate was stirred for about 30 minutes, cooled to −20°C, and filtered through a tared frit or tared Whatman #42 filter paper in a Büchner funnel.

The white polymer product was dried under vacuum for 24 hours, and the weight was determined on an analytical balance. Yield of polymer was calculated on the basis of monomer weight minus the $(CH_3)_3SiOCH_2CF_3$ condensate by-product: 50–99% (see Table 2).

Solution Polymerization with Acid Initiators

Diglyme and nitromethane were refluxed over CaH_2 overnight and distilled over to calcium hydride. All solution polymerizations were conducted in 5 mm NMR tubes which were dried and sealed as specified in the Screening Study above. Antimony pentachloride solution (1.0 M in CH_2Cl_2 from Aldrich Chemical Co.) was used as received. The acetic acids were dissolved in dry CH_3NO_2 to 1.3 M. Liquid monomer (1.5 mmol) was diluted to 1.5 M with either dry nitromethane or diglyme, and introduced to the tube by dry syringe. The appropriate amount of acid solution was added by dry microsyringe, and the contents of each tube were mixed thoroughly.

The sealed NMR tubes thus prepared were heated in a mineral oil bath at the indicated temperature and time period. In all experiments the temperature reported is the external temperature of the oil bath. Yields of products were determined from the ^{31}P-NMR peak integration. ^{31}P-NMR spectra were recorded at the indicated intervals for the kinetic experiments.

Characterization of Reaction Products

NMR spectra were recorded on an IBM NR/300 MHz FT-NMR. Trimethyl phosphite in C_6D_6 was used as an external standard for ^{31}P-NMR spectra, with $\delta p = 141.0$ ppm (same as 0 ppm for 85% phosphoric acid). The lock solvent for all kinetic experiments was $CDCl_3$ and was isolated from the reactants by employing a concentric tube-in-tube arrangement.

The 5-mm NMR sample tube was mounted inside a 10-mm NMR tube via a Teflon insert (Wilmad Scientific). About 2 mL of lock solvent was placed in the outer 10 mm tube; the monomer, solvent, and initiator were loaded in the inner 5 mm tube under an argon blanket and rubber septum seal.

The ^{1}H-NMR spectrum of the condensate was recorded in $CDCl_3$ solution in a 5-mm NMR tube, with the $C\underline{H}Cl_3$ peak at 7.24 ppm as internal standard. The ^{1}H-NMR spectra of the polymers were recorded in d_6-acetone in a 5-mm NMR tube, with the acetone proton peak at 2.04 ppm as internal standard. The ^{29}Si-NMR spectra were recorded with hexamethyldisiloxane external standard (6.85 ppm).

A Nicolet 5DXB FT-IR was used to obtain IR spectra of the solid poly[bis(trifluoroethoxy)phosphazene] by KBr pellet. Polymer IR band assignments: 2981 cm^{-1}, aliph. CH; 1462 cm^{-1}, CH_2; 1427 cm^{-1}, P—O—C; 1271-1308 cm^{-1} br, P=N; 1173 cm^{-1}, P—O; 1089 cm^{-1}, C—O; 963 cm^{-1}, P—O; 660 cm^{-1}, CF_3.

A Seiko I DSC 220C (SSC /5200) with SSC 5040 Disk Station provided the thermal measurements of polymer samples with two 10°C/min heating and 20°C/min cooling cycles. Sample size was approximately 10 mg of solid polymer; the data were taken from the second heating curve.

A Waters Model 510 Size Exclusion Chromatograph with three Ultrastyragel columns (10,000, 1000, 100 Å) and a Model 410 Differential Refractometer with internal temperature of 35°C was used to measure the molecular weight of the polymer products. A polymer sample was prepared at 0.5% in THF (HPLC grade) and filtered through a 0.5-μ Teflon filter prior to injection. About 20 μL of this solution was injected into the carrier solvent stream (0.1% tetra-*n*-butyl ammonium bromide in THF [31] at a flow rate of 1.0 mL/minute. Data acquisition and calculations were performed via a Nelson 900 Analytical Interface on a Samsung IMS 286 personal computer. Calibration was based on polystyrene standards from Showa-Denko.

Elemental analysis of poly[bis(trifluoroethoxy)phosphazene] prepared by $SbCl_5$ initiator was performed by Midwest Microlab, Indianapolis, Indiana. Theoretical %: C, 19.75; H, 1.65; N, 5.76; P, 12.76; Cl, none; F, 46.91; O, 13.17. Found %: C, 19.32; H, 1.66; N, 5.69; P, 11.95; Cl, none; F, 45.35; O, fluorine interference.

RESULTS AND DISCUSSION

Screening Studies

Various acids were tested as potential catalysts for the polymerization of *P*-tris(trifluoroethoxy)-*N*-trimethylsilyl phosphoranimine, $(CF_3CH_2O)_3P{=}N{-}Si(CH_3)_3$, hereinafter referred to as the "monomer." Table 1 shows a compilation of results obtained in a series of experiments at different temperatures and reaction times.

As shown in the table, the silyl and methyl triflates failed to produce polymer even at 190°C, and it was initially thought that acids were ineffective as polymerization catalysts [3]. However, subsequent efforts with a range of acidic compounds have shown that a few are successful initiators of polymerization with respect to this monomer.

Among the protonic acids, sulfuric ("fuming"), *p*-toluene sulfonic, sulfamic, and chloroacetic were found to readily produce polymer upon heating as shown. Of these catalysts, chloroacetic gave the cleanest reaction. The others produced significant yields of unidentified by-products as well as polymer. It should be noted that the use of sulfamic and toluenesulfonic acids as catalysts for the ring-opening polymerization of hexachlorocyclotriphosphazene to poly(dichlorophosphazene) was previously reported by other workers [18].

The most effective Lewis acid was antimony pentachloride, $SbCl_5$. Other Lewis acids evaluated in the screening phase of the work were either unreactive or less effective. In some cases the acids were insoluble in the monomer and were tested as heterogeneous catalysts.

It is noteworthy that the trityl hexachloroantimonate salt was also a useful catalyst which gave quantitative conversion to polymer within 2 hours at 150°C. In order to determine the effect of the trityl cation on the reaction, the trityl pentachlorostannate salt was studied and found to be unreactive with respect to polymeriza-

TABLE 1. Screening Study of Acid Catalysts, 1 mol% of Monomer

Electrophile	Time, hours	Temperature, °C	Solvent	% Polymer, NMR	M_n	M_w/M_n
$(CH_3)_3SiOTf$	2.2	100	–	0	–	–
	1.0	190	–	0	–	–
CH_3OTf	2.2	100	–	0	–	–
	1.0	190	–	0	–	–
CF_3SO_3H	2.0	125	–	0	–	–
H_2SO_4 99%	1.0	125	Diglyme	50	–	–
pTSA	4.0	125	–	75	11,418	1.64
$ClCH_2COOH$	3.3	125	–	60		
$EtAlCl_2$	4.0	125	–	20		
Et_2AlCl	5.0	125	–	20		
$ZnCl_2$[a]	1.0	125	–	0		
$BF_3 \cdot Et_2O$	3.0	125	–	5		
$SbCl_5$	3.0	125	–	74	23,257	1.47
$(Ph)_3CSnCl_5$	2.3	125	–	0		
$SbCl_5$	1.0	145	–	75	28,872	2.47
$(Ph)_3CSbCl_6$	2.0	150	–	99	11,000	2.68[b]
H_2NSO_3H[a,c]	6.0	150	–	75	12,112	1.88
$AlCl_3$[a]	3.5	150	–	10		
BCl_3	2.5	150	–	0		
BBr_3	1.0	145	–	0		
$SnCl_4$	2.5	150	–	0		
$TiCl_4$	2.5	150	–	0		

[a] Heterogeneous catalyst.
[b] Bimodal molecular weight distribution.
[c] 2 to 4 mol%.

tion of the monomer. This indicated that the trityl cation was not the initiating species in the antimonate salt polymerization reaction.

Since the species $[SbCl_6]^-$ is a very soft anion and poor nucleophile, it is an unlikely candidate as the active agent in the reaction. On the other hand, the trityl hexachloroantimonate is in equilibrium with trityl chloride and $SbCl_5$:

$$\mathrm{Ph_3C^+SbCl_6^-} \rightleftharpoons \mathrm{Ph_3CCl} + \mathbf{SbCl_5}$$

Among the Lewis acids evaluated, only $SbCl_5$ showed significant reactivity as a polymerization initiator with this particular *N*-silyl phosphoranimine. Although $TiCl_4$ produced a yellow precipitate that is probably an acid-base adduct, the precipitate dissolved upon heating and no polymer was obtained as shown in Table 1.

It is likely that the relatively weak basicity of the phosphoranimine accounts for this selectivity. For example, titanium tetrachloride was found to be unreactive with the hexachlorocyclotrimer as previously mentioned. On the other hand, $TiCl_4$ readily forms an adduct with the hexamethylated cyclophosphazene trimer [10]. This indicates that inductive effects of the phosphorous substituents of the phosphazene play a key role in the reaction. The electron-donating methyl groups of the permethylated trimer result in a stronger phosphazene base, and thus an increased reactivity with the acid is observed.

Since antimony pentachloride was found to be the best Lewis acid polymerization catalyst in the present work, this compound was studied in a series of bulk and solution polymerizations.

Bulk Polymerization with $SbCl_5$

The bulk polymerization reaction was utilized to examine the polymer product in detail. A bulk reaction of monomer with 1% $SbCl_5$ was heated to 120-130°C for 3 hours.

The ^{1}H-NMR and ^{31}P-NMR spectra of the precipitated and washed white polymer were similar to that of the polymer obtained with the fluoride initiator [1, 6]. The δ_H chemical shift of the trifluoroethoxy protons was found at 4.54 ppm in d_6-acetone solution. The ^{1}H-NMR spectrum also showed trace signals of silylmethyl protons at 0.10, 0.18, and 0.29 ppm, indicating trimethylsilyl end groups.

The ^{31}P-NMR spectrum of the polymer showed a somewhat broad resonance at 6.85 ppm in d_6-acetone as the only signal. The polymerization residue, obtained by evaporating the chloroform precipitation solvent, showed the presence of oligomers including cyclic trimer and tetramer.

The molecular weight of the precipitated polymer was M_n = 28,316 with a polydispersity of 1.43 as shown in Table 2.

The FT-IR spectrum of the polymer was a good match to the spectra of the polymer produced by fluoride initiation [6] and the polymer obtained by thermal decomposition of the monomer [19] (Fig. 1).

A repeat bulk polymerization with this catalyst produced similar results with excellent agreement between the NMR and IR spectra. Table 2 shows the molecular

TABLE 2. Bulk Polymerization Data, $SbCl_5$ Initiator

$[M]_0$, bulk	% $SbCl_5$	T, °C	t, hours	M_n	M_w/M_n	% Conversion
3.0	1.0	125	3	28,316	1.43	57[a]
3.0	1.0	125	3	23,257	1.47	74
3.0	1.0	130	3	38,700	1.74	99
3.0	1.0	130	3	44,289	1.77	50[a]
3.0	1.0	145	1	28,872	2.47	75
3.0	1.0	150	17	51,355	1.47	100
3.0	1.0	200	17	59,786	2.17	100
3.0	1.0	240	17	(black discoloration: discarded)		

[a] Unstirred.

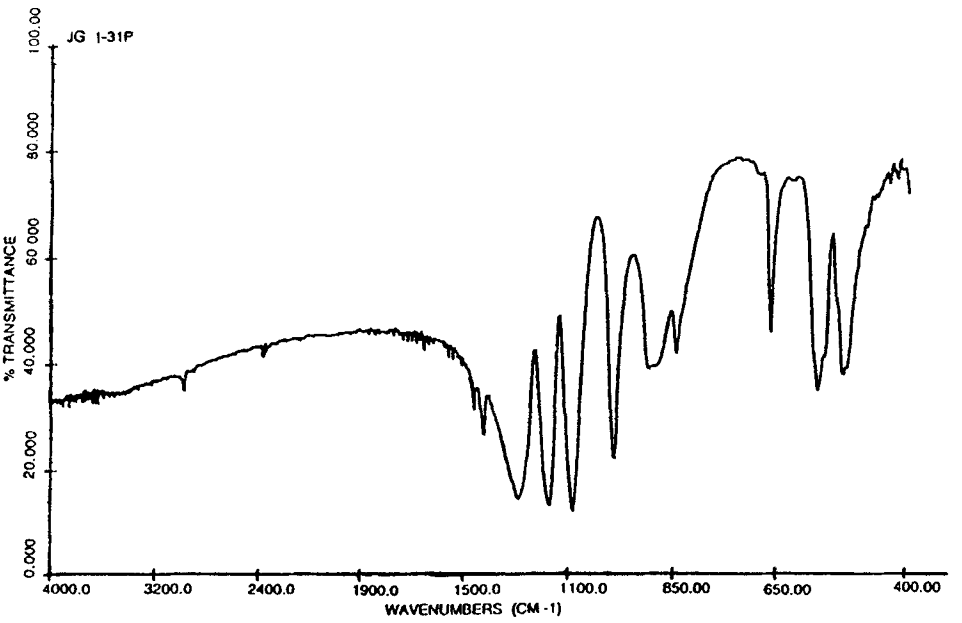


FIG. 1. FT-IR spectrum of poly[bis(trifluoroethoxy)phosphazene] (PBFP) isolated from bulk polymerization of monomer with 1% $SbCl_5$ initiator.

weights, polydispersities, and conversions produced by bulk polymerization under various times and temperatures.

The high temperature reactions (17 hours) produced the highest molecular weights, and may result from some contribution of macrocondensation of polymer chains after consumption of monomer. A trimethylsilyl chain end can condense with a trifluoroethoxy chain end to couple chains and enhance molecular weight. At 240°C, some decomposition products were observed as indicated in the table.

On the basis of these results, it was concluded that poly[bis(trifluoroethoxy)-phosphazene] is formed from the $SbCl_5$-catalyzed polymerization of the *P*-tris(trifluoroethoxy)-*N*-trimethylsilyl phosphoranimine monomer in a similar way to the nucleophilically catalyzed process:

$$(CF_3CH_2O)_3P{=}N{-}Si(CH_3)_3 \xrightarrow[\Delta]{SbCl_5} \overset{CF_3CH_2O\quad OCH_2CF_3}{(P{=}N)_n} + \overset{CF_3CH_2O\quad OCH_2CF_3}{(P{=}N)_{n=3,4}}$$

The DSC trace of the polymer is shown in Fig. 2 and was compared to the trace of the same polymer prepared from the same monomer and tetra-*n*-butyl ammonium fluoride initiator.

Though chemically similar, the polymers have very different thermal properties, indicating differences in morphology or microstructure. In addition to the *T*(1) transition at 74.5°C, another transition at 45°C is seen in the trace of the $SbCl_5$ polymer, and a very pronounced glass transition (T_g) at −68.7°C is displayed, in

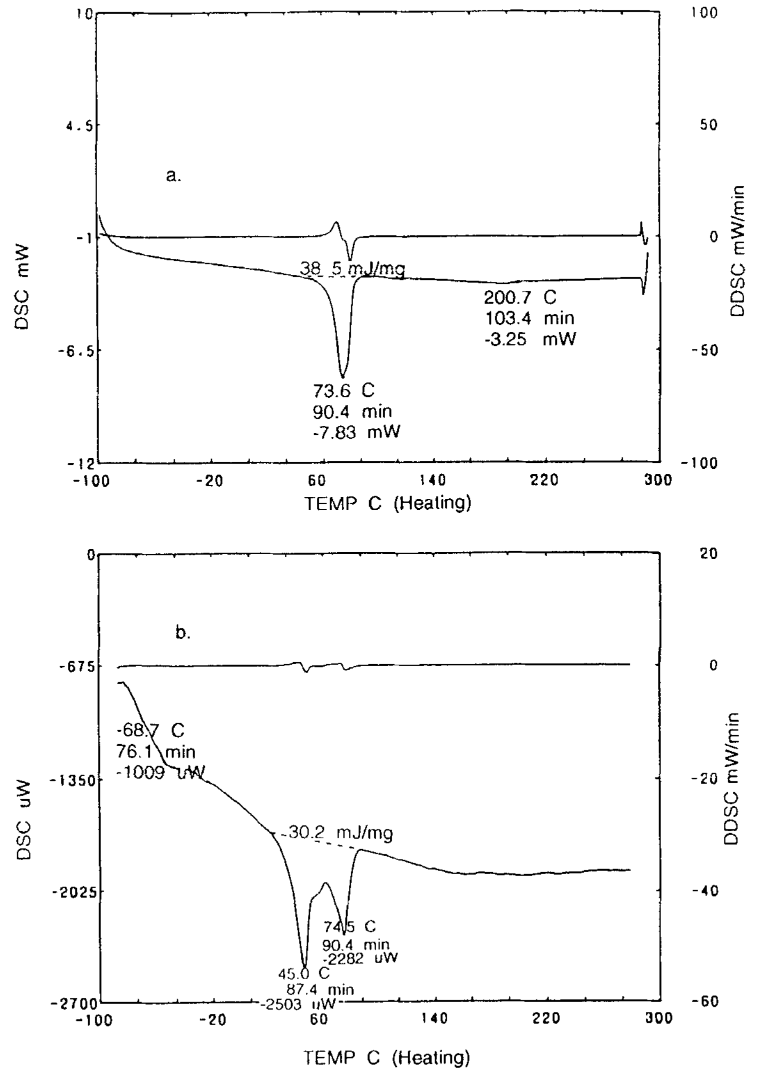


FIG. 2. DSC thermograms of PBFP prepared with (a) 1% TBAF and (b) 1% $SbCl_5$.

contrast to the trace of the fluoride-initiated polymer. Furthermore, while a T_i isotropization temperature is detected in the fluoride-initiated polymer at around 200°C, such transition was very weak in the $SbCl_5$-initiated polymer sample.

The advent of a second peak in the vicinity of the $T(1)$ transition temperature of poly[bis(trifluoroethoxy)phosphazene] is not unprecedented. It has been previously shown that the nature of the $T(1)$ transition of this polymer is highly dependent on the sample's thermal history, and a second peak near $T(1)$ may in fact be eliminated by subsequent annealing or heating cycles [20].

However, the DSC data shown in Fig. 2 were obtained from the second heating curves of solid polymer samples that were prepared and processed under similar conditions, and thus are comparable. The second peak in the $T(1)$ region may be due to different structure of the backbone as discussed later. The DSC experiment was repeated with a duplicate $SbCl_5$ polymer sample, and a similar trace was obtained.

Solution Polymerization with $SbCl_5$

A comparison of the solution polymerization of the monomer in diglyme to the monomer in nitromethane was conducted with 1 mol% antimony pentachloride as the catalyst at a temperature of 100°C. Nitromethane was selected as a more acidic solvent ($pK_a \approx 10$) than the ether, and it was thought that such a solvent could be beneficial to an acid-initiated polymerization. Furthermore, it was found that a sample of poly[(bistrifluoroethoxy)phosphazene] was soluble in this solvent, thus allowing the monitoring of reaction progress by solution NMR spectroscopy.

It must be noted, however, that a recent report has warned that *mixtures of nitromethane and Lewis acids might be explosive* [21]. Although many small-scale NMR tube reactions of this phosphoranimine monomer with antimony pentachloride in nitromethane solution were conducted in the course of this work without incident, this *warning should be heeded before any scale-ups of this reaction are attempted.*

The nitromethane system produced faster conversion to polymer than the diglyme system. After 1.75 hours at 100°C, the nitromethane sample contained 6% monomer, 61% polymer, 3 to 4% phosphate (hydrolysis), and 29% cyclic trimer, tetramer, and other species, by ^{31}P-NMR integration. Molecular weight of the polymer was low, $M_n = 7600$, with polydispersity 1.17 by GPC.

The diglyme sample contained 75% monomer, 13% polymer, 9% oligomers, and 3% phosphate under the same conditions of time and temperature. After 2 additional hours the distribution was 19% monomer, 64% polymer, 13% oligomers, and 4% phosphate. Heating the reaction for 2 more hours (total = 5.75 hours) converted 99% of the monomer.

The molecular weight of this polymer was also low, $M_n = 9500$, with polydispersity 1.26. The diglyme sample turned a very dark brown color in contrast to the nitromethane system which was a clear bright yellow solution. The faster reaction in nitromethane is attributed to the higher dielectric constant of this solvent (≈ 36) compared to the ether (≈ 7), and to partial deactivation of the Lewis acid by the more nucleophilic diglyme.

The advent of a significant amount of cyclic tetramer (-1 to -2 ppm in ^{31}P-NMR [22]) in addition to cyclic trimer ($+18.4$ ppm) is a feature of the $SbCl_5$-catalyzed polymerization that is not seen with the fluoride-initiated polymerizations previously discussed. This signal does not arise from a trifluoroethyl phosphate because the phosphate signals are split due to J_{POCH} coupling (6–9 Hz) in the proton-coupled ^{31}P-NMR spectrum [23], whereas this resonance is a broad unresolved singlet. The ^{31}P-NMR spectrum in Fig. 3 shows residual monomer, high polymer, cyclic tetramer, and cyclic trimer, as indicated.

The GPC trace of the $SbCl_5$ solution polymerization in nitromethane also showed tetramer and trimer in addition to polymer.

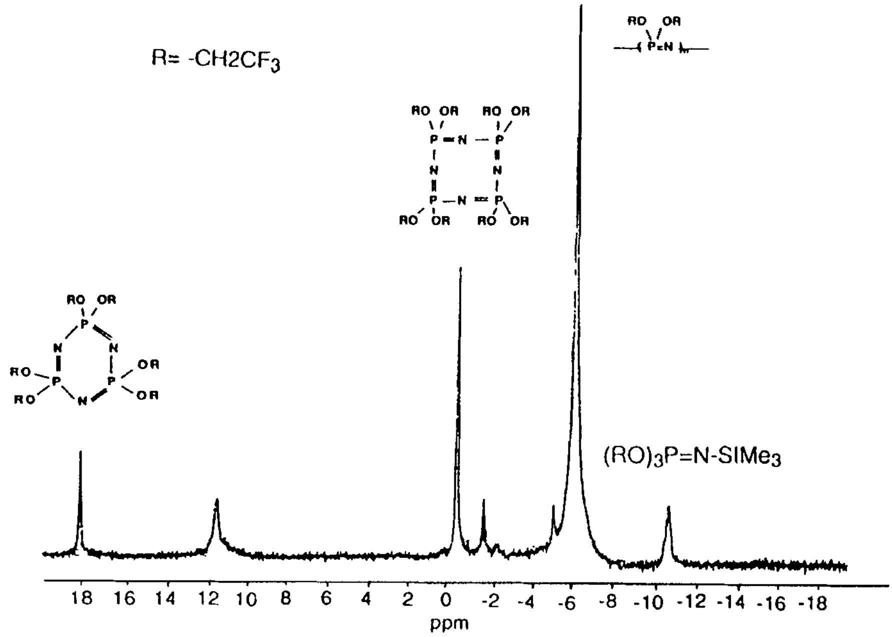


FIG. 3. ^{31}P-NMR spectrum of solution polymerization in the presence of $SbCl_5$: $[M]_0 = 1.5$ M in CH_3NO_2, $[I]_0 = 0.015$ M $SbCl_5$.

Kinetics of $SbCl_5$ Solution Polymerization

The kinetic study of the polymerization of the phosphoranimine in the presence of antimony pentachloride was conducted in nitromethane solution. Figure 4 shows a plot of the monomer consumption in solution polymerization as a function

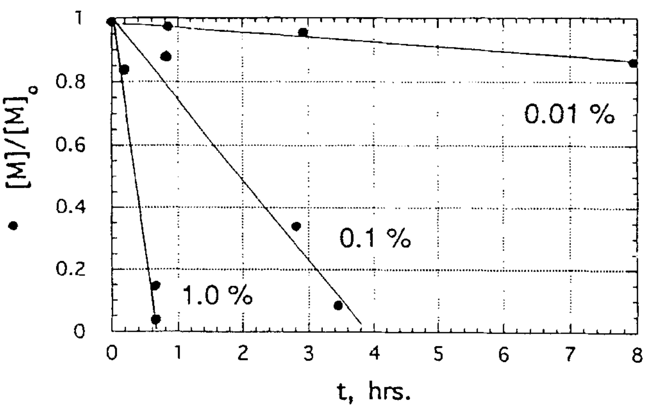


FIG. 4. Effect of $SbCl_5$ initiator level on solution polymerization rate; $[M]_0 = 1.5$ M in CH_3NO_2, $T = 125$ °C (reflux).

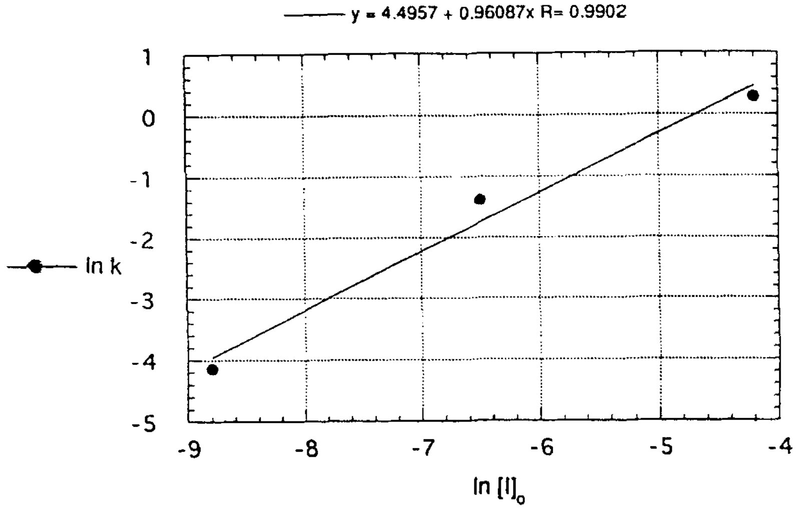


FIG. 5. Reaction rate as a function of $[I]_0$, $SbCl_5$.

of time, and a good fit for zero kinetic order in monomer concentration was obtained for the three initiator levels studied.

The plot in Fig. 4 shows that the reaction rate increases with initiator concentration. The value of k, the rate coefficient of the reaction, was obtained as the slope of the line, $d[M]/dt$.

Figure 5 displays the rate as a function of initiator concentration, and the slope of this plot provided the order of the reaction in initiator concentration. The value of 0.96 for initiator order (Fig. 5) means that the reaction is first order in initiator, and therefore, the apparent rate of propagation k_p is determined as

$$R_p = -d[M]/dt = k_p[M]^0[I]_0^n, \quad n = 1 \tag{1}$$

$$k_p = (-d[M]/dt)/[I]_0 \tag{2}$$

$$k_p = k/[I]_0 \tag{3}$$

A major difference in the reaction products was also noted. The ^{31}P-NMR spectra at 1.0, 0.1, and 0.01% initiator showed that the lowest initiator level produced the highest yield of polymer and less oligomers. In general, $SbCl_5$ catalysis produced significantly more oligomeric side products in solution polymerization than the fluoride-initiated polymerization [1-6].

The effect of temperature is shown in Fig. 6, and the apparent rates of propagation were determined from Eq. (3). The apparent rate constants of propagation k_p, ranged from 2 to 12 × 10^{-3} second^{-1} over the temperature range of 80 to 100°C.

Using the values of k_p obtained from Fig. 6, the Arrhenius-Eyring plot (Fig. 7) was constructed from the following relations [24, 25]:

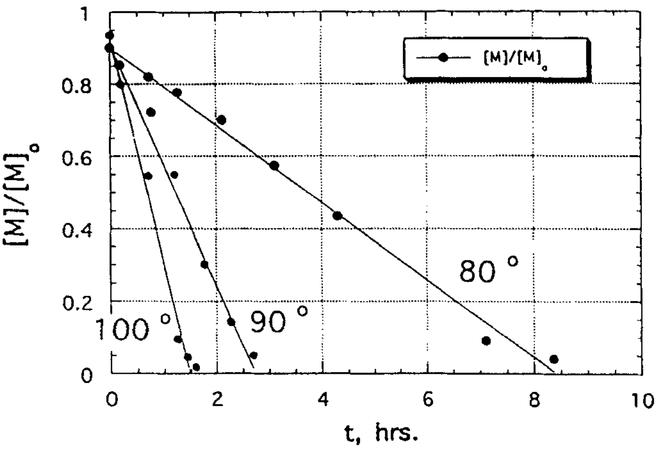


FIG. 6. Effect of temperature (°C) on solution polymerization rate; $[M]_0 = 1.5$ M in CH_3NO_2, $[I]_0 = 0.015$ M $SbCl_5$.

$$k_p = Ae^{-E_a/RT};\ A = (kT/h)e^{n}e^{\Delta S^{\ddagger}/R}$$

$$\ln k_p = \ln A - E_a/RT$$

$$d\ln k_p/d(1/T) = -E_a/R \text{ (slope of Arrhenius plot)}$$

$$\Delta H^{\ddagger} = E_a - RT$$

$$\Delta S^{\ddagger} = R\ln A - R\ln(kT/h) - R$$

where h = Planck, k = Boltzmann, R = gas constants, n = reaction order.

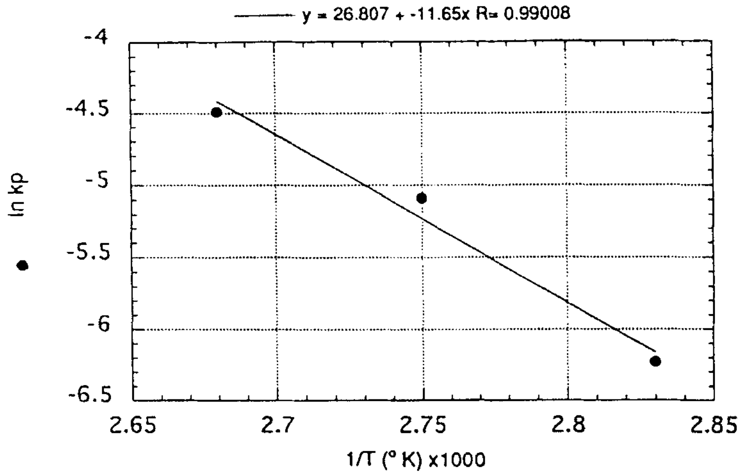


FIG. 7. Arrhenius-Eyring plot of $SbCl_5$-initiated solution polymerization.

TABLE 3. Effect of Temperature on M_n

T, °C	$[M]_0$, mol/L	$[I]_0$, mol/L	M_n	M_w/M_n	% Conversion
125	1.5	0.015	15,584	1.28	95
100	1.5	0.015	15,699	1.26	73
80	1.5	0.015	14,825	1.29	74

The activation enthalpy $\Delta H^\ddagger$ was 23 kcal·mol^{-1} and $\Delta S^\ddagger$ was -8 cal·mol^{-1}·deg^{-1}, as determined from the slope and y-intercept and the above equations.

The effect of monomer concentration on the polymerization rate was neglible for $[M]_0 = 1.5$ and 2.0 M, with a somewhat reduced rate noted for $[M]_0 = 0.5$ M.

The ^{31}P-NMR spectra also showed that at low monomer concentration, a higher proportion of oligomers was obtained relative to polymer. In this experiment, an $[M]_0 = 0.5$ M reaction at 125°C (reflux) gave a product distribution of 59% polymer, 41% oligomers. The 1.5 M reaction produced 78% polymer, 22% oligomers; the 2.0 M polymerization also resulted in 78% polymer, 22% oligomers. By contrast, bulk polymerization was found to produce over 90% polymer and ca. 5% oligomers, as determined by ^{31}P-NMR signal integration.

Finally, an experiment to assess the effect of a less polar solvent was attempted by running the reaction at 125°C (reflux) in a 50:50 blend of nitromethane:xylene. The xylene-modified sample was similar to the nitromethane reaction, however, with the apparent rate constants of propagation 2.44×10^{-2} second^{-1} for the 100% nitromethane system, and 2.16×10^{-2} for the xylene/nitromethane blend. Higher xylene proportions were not studied due to the insolubility of the polymer in this solvent.

Polymer Molecular Weight Distribution: Solution Polymerization

The molecular weights were generally lower than those obtained by fluoride initiation, but were in the range of 10^4 at the lowest detectable amount and at relatively low conversion. Tables 3 to 6 display the molecular weight data at high conversion.

No sharp increase in molecular weight was observed at high conversion, which indicated that macrocondensation [8] did not occur under these conditions. The molecular weight reached a maximum at partial conversion and leveled off, most

TABLE 4. Effect of $[M]_0$ on M_n

T, °C	$[M]_0$, mol/L	$[I]_0$, mol/L	M_n	M_w/M_n	% Conversion
125	0.5	0.005	16,425	1.18	99
125	1.5	0.015	15,584	1.28	95
125	2.0	0.020	12,177	1.45	92

TABLE 5. Effect of $[I]_0$ on M_n

T, °C	$[M]_0$, mol/L	$[I]_0$, mol/L	M_n	M_w/M_n	% Conversion
125	1.5	0.015	15,584	1.28	95
125	1.5	0.0015	17,284	1.29	90
125	1.5	0.00015	25,029	1.39	94

likely due to transfer reactions, as illustrated in Fig. 8. The temperature range of 80 to 125°C (reflux) had little effect on the final molecular weight of the polymer.

In terms of monomer concentration, however, the molecular weight decreased at higher monomer levels, and a broader molecular weight distribution was obtained. These data indicate that more transfer reactions can occur at the higher monomer concentrations.

As the initiator concentration decreased, molecular weight increased. At the 0.01% level of $SbCl_5$, the higher molecular weight corresponds to the higher yield of polymer relative to oligomers as discussed above. A slightly broader molecular weight distribution was also noted.

The addition of 50% xylene to the solution polymerization had no significant effect on the molecular weight of the polymer, as shown in Table 6.

The zero order (in monomer) kinetics and the molecular weight behavior are in sharp contrast to those obtained in the fluoride study [1-6]. The inverse relationship of molecular weight and initiator amount is similar to classical chain polymerization, but transfer reactions probably mediate molecular weight advancement.

The appearance of high molecular weight polymer at partial conversion and the kinetic order of the reaction both support a chain-growth process. The transition state is apparently polar, and is only slightly more ordered than the reactants, as indicated by the weakly negative entropic change.

Mechanistic Studies

A bulk polymerization reaction was studied to determine the nature of the liquid condensate that is produced as a by-product. Neat monomer with 1 mol% $SbCl_5$ was heated to 120-130°C for 3 hours, and about 1 mL of condensate was collected at partial conversion in a trap as a clear, colorless liquid.

TABLE 6. Effect of Solvent on M_n

T, °C	$[M]_0$, mol/L	$[I]_0$, mol/L	M_n	M_w/M_n	% Conversion
125	1.5 (CH_3NO_2)	0.015	15,584	1.28	95
125	1.5 (nm/xylene)	0.015	15,334	1.36	93[a]

[a] Homogeneous.

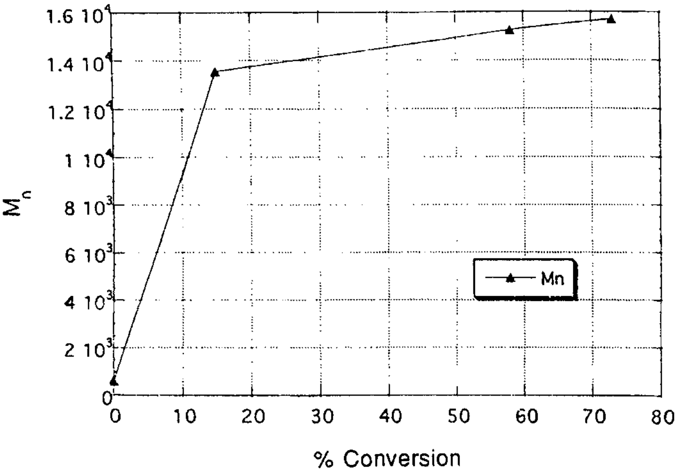


FIG. 8. Molecular weight as a function of conversion, $SbCl_5$-initiated solution polymerization.

The ^{1}H-NMR spectrum of the condensate showed that this liquid contained predominantly $(CH_3)_3SiOCH_2CF_3$, as during the earlier study of the fluoride-initiated system [26].

However, in addition to the silyl ether signals at 0.15 and 3.88 ppm, a small signal at 0.4 ppm indicated the presence of trimethylsilyl chloride, $(CH_3)_3SiCl$. The formation of this compound indicates that the catalyst loses a chloro group as a result of reaction with the monomer.

Figure 9 shows a plot of the monomer consumption in solution polymerization, $[M]_0$ = 1.5 M in CH_3NO_2 at 125°C (reflux) as a function of time, and in the presence of 2 mol% 2,6-di-*tert*-butyl-4-methylpyridine (DTBMP) to determine the possible role of protonic species in the initiation of polymerization. DTBMP is a sterically hindered, nonnucleophilic base which distinguishes between Brønsted and Lewis acids [27].

Zero order in monomer concentration was noted as before. The rates of polymerization were determined from the slopes as follows:

$$R_p = -d[M]/dt = 4.2 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}\cdot\text{s}^{-1} \text{ without DTBMP}$$

$$R_p = -d[M]/dt = 4.05 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}\cdot\text{s}^{-1} \text{ with DTBMP}$$

The plots in Fig. 9 clearly shows that the presence of the proton trap did not significantly affect the rate of polymerization of the monomer. This is evidence that the true initiator is $SbCl_5$ rather than protonic impurities.

The molecular weights and molecular weight distributions of the polymers produced were virtually identical for the two reactions: M_n = 16,593 with polydispersity (PDI) = 1.44 and M_n = 16,401 with PDI of 1.44. The hindered pyridine thus had no effect on the chain assembly process.

An experiment involving high levels of $SbCl_5$ relative to the monomer was conducted and examined by ^{29}Si-NMR spectroscopy. Upon mixing the monomer

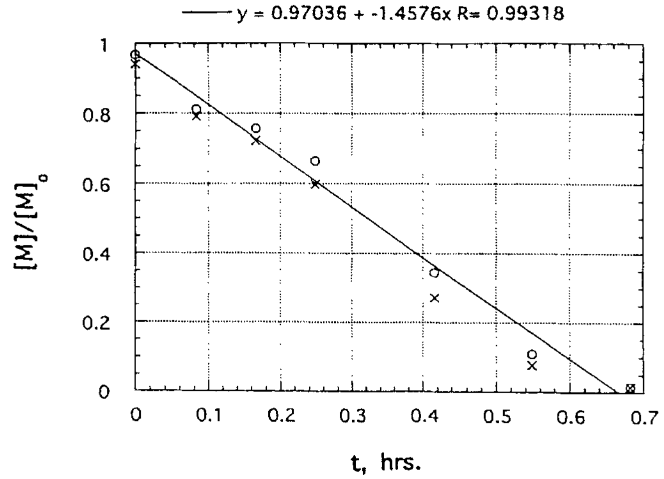


FIG. 9. $SbCl_5$-initiated solution polymerization with (○) and without (×) 2 mol% DTBMP proton trap; $[M]_0$ = 1.5 M in CH_3NO_2, $[I]_0$ = 0.015 M $SbCl_5$, T = 125°C (reflux).

and acid at a mole ratio of 2:1, an exotherm was noted in the NMR tube at room temperature. The ^{29}Si spectrum showed that the major silicon product of the reaction was trimethylsilyl chloride, $(CH_3)_3SiCl$, exhibiting a strong singlet at +31.5 ppm in the methylene chloride solvent. A residual doublet of the monomer was noted at −7.4 ppm, $J_{Si\text{-}P}$ = 29.4 Hz, in agreement with a previous report [28].

In addition, a new silicon doublet at −9.7 ppm appeared as a reaction product, J = 37.6 Hz. Since the coupling constant is of similar magnitude compared to the phosphorous-silicon coupling observed in the monomer, this doublet may represent a new *N*-silyl phosphoranimine species such as an $SbCl_5$:phosphoranimine coordinated complex, as proposed in the mechanism below. This complex could be formed initially, then decompose with evolution of trimethylsilyl chloride. No other signals were observed in the ^{29}Si-NMR spectrum of the reaction.

The ^{31}P-NMR spectrum of this reaction was very complicated, with multiple resonances in clusters ranging from +10.5 to −14 ppm, and was indecipherable. Thus at high acid concentration, numerous phosphorus products are produced.

The appearance of the chlorosilane as a reaction product was previously noted in the proton spectrum of the isolated condensate. This result indicates that the Lewis acid donates a chloro group which cleaves the silyl group from the monomer.

The question of the possible catalytic effect of trimethylsilyl chloride on the polymerization was addressed by adding 1 mol% of this compound to the monomer, and heating the mixture at 125°C for 2 hours. The ^{31}P-NMR spectrum of the reaction showed only 2% polymer and 96% unreacted monomer; the rest was oligomer. Since antimony pentachloride provides rapid conversion of monomer to polymer in high yield under these conditions, the chlorosilane cannot be the active agent in the initiation of polymerization.

Nitromethane was found to be relatively unreactive with the phosphoranimine monomer after heating a 1.5 M solution to 125°C, or reflux conditions for 2 hours.

Summary: $SbCl_5$ Polymerization

The data indicate that antimony pentachloride is the true initiator in the polymerization of the monomer, $(CF_3CH_2O)_3P{=}N{-}Si(CH_3)_3$. Protonic impurities and the trimethylsilyl chloride by-product are not involved in the initiation of the reaction. The Lewis acid apparently reacts with the phosphoranimine via ligand exchange of a chloro group at the initiation step.

Kinetic data shows that the solution polymerization is a chain-growth process with a polar (probably ionic) transition state. The reaction is zero order in monomer concentration and first order in initiator concentration.

The appearance of a small resonance at the base of the polymer peak in the ^{31}P-NMR spectrum indicates phosphorus nuclei in a similar environment and may be taken as evidence of branching. Such signals have been noted in the spectra of other polyphosphazenes as branch sites [18], and it seems reasonable to make the assignment in this case as well.

Branching is also consistent with the more amorphous character of the polymer product as shown by the pronounced T_g in the DSC trace, and may explain the dual peaks in the 45 to 75°C region. However, the relatively narrow molecular weight distribution of the polymers indicates that only a few short branch sites are likely to be present.

In consideration of this evidence, the mechanism of polymerization shown in Scheme 1 is proposed.

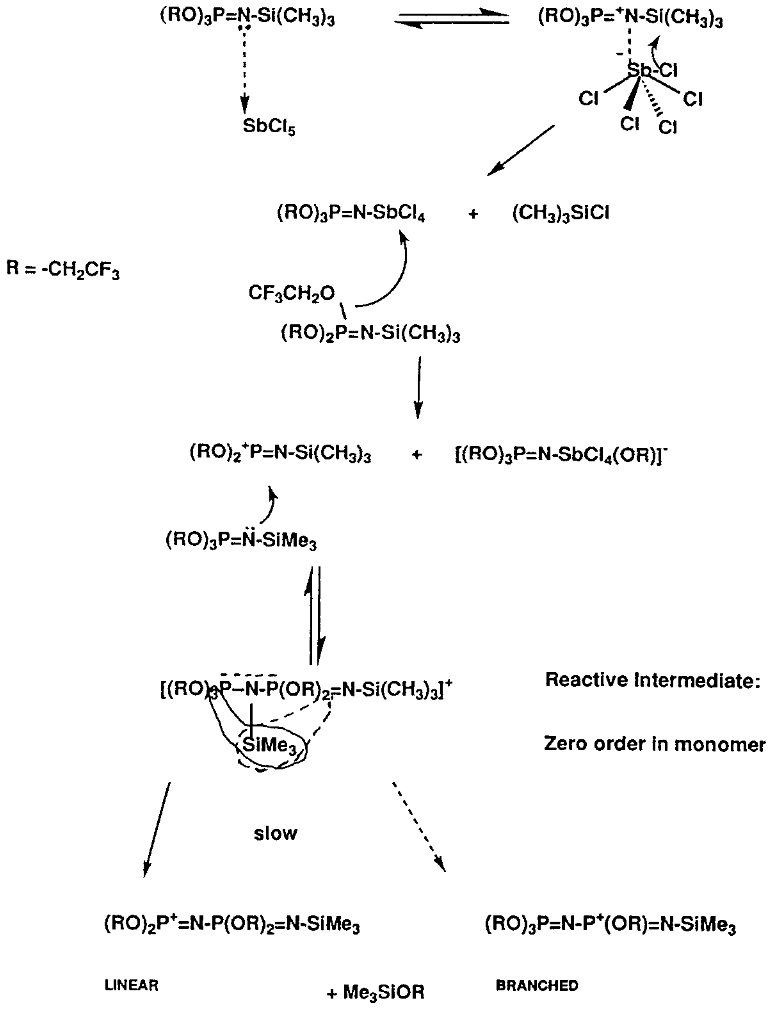
This mechanism acknowledges the known affinity of Lewis acids for phosphoranimines, and is consistent with the evidence produced in this study. The zero order in monomer kinetics of the reaction indicates that the polymerization rate is not dependent on monomer concentration. It is thus likely that a reactive intermediate is formed in fast equilibrium with the monomer, followed by slow unimolecular elimination of trimethylsilyl trifluoroethoxide.

Furthermore, while an anionic mechanism (with active site as a phosphazene-nitrogen anion, $P{=}N^-$) results in a linear chain [1-6], a cationic chain assembly process can lead to branching. If a trifluoroethoxy ligand is expelled from the penultimate P-atom, a short branch point is created and a new active site (phosphonium ion) results from transfer of the charge to an "internal" phosphorus atom. If the fluoroalkoxy group is eliminated from the terminal P-atom, the active site remains at the end phosphorus atom, and a linear chain is propagated.

^{1}H-NMR spectra of the isolated polymer show signals for silylmethyl protons, indicating trimethylsilyl groups as the chain ends. Although it seems unlikely that antimony moieties are incorporated into the chain, the ultimate fate of this fragment of the initiator is not known at this time.

Elemental analysis of the polymer indicated that there are no chloro groups incorporated in the chain, as shown by the data in the Experimental section.

Additional studies of this polymerization are necessary in order to determine the exact nature of the active chain ends and to further test the hypothesized mechanism.



SCHEME 1.

Haloacetic Acid Initiation of Polymerization

The polymerization of the phosphoranimine monomer in the presence of chloroacetic acid produced polymer with only a minor amount of side products (Table 1). A series of haloacetic acids was studied as polymerization initiators.

Figure 10 shows that a plot of the log of the monomer consumption with time is essentially linear with one exception, indicating the polymerization is first order in monomer:

$$R_p = -d[M]/dt = k_p[M]^1[I]_0^n$$

$$k = -d\ln[M]/dt$$

Table 7 shows the data obtained in this study.

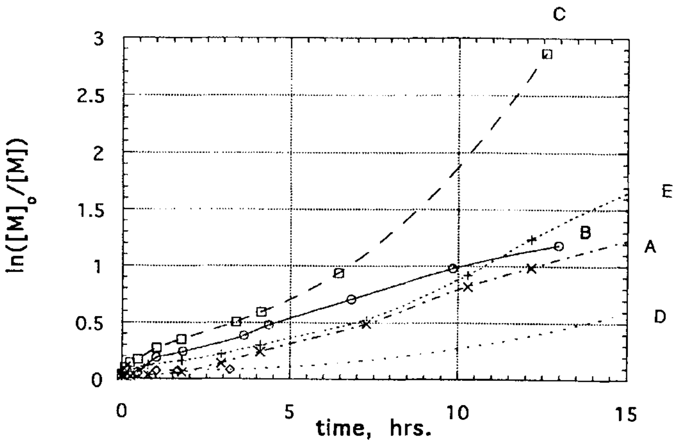


FIG. 10. Conversion of monomer in the presence of haloacetic acids: $[M]_0 = 1.5$ M in CH_3NO_2, $[I]_0 = 0.015$ M, $T = 125°C$ (reflux). A = acetic, B = chloroacetic, C = dichloroacetic, D = trichloroacetic, E = trifluoroacetic.

A plot of the rate coefficient k as a function of pK_a is shown in Fig. 11. There was no correlation of polymerization rate with the relative acidity of the initiators. An interesting feature of these polymerizations is the fact that the stronger acids show significant induction periods, as shown in Fig. 10.

The molecular weights of the polymers obtained in this study were all monomodal, and indicate that the *weaker* acids promote higher molecular weights.

Trifluoroacetic acid was the only strong acid that produced a relatively higher molecular weight. This result prompted a further experiment in which 1.5 mol% of DTBMP, the proton trap previously discussed, was combined with 1 mol% of chloroacetic acid (1.3 M in CH_3NO_2) with the monomer in nitromethane solution.

Upon heating the homogeneous sample in a 125°C oil bath for 2 hours, the ^{31}P-NMR spectrum revealed that polymer was obtained in about 30% (integration)

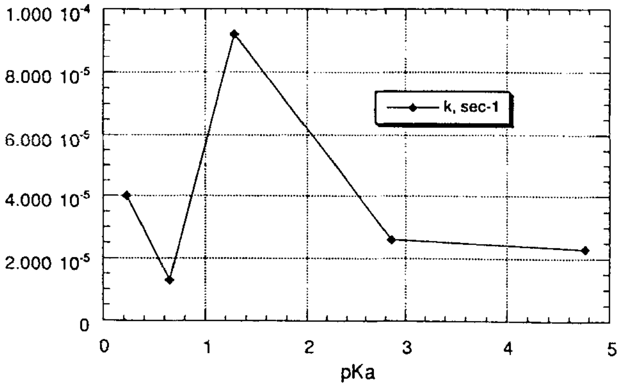


FIG. 11. Rate vs pK_a of haloacetic acids, for $[I]_0 = 0.015$ M.

TABLE 7. Polymerization Data, Haloacetic Acid Initiators

Acid	pK_a [Ref.]	k,[a] s^{-1}	M_n	M_w/M_n	% Conversion
CH_3COOH	4.76 [25]	2.3×10^{-5}	38,698	1.52	80
$CH_2ClCOOH$	2.86 [25]	2.6×10^{-5}	30,233	1.48	70
$CHCl_2COOH$	1.29 [25]	9.2×10^{-5}	21,329	1.41	94
CCl_3COOH	0.65 [25]	1.3×10^{-5}	17,298	1.32	83
CF_3COOH	0.23 [32]	4.0×10^{-5}	29,248	1.37	89

[a] For $[I]_0 = 0.015$ M; $[M]_0 = 1.5$ M in CH_3NO_2 at 125°C.

yield. Comparing this time to the kinetic plot for chloroacetic in Fig. 10 shows that this polymerization was slightly faster than the chloroacetic acid *without* the proton trapping agent.

A control sample containing only monomer at the same concentration ($[M]_0 = 1.5$ M) in nitromethane solution produced only ≈2% polymer under the same conditions of time and temperature; thus the solvent is excluded as the initiating agent.

Two possibilities could explain the unexpected behavior in the presence of the proton trap. First, the hindered amine may not have scavenged the protons in the system, and the monomer was protonated instead. However, this phosphoranimine is known to be weakly basic due to the inductive effects of the three trifluoroethoxy groups on the phosphorus atom [10]. The nitrogen atom of the sterically hindered pyridine should be more basic and allow it to successfully compete with the monomer for the protons in the system; thus this possibility seems remote.

In the second scenario, the DTBMP did trap the protons, and some other species is the true initiator. The failure of excess DTBMP to inhibit this "acid-catalyzed" polymerization raises serious doubts about the role of protons as the active species of initiation.

The question of the conjugate base, the chloroacetate anion, must be considered at this point. The affinity of oxoanions for silyl groups is well known, and it is certainly possible that the acetic acids react with the monomer in this manner to form silyl esters as condensation by-products of the polymerizations. Trimethylsilyl chloroacetate, $(CH_3)_3SiOC(O)CH_2Cl$, has been previously prepared and characterized by ^{29}Si NMR, $\delta_{Si} = 26.6$ ppm [29], and might be detected in model reaction studies of chloroacetic acid with the monomer.

Viewed from the perspective of the anion, the weaker conjugate bases (poorer nucleophiles) generally showed the more pronounced induction times. If protons are excluded as the initiating species in favor of the conjugate anion, then the lack of catalytic activity of triflic acid (see Table 1) is understandable, since the triflate anion is an extremely weak nucleophile.

The future study of this polymerization reaction should be directed toward the role of the acetate anion as the initiator. Although the reaction is initiated by a Brønsted acid, the polymerization is probably an anionic process, catalyzed/initiated by the haloacetate anion.

CONCLUSIONS

This study has shown that it is possible to polymerize an *N*-silylated phosphoranimine under mild conditions using a catalytic amount of either a Lewis or protonic acid. The evidence in the case of antimony pentachloride supports a monomer-Lewis acid ligand exchange reaction as the initiating step, and a chain-growth polymerization that is zero order in monomer. The resulting polyphosphazene displays markedly different thermal properties compared to the polymer prepared by fluoride (anionic) polymerization of the same phosphoranimine monomer. The NMR, IR, SEC, and thermal data indicate that slightly branched poly[(bistrifluoroethoxy)phosphazene] of low to moderate molecular weight (10^4) is the principal product of the reaction.

Another significant difference between the fluoride process and the $SbCl_5$ reaction is the higher amount of cyclic oligomers produced by the acid-initiated solution polymerization. Both reactions are examples of chain-growth condensation polymerizations. As such, the cyclics are likely formed by back-biting reactions of active chain ends occurring during the chain-building process. On the basis of the evidence obtained to date, a cationic chain assembly process is postulated as a likely mechanism that would lead to chain branching.

The data obtained in the study of the haloacetic acids indicate that protons are not involved in the initiation step. The mechanistic results implicate the acetate anion as the true initiator in these polymerizations.

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