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Articles

Synthesis and Characterization of Poly(alkyl/arylphosphazenes)

Robert H. Neilson* and Rahim Hani

Department of Chemistry, Texas Christian University, Fort Worth, Texas 76129

Patty Wisian-Neilson,* John J. Meister, and Aroop K. Roy

Department of Chemistry, Southern Methodist University, Dallas, Texas 75275

Gary L. Hagnauer

Polymer Research Division, Army Materials Technology Laboratory, Watertown, Massachusetts 02172.

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ABSTRACT: Several alkyl/aryl-substituted phosphazene polymers $[R(R')PN]_n$ (**1**, R = R′ = Me; **2**, R = R′ = Et; **3**, R = Me, R′ = Ph; **4**, R = Et, R′ = Ph) and copolymers $\{[R(Ph)PN]_x[R_2PN]_y\}_n$ (**5**, R = Me; **6**, R = Et) were prepared by the thermally induced condensation polymerization of the corresponding *N*-silyl-*P*-trifluoroethoxyphosphoranimines $Me_3SiN{=}P(OCH_2CF_3)RR'$. With the exception of the diethyl derivative **2**, which is insoluble in all common solvents, these polymers were characterized by a variety of dilute solution techniques (viscosity measurements, membrane osmometry, size-exclusion chromatography, and light scattering), by thermal analysis (DSC and TGA), by multinuclear NMR spectroscopy, and by X-ray diffraction measurements. The polymers have molecular weights ($\bar{M}_w$) ranging from ca. 25 000 to 200 000 with symmetrical molecular weight distributions ($\bar{M}_w/\bar{M}_n \sim 2.0$) and, in general, exhibit solution behavior typical of random coil polymers in "good" solvents (e.g., THF or $CHCl_3$). The Mark–Houwink constants for polymer **3** were estimated from the viscosity and light scattering results. The DSC measurements show that (a) poly(dimethylphosphazene) (**1**) is a semicrystalline thermoplastic with $T_g = -46$ °C and $T_m = 143$ °C, (b) poly(diethylphosphazene) (**2**) is highly crystalline with $T_m = 217$ °C, and (c) the phenyl-substituted polymers **3**–**6** are amorphous with glass transition temperatures ranging from −5 °C (**6**) to 37 °C (**3**). The crystallinity of **1** and **2**, presumably the reason for the insolubility of **2**, was confirmed by X-ray diffraction measurements. The thermal stability of these polymers is generally quite high as indicated by decomposition onset temperatures (TGA) of ca. 350–400 °C. High-field ^{13}C NMR spectral data show that the structure of the homopolymer **3** is completely atactic even though there are two different substituents present on each phosphorus atom. A chain growth process is suggested as the polymerization mechanism on the basis of studies of the polymer molecular weight vs. the extent of reaction.

Introduction

Inorganic polymers with a backbone of alternating phosphorus and nitrogen atoms, known as poly(phosphazenes), $[R_2PN]_n$, have attracted increasing attention in recent years.[1] Many such polymers with a variety of substituents at phosphorus have been prepared, and they often exhibit useful properties including low-temperature flexibility, resistance to chemical attack, flame retardancy, stability to UV radiation, and reasonably high thermal stability.[2] Compounds containing biologically or catalytically active side groups are also being investigated.[3]

The most commonly used synthetic route to poly(phosphazenes) is the ring-opening/substitution method developed by Allcock and co-workers. This procedure involves the initial preparation of poly(dihalophosphazene), $[X_2PN]_n$, (X = Cl, F) by the ring-opening polymerization of the cyclic trimer and subsequent nucleophilic displacement of the halogens along the chain (eq 1). In each

$$\begin{aligned}(Cl_2PN)_n &\xrightarrow{NaOR} -[P(OR)_2{=}N]_n- \\ (Cl_2PN)_n &\xrightarrow{RNH_2} -[P(HNR)_2{=}N]_n-\end{aligned} \qquad (1)$$

case, the substituents at phosphorus must be introduced after polymerization since the fully substituted cyclic phosphazenes do not polymerize.[4,5]

A common feature of poly(phosphazenes) prepared in this manner is that the organic substituents are bonded to phosphorus through oxygen or nitrogen links, thereby providing pathways for decomposition or depolymerization on heating above about 200 °C. It has been postulated that

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Table I
Typical Preparative Data for Poly(alkyl/arylphosphazenes)[a]

polymer	scale, mmol	yield,[b] %	temp,[c] °C	time, h	analysis[d] % C	analysis[d] % H
1, $[N{=}PMe_2]_n$	510	92[e]	160	302	31.75 (32.01)	8.06 (8.21)
2, $[N{=}PEt_2]_n$	25	92	200[f]	115	46.47 (46.60)	9.79 (9.78)
3, $[N{=}PPhMe]_n$	201 18	92 95	175 175[f]	305 305	61.58 (61.32)	6.13 (5.88)
4, $[N{=}PPhEt]_n$	217	93	175	327	63.56 (63.57)	6.74 (6.67)
5, $\{[N{=}PMe_2]_x[N{=}PPhMe]_y\}_n$	82	98[e]	175	130	51.10 (50.95)	6.92 (6.65)
6, $\{[N{=}PEt_2]_x[N{=}PPhEt]_y\}_n$	87	96[e]	185	157	56.46 (56.69)	7.92 (7.93)

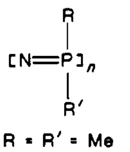
[a] Reactions carried out under vacuum in a stainless steel vessel (ca. 300-mL capacity) unless otherwise noted. [b] Based on recovered $Me_3SiOCH_2CF_3$ unless otherwise noted. [c] Temperatures 10–15 °C higher can be employed with minor reduction in reaction time. [d] Calculated values in parentheses. [e] Based on actual mass of isolated polymer. [f] Reaction carried out in a sealed glass ampule (ca. 20-mL capacity).

directly P–C bonded alkyl or aryl side groups might enhance the thermal or chemical stability of the polymers and give rise to interesting physical properties.[5–7] Furthermore, the alkyl-substituted poly(phosphazenes), $[R_2PN]_n$, are isoelectronic with the well-known siloxane polymers, $[R_2SiO]_n$, and the extent of this analogy would be interesting to pursue. The published attempts to prepare the directly P–C bonded polymers by the substitution method have generally not been successful. Treatment of poly(dihalophosphazenes) with organometallic reagents (e.g., RMgX or RLi) results in either incomplete substitution under mild conditions or undesired reactions such as chain cleavage and/or cross-linking under more vigorous conditions.[6–9]

During the last few years, a new general method for the synthesis of poly(phosphazenes) has been under investigation in our laboratory. The approach is based on the premise that suitably constructed *N*-silylphosphoranimines can eliminate substituted silanes to form cyclic and/or linear phosphazenes (eq. 2). This type of *condensation-polymerization* reaction has several potential advantages, the most important of which is the ability to incorporate the desired phosphorus substituents directly into the starting Si–N–P compound. Therefore, by designing the appropriate precursors, it should be possible to widely vary the pattern of substituents in the phosphazene products. Indeed, this procedure has resulted in the successful preparation of the first fully P–C bonded poly(phosphazene), $[Me_2PN]_n$ (1), as described in preliminary reports.[10–12]

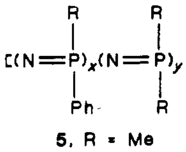
$$Me_3SiN{=}PRR'X \rightarrow Me_3SiX + -[N{=}PRR']_n- \quad (2)$$

We report here the results of a more complete study of the synthesis of a representative series of polymers (1–4) and copolymers (5 and 6) by the condensation-polymerization method. In addition, the characterization of these new materials by dilute solution techniques (viscosity, membrane osmometry, light scattering, and size-exclusion chromatography), thermal analysis (DSC and TGA), and X-ray diffraction is described.



$$[N{=}\overset{R}{\underset{R'}{P}}]_n$$

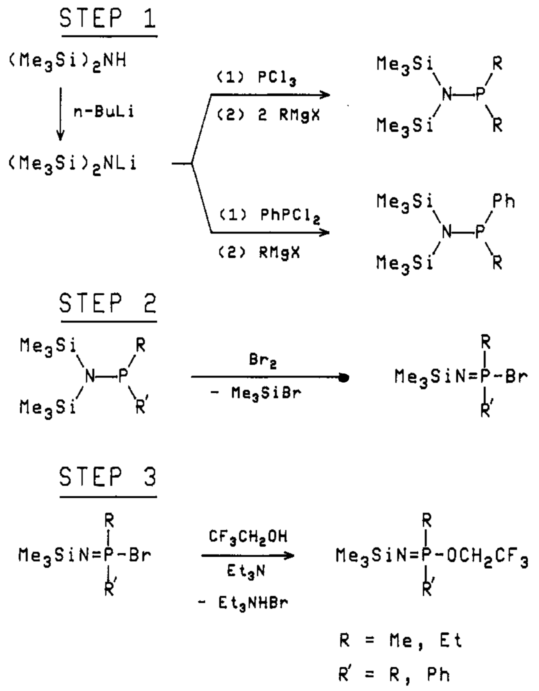
1, R = R′ = Me
2, R = R′ = Et
3, R = Me, R′ = Ph
4, R = Et, R′ = Ph



$$[(N{=}\overset{R}{\underset{Ph}{P}})_x(N{=}\overset{R}{\underset{R}{P}})_y]_n$$

5, R = Me
6, R = Et
x = y

Scheme I



Results and Discussion

Synthesis and Solubility. The *N*-silyl-*P*-trifluoroethoxyphosphoranimine reagents, used as "monomers" in this polymer synthesis, are readily prepared from either PCl_3 or $PhPCl_2$ in a straightforward, three-step reaction sequence outlined in Scheme I. As described elsewhere,[13–15] these compounds are obtained as colorless, distillable, air-sensitive liquids in yields of 40–65% based on starting PCl_3 or $PhPCl_2$. The highest yields are achieved with the Ph(Me)P and Ph(Et)P derivatives, while that of the Me_2P analogue is usually somewhat lower.

On heating in either sealed glass ampules or a stainless steel vessel, these phosphoranimines readily eliminate $Me_3SiOCH_2CF_3$ (eq 3) to form the polymeric phosphazenes 1–4. The copolymers 5 and 6 are prepared by heating equimolar mixtures of the dialkyl- and phenyl/alkyl-substituted phosphoranimines.

$$nMe_3SiN{=}PRR'(OCH_2CF_3) \xrightarrow{\Delta} [N{=}PRR']_n + nMe_3SiOCH_2CF_3 \quad (3)$$

The reaction conditions, yields, and elemental analyses for polymers 1–6, prepared in some typical experiments,

Table II
NMR Spectroscopic Data[a,b]

compd	signal	^{1}H NMR,	^{13}C NMR		^{31}P NMR,
		δ	δ	J_{PC}	δ
1, $[N{=}PMe_2]_n$	Me	1.4[c]	22.5	90.2	8.3
3, $[N{=}PPhMe]_n$	Me	1.3–1.6[d]	21.7	91.6	1.5–1.9[e]
			22.3	92.3	
			22.8	90.8	
	Ph	H_{3-5} 7.2	$C_{3,5}$ 127.7	11.5	
		$H_{2,6}$ 7.8	C_4 129.5	9.9	
			$C_{2,6}$ 131.0	9.9	
			C_1 139.7	129.0	
			140.1	125.9	
			140.5	126.5	
4, $[N{=}PhEt]_n$	CH_3	0.9	7.9	2.9	6.8–7.9[e]
	CH_2	1.9	28.1	98.1	
			28.6	96.1	
			29.1	93.1	
	Ph	H_{3-5} 7.2	$C_{3,5}$ 127.4		
		$H_{2,6}$ 7.9	C_4 129.5		
			$C_{2,6}$ 131.9		
			C_1 134–140[d]		
5, $[N{=}PMe_2]_x[N{=}PPhMe]_y$	Me	1.5	22.2	90.1	2.5
			22.4	90.5	10.0
	Ph	H_{3-5} 7.2	$C_{3,5}$ 127.6		
		$H_{2,6}$ 7.8	C_4 129.6		
			$C_{2,6}$ 130.7		
			C_1 138–141[d]		
6, $[N{=}PEt_2]_x[N{=}PPhEt]_y$	CH_3	1.0	7.6		6.1–7.5[e]
			7.9		17.2–17.8[e]
	CH_2	1.7	26.2	90.8	
		2.0	28.6	93.1	
			28.9	94.7	
	Ph	H_{3-5} 7.3	$C_{3,5}$ 127.4		
		$H_{2,6}$ 8.0	C_4 129.4		
			$C_{2,6}$ 131.9		
			C_1 138–141[d]		

[a] Spectra recorded on a Varian XL-300 spectrometer with $CDCl_3$ as the solvent. Chemical shifts are downfield from Me_4Si for ^{1}H and ^{13}C NMR spectra and from H_3PO_4 for ^{31}P spectra. [b] Broad resonances except where coupling constants (J_{PH} or J_{PC}) are listed or unless otherwise noted. [c] Sharp doublet; J_{PC} = 12.6 Hz. [d] Several overlapping doublets. [e] Several overlapping signals.

are summarized in Table I. These thermolysis reactions normally produce polymeric products, free of the cyclic analogues, in essentially quantitative yield and in sufficient purity to give satisfactory elemental analysis upon removal of the silyl ether byproduct under vacuum. Final purification is generally achieved by precipitation of the polymer into a nonsolvent such as hexane.

As is the case with most poly(phosphazenes), the physical properties of these alkyl/aryl derivatives are found to be very dependent upon the nature of the substituents along the polymer backbone. This fact is illustrated, for example, by the solubility behavior of these materials. With the exception of poly(diethylphosphazene) (**2**), which is insoluble in all common solvents (see below), the new polymers are readily soluble in CH_2Cl_2 and $CHCl_3$, facilitating their characterization by NMR spectroscopy (Table II). In addition, the phenyl-substituted compounds (**3**–**6**) are soluble in THF and various aromatic solvents. None of the polymers are water-soluble; however, $[Me_2PN]_n$ (**1**) is soluble in a 50/50 water/THF mixture. It is also interesting to note that, while the pure compound is insoluble in THF, polymer **1** does not precipitate for several hours when a concentrated solution (ca. 10%) of it in CH_2Cl_2 is poured into THF.

NMR Spectral Data. All of the soluble polymers (**1** and **3-6**) give high-resolution NMR spectra (Table II) that are completely consistent with their proposed structures. The ^{31}P NMR spectra of the homopolymers **1**, **3**, and **4** consist of single peaks (with some fine structure noted for **3** and **4**) as expected, while those of the copolymers **5** and **6** contain two distinct sets of resonances, corresponding to the two different structural environments of the phosphorus centers along the polymer backbone (Figure 1). As observed for other types of poly(phosphazenes),[16] the ^{31}P chemical shifts of these alkyl/aryl-substituted polymers are consistently ca. 15–30 ppm upfield from those of the analogous cyclic trimers and tetramers.

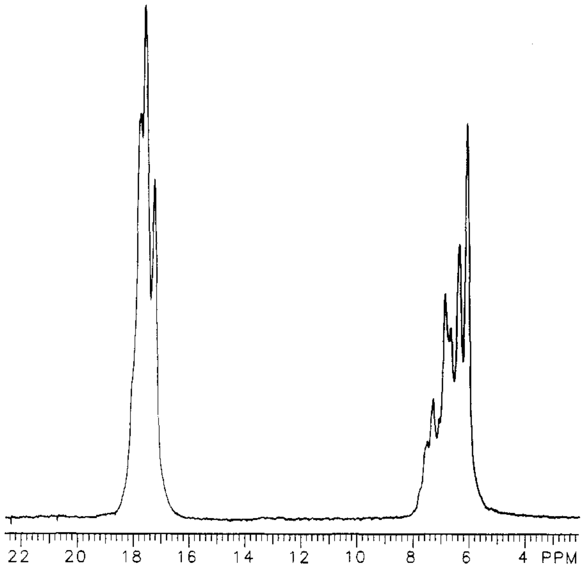


Figure 1. Phosphorus-31 NMR spectrum (121.421 MHz) of the $\{[Ph(Et)PN]_x[Et_2PN]_y\}_n$ copolymer **6**.

The ^{1}H NMR spectra of these polymers generally consist of relatively broad, featureless signals with the exception of the dimethyl compound **1**, for which a sharp doublet is observed. In contrast, some important structural in-

Table III
Viscosity, Membrane Osmometry, and Size-Exclusion Chromatography (SEC) Data

polymer	$[\eta]^a$	$\bar{M}_n{}^b$	SEC analysis^c $\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
1,^{d} $[N{=}PMe_2]_n$	0.710	67000	63700	108300	1.7
3, $[N{=}PPhMe]_n$	0.398	102800	94500	162200	1.7
	0.341	87900	81800	136000	1.7
4, $[N{=}PhEt]_n$	0.174	32700	29000	65300	2.2
5, $\{[N{=}PMe_2]_x[N{=}PPhMe]_y\}_n$	0.307	53000	57600	93900	1.6
6, $\{[N{=}PEt_2]_x[N{=}PPhEt]_y\}_n$	0.156	20900	14800	24200	1.6

[a] Intrinsic viscosity (dL/g) in THF at 30 °C. [b] By membrane osmometry in THF at 30 °C. [c] Operating conditions: mobile phase, THF containing 0.1% $(n\text{-Bu})_4N^+Br^-$; flow rate, 1.5 mL/min; temperature, 30 °C; columns, 500-, 10^4-, 10^5-Å μStyragel; sample size, ca. 0.05 mL; concentration, 0.1%. [d] Insoluble in THF; data obtained in $CHCl_3$.

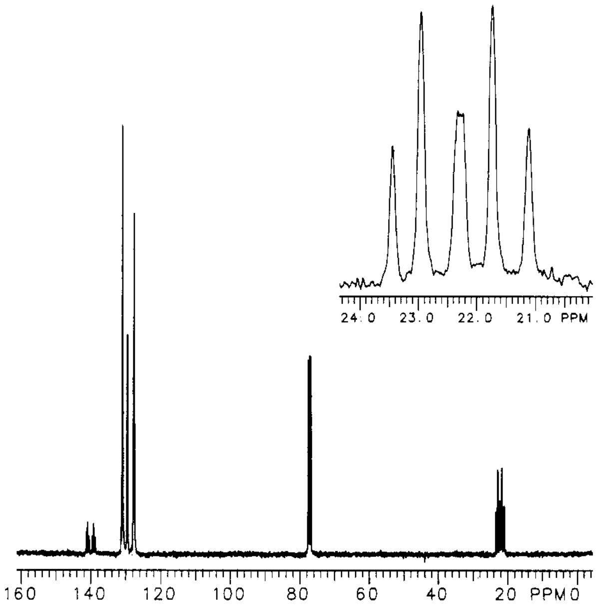


Figure 2. Carbon-13 NMR spectrum (75.429 MHz) of the $[Ph(Me)PN]_n$ polymer 3.

formation is provided by ^{13}C NMR spectroscopy, particularly for the phenyl/alkyl derivatives 3 and 4. These materials are rare[17] examples of poly(phosphazenes) that *contain two different substituents at each phosphorus atom in the chain and, thus, have the possibility of being stereoregular.* The fact that the structures are completely *atactic*, however, is clearly shown by the ^{13}C NMR spectra. In particular, the high-field ^{13}C NMR spectrum of 3 (Figure 2) contains three doublets in the P–Me region (ca. 22 ppm) in a 1:2:1 intensity ratio. This spectral feature clearly indicates a triad structure in which the methyl group's nearest neighbors (A and B), on the same side of the polymer chain, have equal probabilities of being either Me or Ph groups. The same reasoning accounts for the observation of three doublets (ca. 140 ppm) for the P-bonded phenyl carbon.

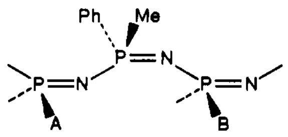


Table IV
Light Scattering Results for Poly(methylphenylphosphazene), $[Ph(Me)PN]_n$, in THF Solution

sample	$[\eta]^a$	$\bar{M}_w(SEC)^b$	$\bar{M}_w(LS)^c$	$A_2{}^d$
A	0.224	64500	73000	1.7×10^{-3}
B	0.341	103800	133000	5.8×10^{-4}
C	0.337	109100	139000	9.1×10^{-4}
D	0.442	149800	202000	7.5×10^{-4}

[a] Intrinsic viscosity in dL/g. [b] Weight-average molecular weight from size-exclusion chromatography. [c] Weight-average molecular weight from light scattering. [d] Second virial coefficient in mL·mol/g^2.

Dilute Solution Characterization. This series of poly(alkyl/arylphosphazenes) was studied by a variety of standard dilute solution techniques including viscosity measurements, membrane osmometry, size-exclusion chromatography, and light scattering. Taken together, these studies demonstrate that *the poly(alkyl/arylphosphazenes) exist as extended, flexible chains in good solvents such as THF or $CHCl_3$, with average chain lengths of several hundred to a thousand repeat units and symmetrical molecular weight distributions ($\bar{M}_w/\bar{M}_n \cong 2$).* The data obtained in these studies are summarized in Tables III and IV.

The intrinsic viscosities (Table III) were determined at 30 °C in $CHCl_3$ for the dimethyl polymer 1 and in THF for the phenyl-substituted polymers 3–6. In all cases, the plots of reduced viscosity vs. concentration were quite linear at low concentration (ca. 0.1–1.0%) with Huggins constants in the range (ca. 0.30–0.45) characteristic[18] of good polymer/solvent interactions. In order to investigate solvent effects in more detail, a sample of $[Ph(Me)PN]_n$ was studied in a series of solvents (THF, $CHCl_3$, toluene, DMF, and THF containing 0.1% tetra-*n*-butylammonium bromide). The intrinsic viscosity (ca. 0.41 dL/g) and the Huggins constant remained essentially the same in $CHCl_3$, toluene, and THF (with or without the ammonium salt additive), thus showing all of these to be very good solvents for the polymer. By contrast, in DMF, the viscosity decreased to 0.24 dL/g and the Huggins constant increased to 0.71, suggesting anomalous solution behavior in this more polar solvent.

Absolute number-average molecular weights ($\bar{M}_n$) of the same series of polymers were determined by membrane osmometry at 30 °C using the same solvents and concentrations as in the viscosity measurements (Table III). All of the samples afforded linear plots of $(\pi/c)^{1/2}$ vs. c (c is the concentration) with second virial coefficients of ca. 10^{-4} mL·mol/g^2. No significant degree of diffusion through the cellulose acetate membranes, due to possible low molecular weight impurities, was noted for any of the samples. The molecular weights ($\bar{M}_n$) fall in the general range of 20000–100000, with those of the dimethyl (1) and phenyl/methyl (3) polymers and the corresponding copolymer (5) typically being greater than 50000. The analogous phenyl/ethyl compounds (4 and 6) have somewhat lower molecular weights, but, since they have not been studied as extensively, it is not known whether this is due to the greater steric bulk of the ethyl group or to other factors such as reaction time and/or temperature.

Initially, the rapid and routine characterization of these poly(phosphazenes) was hindered by their anomalous behavior in size-exclusion chromatography (SEC) experi-

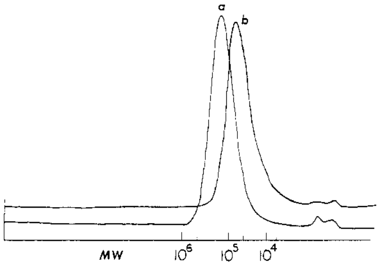


Figure 3. Molecular weight distributions (determined by SEC): (a) $[Ph(Me)PN]_n$ (**3**, $\bar{M}_w$ = 162 200) and (b) $[Ph(Et)PN]_n$ (**4**, $\bar{M}_w$ = 65 300).

ments. The analysis of these materials was attempted on commercial columns, with either Styragel or glass bead packings, at a variety of temperatures and concentrations. In addition, several different solvents including mixed-solvent systems were investigated. In almost all cases, grossly distorted, severely tailing, nonreproducible chromatograms were obtained, suggestive of an adsorption type of interaction between the polymer and the column materials. The results of these experiments were obviously inconsistent with the membrane osmometry and viscosity studies.

Recently, however, we found that *these SEC problems are completely circumvented by the addition of a small amount (ca. 0.1 wt %) of an ionic species such as* $(n\text{-}Bu)_4NBr$ *to the THF mobile phase.* Under these conditions, classic SEC behavior is observed and consistent, nontailing chromatograms are obtained (Figure 3). Moreover, the molecular weights ($\bar{M}_n$) measured by SEC, relative to narrow molecular weight polystyrene standards, agree very well (within ca. 20–30%) with the values determined by membrane osmometry (Table III). Similar effects are observed with other ammonium salt additives in THF as well as in $CHCl_3$ and CH_2Cl_2 solution. As long as the salt is present, other experimental variables including temperature, polymer concentration, type of column, flow rate, etc., have negligible effects on the observed molecular weight distribution. The fact that the solution viscosity, as mentioned above, is unaffected by the presence of the salt shows that there has been no significant change in the nature of the polymer/solvent interaction.

Although the exact reason for this dramatic improvement in the chromatography is not known, we speculate that the ionic solute simply prevents whatever type of polar interaction was occurring in the prior experiments. Other new findings[19] relevant to this question indicate that the backbone nitrogen sites in these poly(alkyl/arylphosphazenes) are more easily protonated than those in the more conventional polymers bearing alkoxy, aryloxy, or amino substituents. Consistent and reasonable SEC results for some silylated derivatives of $[Ph(Me)PN]_n$, under the same conditions, have recently been reported.[20]

The absolute weight-average molecular weights ($\bar{M}_w$) of several samples of $[Ph(Me)PN]_n$ from different preparations were determined by light scattering measurements (4880-Å argon ion laser line) in dilute THF solutions. The $\bar{M}_w$ values, which range from 73 000 to 202 000, are consistently (ca. 30%) higher than those obtained by SEC determinations (Table IV). These results, when combined with the membrane osmometry data, clearly confirm that the SEC experiments do provide valid representations of the molecular weight distributions of these poly(alkyl/arylphosphazenes). The second virial coefficients A_2 determined by light scattering are consistent with the osmometry values. For most samples, the radius of gyration $\langle S^2\rangle_z^{1/2}$ was too low for an accurate assessment. The $\langle S^2\rangle_z^{1/2}$ value for sample D (Table IV), probably because of the polymer's higher molecular weight, was analyzed and found to equal 249 Å, which is consistent with the polymer having a randomly coiled configuration in solution. Indeed, the calculated ratio $\langle S^2\rangle_z^{1/2}/\bar{M}_w$ (ca. 0.31 Å^2·mol/g) is essentially identical with the value obtained for high molecular weight poly(dichlorophosphazene).[21]

Also, a good correlation between $\bar{M}_w$ (light scattering) and intrinsic viscosity is observed for $[Ph(Me)PN]_n$ over the molecular weight range of the samples studied (Table IV). Thus, the Mark–Houwink relationship, $[\eta] = K(\bar{M}_w)^a$, yields values of $K = 1.44 \times 10^{-4}$ (with $[\eta]$ in dL/g) and a = 0.66. These data again indicate a well-solvated, extended-chain structure of the polymer in THF.

Table V
Thermal Analysis Data

polymer	DSC[a] T_g	DSC[a] T_m	TGA[b]
1, $[N{=}PMe_2]_n$	−46	143	401
2, $[N{=}PEt_2]_n$		217	353
3, $[N{=}PPhMe]_n$	37		354
4, $[N{=}PPhEt]_n$	20		342
5, $\{[N{=}PMe_2]_x[N{=}PPhMe]_y\}_n$	−3		390
6, $\{[N{=}PEt_2]_x[N{=}PPhEt]_y\}_n$	−5		365

[a] Glass transition (T_g) and melting temperatures (T_m) in degrees Celsius. [b] Decomposition onset temperature at a heating rate of 10 °C/min in argon. Decomposition temperatures ca. 20–50 °C lower are observed in air.

Thermal Analysis Results. The data obtained from thermal analyses (DSC and TGA) of the polymers are summarized in Table V. Not surprisingly, we find that the nature of the substituents has a pronounced effect on properties such as glass transition and melting temperatures and on the overall thermal stability of these poly(alkyl/arylphosphazenes).

The symmetrically substituted poly(dialkylphosphazenes) **1** and **2** show sharp endothermic melt transitions [4.0 and 7.7 kJ/(mol repeat unit), respectively], indicating a fairly high degree of crystallinity in the materials. On the other hand, none of the phenyl-substituted polymers (**3** and **4**) and copolymers (**5** and **6**) show a melt transition; therefore, the side-group asymmetry disrupts the crystalline order in the solid state. These results were the basis for the X-ray diffraction experiments that are discussed below. Moreover, the general amorphous nature of the phenyl/alkyl homopolymers **3** and **4**, indicated here, is consistent with their structure being assigned as atactic on the basis of ^{13}C NMR spectroscopy (see above).

In the DSC experiments, poly(dimethylphosphazene) (**1**) shows a glass transition of −46 °C which increases to −3 and 37 °C for the 25% (**5**) and 50% (**3**) phenyl-substituted analogues. A similar trend is noted for the phenyl/ethyl derivatives (**4** and **6**), although poly(diethylphosphazene) itself does not exhibit a discernible glass transition. Current studies are in progress on a much larger series of polymers and copolymers in order to better understand the structure/property relationships common to the poly(alkyl/arylphosphazenes).

Thermogravimetric analysis (TGA) of these poly(phosphazenes) show their decomposition onset temperatures in an inert atmosphere to be ca. 350–400 °C, depending on the side group. These temperatures are ca. 25–75 °C higher than that reported for commercial materials based on the fluoroalkoxy-substituted polymer, $[(CF_3CH_2O)_2PN]_n$[22]. Preliminary indications, therefore, are that the incorporation of directly P–C bonded alkyl and/or aryl groups does increase the thermal stability of poly(phosphazenes), as anticipated.[5-7] Interestingly, methyl rather than phenyl side groups yield the more

Table VI
Molecular Weight vs. Percent Polymerization of $[Ph(Me)PN]$[a]

expt no.	reactn time, days	% polymn[c]	SEC analysis[b] $\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
1	4	22	61 600	1.8
2	8	63	67 400	1.7
3	12	>93	127 600	2.1
4	16	>93	129 600	2.0

[a] Reactions run in sealed glass ampules at 175 °C with equal amounts of monomer in each experiment. [b] See footnote c, Table III, for conditions. [c] Based on recovered $Me_3SiOCH_2CF_3$.

stable materials, as shown by the results for polymers **1**, **3**, and **5**. We have also recently reported that silylmethyl groups (i.e., Me_3SiCH_2) have a significant stabilizing influence.[20]

X-ray Diffraction Studies. Samples of the poly(dialkylphosphazenes) **1** and **2** displayed X-ray powder diffraction patterns characteristic of crystalline regions in the materials. The peaks in the diffraction of **1** were of lower amplitude and greater angular breadth than those of **2**. These data indicate that poly(diethylphosphazene) **2** is highly crystalline while poly(dimethylphosphazene) **1** is more amorphous with smaller crystalline zones. This high degree of crystallinity is probably responsible for the insolubility of **2** as noted above. All of the phenyl-substituted polymers **3–6** were found to be quite amorphous in the X-ray diffraction studies, a result that is further evidence for an atactic structure of the poly(alkylphenylphosphazenes) **3** and **4** and for a random substitution pattern in the copolymers **5** and **6**.

Mechanistic Implications. The successful synthesis of poly(alkyl/arylphosphazenes) by the condensation-polymerization process leads to a number of questions concerning the mechanism of this reaction (eq 3). It was initially assumed that a step-growth mechanism, as is usually the case for condensation reactions,[18] was operative since the polydispersity ($\bar{M}_w/\bar{M}_n$) values of the polymers are close to the theoretical limit of 2.0 expected for a step-growth process.[18]

The possibility of a step-growth mechanism is precluded, however, by the results of experiments in which the polymerization is stopped prior to completion (Table VI). Even when the reaction is ca. 20% complete, the contents of the polymerization ampule are found to be fairly high molecular weight polymer and unreacted monomer. No indication of the presence of linear or cyclic oligomers is found in the NMR spectroscopic and SEC studies of these reaction mixtures. Such data clearly indicate that some type of *a chain-growth mechanism must be occurring*. More extensive studies aimed at the elucidation of the detailed mechanisms of the initiation, propagation, and termination steps of this process are currently in progress.

Experimental Section

Synthesis. The *N*-silyl-*P*-trifluoroethoxyphosphoranimine "monomers" were prepared and characterized by NMR spectroscopy as described elsewhere.[13-15] Complete details[15] of the thermal decomposition reactions are also available; however, a typical experiment is described here. A heavy-walled glass ampule (ca. 20-mL capacity) with a constriction was purged with dry nitrogen and charged with $Me_3SiN{=}P(OCH_2CF_3)Me_2$ (6.46 g, 26.1 mmol). After the ampule was degassed by the freeze–pump–thaw method, it was sealed at the constriction with a torch and was heated in a thermoregulated oven at 160 °C for 65 h. The ampule was opened and the volatile component ($Me_3SiOCH_2CF_3$, 4.45 g, 99.0% yield) was trapped on a vacuum line. The remaining white solid was dissolved in CH_2Cl_2 and precipitated by pouring the solution into hexane. Drying under vacuum gave **1** (1.93 g, 99.0% yield). Larger quantities of the polymer were prepared by carrying out the thermolysis in a stainless steel reaction bomb (ca. 300-mL capacity) fitted with a valve for removal of the volatile byproduct. In this manner, for example, $Me_3SiN{=}P(OCH_2CF_3)Me_2$ (127 g, 0.51 mol) was heated at 160 °C for 302 h to give complete thermolysis to $[Me_2PN]_n$ (**1**). Alternatively, a large capacity (ca. 100-mL, 25-mm inner diameter) heavy-walled glass ampule could be used as the reaction vessel.

The other homopolymers **2–4** were prepared according to the same procedure under the conditions listed in Table I. The copolymers **5** and **6** were similarly prepared by charging the reaction vessel with equimolar quantities of the respective monomers prior to sealing under vacuum.

Measurements. Elemental analyses (Table I) were obtained from Schwarzkopf Microanalytical Laboratory, Woodside, NY. Proton, ^{13}C, and ^{31}P NMR spectra (Table II) were recorded on a Varian XL-300 spectrometer.

Dilute solution viscosity measurements (Table III) were made at 30 °C with a Cannon Ubbelohde viscometer immersed in a water bath controlled to within 0.1 °C. Membrane osmometry data (Table III) was obtained on a Hewlett-Packard Mechrolab Model 501 high-speed membrane osmometer equipped with an Arro Laboratories Type 600 cellulose acetate membrane. The SEC determinations were done on a Waters 244 ALC/GPC instrument with a 6000A solvent delivery system, a U6K injector, and Model 441 UV absorbance and R400 refractive index (RI) detectors coupled to a Spectra-Physics data system. Typical experimental conditions and SEC results are given in Table III.

Light scattering measurements (Table IV) were made on a Brookhaven instrument operating at the 4880-Å argon ion laser line. Dilute solutions of $[Ph(Me)PN]_n$ (**3**) in THF gave a refractive index increment (dn/dc) of 0.21 mL/g, which was independent of the molecular weight of the sample. Zimm plots were constructed in order to evaluate weight-average molecular weights ($\bar{M}_w$), second virial coefficients, and the *z*-average radii of gyration $\langle S^2\rangle_z^{1/2}$.

Differential scanning calorimetry (DSC) measurements (Table V) were made on a Du Pont Model 910 instrument under nitrogen against an aluminum reference from −150 to 280 °C. Thermogravimetric analyses (TGA) (Table V) were done on a Du Pont Model 951 instrument at temperatures from 30 to 480 °C under flowing argon or air. Data was collected and analyzed on a Du Pont 1090 data station.

The X-ray diffraction measurements were made with a North American Phillips diffractometer equipped with a copper source tube emitting Kα radiation at 40 kV and 18 mA. The rate of monitoring of the angle change was 2° (2θ) per min. Counting was done on a Model 30*XY* Phillips Electronic Instruments counting assembly equipped with a scintillation counter and a graphite monochrometer.

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Registry No. 1 (SRU), 32007-38-8; 1 (homopolymer), 88718-77-8; 2 (SRU), 56296-30-1; 2 (homopolymer), 107037-73-0; 3 (SRU), 88733-82-8; 3 (homopolymer), 88718-66-5; 4 (SRU), 96743-32-7; 4 (homopolymer), 96743-49-6; 5, 96743-50-9; 6, 96743-52-1.

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Living Cationic Polymerization of *N*-Vinylcarbazole Initiated by Hydrogen Iodide

Mitsuo Sawamoto, Jun'ichi Fujimori, and Toshinobu Higashimura*

Department of Polymer Chemistry, Faculty of Engineering, Kyoto University, Kyoto 606, Japan. *Received October 9, 1986*

ABSTRACT: Living cationic polymerization of *N*-vinylcarbazole (NVC) was achieved with hydrogen iodide (HI) as an initiator either at −40 °C in toluene or at −78 °C in methylene chloride containing a catalytic amount of tetra-*n*-butylammonium iodide as a common ion salt. The number-average molecular weight of the polymers obtained under these conditions was directly proportional to NVC conversion or to the NVC/HI feed ratio and in good agreement with the calculated values assuming that one HI molecule forms one living chain. The polymers exhibited a narrow molecular weight distribution with a $\bar{M}_w/\bar{M}_n$ ratio from 1.2 to 1.3. The corresponding polymerizations by iodine or a mixture of HI and iodine (HI/I_2 initiator) were not living, yielding polymers with a broader molecular weight distribution. The scope of living cationic polymerization is also discussed in terms of the stability of the propagating carbocation and the nucleophilicity of the counteranion.

Introduction

N-Vinylcarbazole (NVC) is among the most reactive vinyl monomers in cationic polymerization. Its high cationic polymerizability arises from the electron-donating carbazolyl pendant, which also serves to stabilize the propagating NVC cation by providing a conjugating system where the positive charge is delocalized.

In view of the stability of the NVC-derived growing species, we have been interested in "living" cationic polymerization of this monomer[1,2] and in fact found that the NVC polymerization initiated by iodine yields living polymers with a controlled molecular weight and a narrow molecular weight distribution (MWD).[2] This living system is, however, operative only in a limited range of reaction conditions, i.e., at −78 °C in methylene chloride containing tetra-*n*-butylammonium iodide (n-Bu_4NI) as a common ion salt.

More recent investigations in our laboratories have provided a number of living cationic polymerizations initiated by a mixture of hydrogen iodide (HI) and iodine.[3,4] Although efficient and versatile, the HI/I_2 initiating system has thus far been applied to only vinyl ethers[4] and related monomers.[5] Another characteristic of the binary system is that both HI and iodine are indispensable for living polymerization; HI alone cannot polymerize vinyl ethers but forms a 1:1 adduct [$CH_3CH(OR)$–I], the C–I bond of which must be activated by iodine to initiate living propagation.[6] Namely, HI is the initiator, while iodine acts as the "activator".

The primary object of this study was to extend the scope of the HI/I_2-initiated living polymerization to NVC, a reactive monomer other than vinyl ethers and their analogues. Rather surprisingly, not HI/I_2 but HI alone was found to initiate living polymerization of NVC under conditions wider than those for the corresponding process with iodine. This new combination of monomer and initiator enables us to discuss the scope of living cationic polymerization in terms of the stability of the propagating species (carbocations) and the nucleophilicity of the counteranions derived from initiators.

Experimental Section

Materials. Commercial NVC was recrystallized at least 3 times from *n*-hexane, thoroughly dried in vacuo, and stored in the dark at −20 °C. HI (as an *n*-hexane solution) and iodine were obtained as reported.[3] n-Bu_4NI (polarographic grade) was used as received after prolonged vacuum drying. Polymerization solvents [toluene and methylene chloride (CH_2Cl_2)] and the internal standard for gas chromatography (tetrahydronaphthalene) were purified by the usual methods[3] and doubly distilled over calcium hydride before use.

Procedures. Polymerization was carried out in the dark under dry nitrogen in a baked glass tube equipped with a three-way stopcock.[3] The reaction was initiated by injecting an initiator solution via a dry syringe into a monomer solution and terminated after a certain period with prechilled ammoniacal methanol. When the HI/I_2 initiator was employed, HI and iodine solutions were added successively in this order. The NVC conversion was determined by gas chromatography with tetrahydronaphthalene as an internal standard. The quenched reaction mixture was washed sequentially with 10% aqueous sodium thiosulfate solution and with water, evaporated to dryness under reduced pressure, and vacuum dried to give the product polymers.

The MWD of the polymers was measured by size-exclusion chromatography (SEC) in chloroform at room temperature on a Jasco Trirotar-II instrument equipped with three polystyrene gel columns (Shodex A-802, A-803, and A-804). The polydispersity ratio ($\bar{M}_w/\bar{M}_n$) was calculated from the SEC curves on the basis of a polystyrene calibration. The number-average molecular

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