3686 *Macromolecules* **1996,** *29,* 3686−3693

Synthesis and Characterization of Aminoorganosiloxane-Bearing Polyphosphazenes: New Properties by the Elimination of Hydrogen Bonding

Harry R. Allcock,* Susan E. Kuharcik,† and Constance J. Nelson‡

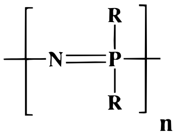
Department of Chemistry, The Pennsylvania State University,
University Park, Pennsylvania 16802

Received October 26, 1995; Revised Manuscript Received February 12, 1996⊗

ABSTRACT: The synthesis of new hybrid polyphosphazene−siloxane polymers is described. These polymers contain a polyphosphazene backbone and [(*N*-methylamino)propyl]siloxane side groups, −N(Me)-$(CH_2)_3SiMe_2OSiMe_3$ or $-N(Me)(CH_2)_3SiMe_2OSiMe_2OSiMe_3$, in ratios of 1:1 and 1:3 with trifluoroethoxy, 2-(2-methoxyethoxy)ethoxy, or *p*-methylphenoxy cosubstituents. The synthetic method utilized allows the polymer properties to be tuned by variations in the cosubstituent ratios. The polymers were characterized by ^{31}P, ^{13}C, and ^{1}H NMR, differential scanning calorimetry (DSC), gel permeation chromatography (GPC), and elemental analysis. The percent loading of siloxane-containing side groups and the nature of the cosubstituents were correlated to the glass transition temperatures. The glass transition temperatures ranged from −83 to −22 °C. The longer, trisiloxane-containing units generated lower glass transition temperatures than did the analogous polymers with disiloxane-containing side groups. Several polymers were further characterized by dynamic mechanical analysis (DMA). In addition to glass transition temperatures, other transitions attributed to the siloxane side groups were detected at approximately −124 °C.

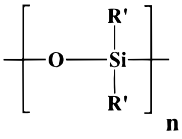
Introduction

Poly(organophosphazenes) (**1**) and poly(organosiloxanes) (**2**) are two main classes of inorganic backbone polymers. These polymer systems share several useful materials properties such as backbone transparency to radiation from the mid-UV to near IR, and relative insensitivity to γ-ray, X-ray, and UV-induced cleavage as compared to organic polymer backbones that contain aliphatic bonds. They are also inherently stable to thermo-oxidative breakdown.[1] In addition, both of these polymer systems have properties which make them good candidates for low-temperature elastomeric behavior. For example, both the siloxane and phosphazene backbones are inherently highly flexible.[2,3] Polysiloxanes and polyphosphazenes, such as $[OSiMe_2]_n$ ($T_g = -130$ °C) and $[NP(OCH_2CH_2CH_2CH_3)_2]_n$ ($T_g = -105$ °C), have glass transition temperatures that are among the lowest known in polymer chemistry. The types of side groups linked to the main chain strongly influence the torsional mobility of the skeletal bonds in these polymer systems. Therefore, properties such as the glass transition temperature and melting temperatures (if present) may be altered by modification of the side group structure. However, side group modification in polysiloxanes is often limited by the available methods of synthesis. The properties of polyphosphazenes are more readily tailored by the use of macromolecular substitution reactions.[4]



$$\left[N{=}P(R)_2 \right]_n$$

1



$$\left[O{-}Si(R')_2 \right]_n$$

2

Polyphosphazenes and polysiloxanes have both been developed as commercial elastomers.[4,5] In principle, hybrid phosphazene−siloxane systems could have both low glass transition temperatures and useful elastomeric behavior, coupled with impermeability to organic liquids and fire resistance. The uses of such polymers in membranes and in hydrophobic surfaces are subjects of additional interest. Several research groups have explored the possibility that hybrid systems of this type may be accessible.[6−15] However, until recently, relatively few successful macromolecular syntheses have been described.[16−24]

An approach being followed in our program is to link organosilicon side groups to a high polymeric phosphazene chain. One method for the attachment of organosiloxane units to a polyphosphazene is by nucleophilic replacement of the chlorine atoms in poly(dichlorophosphazene) with the use of amine-functionalized organosilicon reagents. The reactions of poly(dichlorophosphazene) with primary and secondary nonsilylated amines are well-known.[25] Previously, we reported the reactions of primary (aminopropyl)siloxanes with both small-molecule cyclic phosphazene trimers and linear phosphazene high molecular weight polymers.[24] The advantages offered by the use of (aminopropyl)siloxane reagents include the simplicity of the reactions and the ability to synthesize controlled ratio cosubstituent phosphazene polymers. A disadvantage of the previous work is that phosphazene polymers with more than a 25% loading of the (aminopropyl)siloxane group are rigid, nonelastomeric materials. It was proposed that this may be due to hydrogen bonding near the polymer backbone, which would reduce the flexibility of the polyphosphazene chain.[24]

The objectives of the current research were (1) to incorporate organosiloxane side groups into the polyphosphazene system while eliminating the possibility of hydrogen bonding near the polymer backbone, (2) to synthesize polymers with low glass transition temperatures, and (3) to control the polymer properties by the incorporation of various cosubstituents. To accomplish these goals, *secondary* (aminopropyl)siloxanes were used in conjunction with either (methoxyethoxy)ethoxy, trifluoroethoxy, or *p*-methylphenoxy side groups. Two

---

† Present address: DuPont Experimental Station, Central Research Division, Wilmington, DE.

‡ Present address: 3M Corporate Research Laboratory, St. Paul, MN.

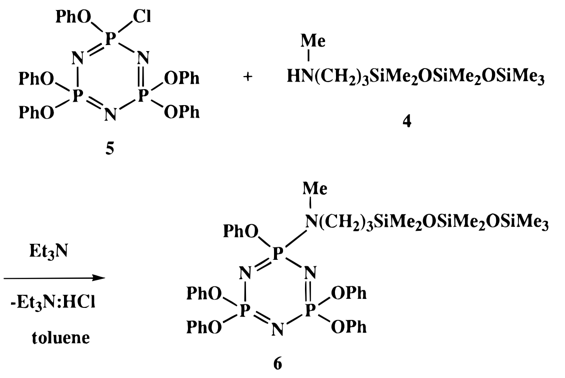
⊗ Abstract published in *Advance ACS Abstracts*, April 1, 1996.

S0024-9297(95)01618-4 CCC: $12.00

Table 1. ^{31}P, ^{1}H, and ^{13}C NMR Characterization Data for [(*N*-Methylamino)propyl]siloxane Starting Materials and Cyclic Trimer 6

compound	^{31}P NMR δ (ppm)	^{1}H NMR signal	^{1}H NMR δ (ppm)	^{13}C NMR signal	^{13}C NMR δ (ppm)
$HN(Me)(CH_2)_3SiMe_2OSiMe_3$ (**3**)	NA	*H*N	1.1 (s, 1H)	N(*Me*)	36.3
		HN(*Me*)	2.4 (s, 3H)	N*C*H$_2$	55.2
		HNC*H*$_2$	2.6 (t, 2H)	NCH$_2$*C*H$_2$	23.5
		HNCH$_2$C*H*$_2$	1.5 (m, 2H)	NCH$_2$CH$_2$*C*H$_2$	15.7
		HNCH$_2$CH$_2$C*H*$_2$	0.5 (m, 2H)	Si*Me*$_2$O	1.9
		Si*Me*$_2$OSi*Me*$_3$	0.0 (m, 15 H)	OSi*Me*$_3$	0.2
$HN(Me)(CH_2)_3SiMe_2OSiMe_2OSiMe_3$ (**4**)	NA	*H*N	1.1 (s, 1H)	N(*Me*)	36.0
		HN(*Me*)	2.4 (s, 3H)	N*C*H$_2$	55.0
		HNC*H*$_2$	2.5 (t, 2H)	NCH$_2$*C*H$_2$	23.2
		HNCH$_2$C*H*$_2$	1.5 (m, 2H)	NCH$_2$CH$_2$*C*H$_2$	15.5
		HNCH$_2$CH$_2$C*H*$_2$	0.5 (m, 2H)	Si*Me*$_2$OSiMe$_2$	1.7
		Si*Me*$_2$OSi*Me*$_2$OSi*Me*$_3$	0.0 (m, 21H)	Si*Me*$_2$OSiMe$_3$	1.1
				OSi*Me*$_3$	0.0
$N_3P_3(OPh)_5[N(Me)(CH_2)_3SiMe_2OSiMe_2OSiMe_3]$ (**6**)	20.1 (t)	N(*Me*)	2.5	N(*Me*)	32.8
	9.0 (d)	NC*H*$_2$	2.8	N*C*H$_2$	51.6
		NCH$_2$C*H*$_2$	1.4	NCH$_2$*C*H$_2$	21.4
		NCH$_2$CH$_2$C*H*$_2$	0.4	NCH$_2$CH$_2$*C*H$_2$	14.9
		Si*Me*$_2$OSi*Me*$_2$OSi*Me*$_3$	0.1	Si*Me*$_2$OSiMe$_2$	1.9
		O*Ph*	6.8−7.4	Si*Me*$_2$OSiMe$_3$	1.3
				OSi*Me*$_3$	0.2
				O*Ph*	150.9, 129.3, 124.5, 121.1

Scheme 1



siloxane reagents of differing lengths were examined: $HN(Me)(CH_2)_3SiMe_2OSiMe_3$ (**3**) and $HN(Me)(CH_2)_3SiMe_2OSiMe_2OSiMe_3$ (**4**). Variations in the ratios of the secondary amino groups to the cosubstituent units should allow a fine-tuning of the polymer properties.

Results and Discussion

Preparation of a Cyclic Trimer Model Compound. It is often easier to synthesize, purify, and characterize small molecule compounds than high molecular weight polymers. In addition, model reactions may provide information on synthetic conditions and substitution reactivities that can be transposed to the high molecular weight polymer level. Thus, the secondary amine, $HN(Me)(CH_2)_3SiMe_2OSiMe_2OSiMe_3$, was allowed to react with the cyclic trimer $N_3P_3(OPh)_5Cl$ (**5**) in the presence of triethylamine as a hydrogen chloride acceptor to yield compound **6** (Scheme 1). The NMR spectral data for the [(*N*-methylamino)propyl]siloxane side groups and cyclic trimer **6** are shown in Table 1.

Another possible synthetic route to **6**, which was considered as an alternative, involved the synthesis of $N_3P_3(OPh)_5\{N(Me)CH_2CH{=}CH_2\}$ followed by hydrosilylation with $HSiMe_2OSiMe_2OSiMe_3$ in the presence of a platinum catalyst. This alternative approach was not used for the following reasons. The use of a preformed aminoorganosiloxane side group such as **3** or **4** offers several advantages. Because the hydrosilylation to yield **3** or **4** is performed before linkage of the side group to the polymer, purification of the products may be easier. Also, previous studies have shown that the ease of a hydrosilylation reaction on an alkene that is attached to a phosphazene skeleton depends on the steric and electronic effects of the spacer group.[13,20] Another advantage is that incomplete reaction, and subsequent cross-linking due to residual double bonds, is avoided. The presence of residual unsaturated sites could cause complications when the reaction is transposed to the high molecular weight polymer level.

Preparation of High Molecular Weight Polymers. First, it must be emphasized that the two organosilyl secondary amines used in this work were incapable of replacing all of the ~30 000 chlorine atoms in poly(dichlorophosphazene). Typically, only 50−60% of the available chlorine atoms were replaced, to yield polymers that were sensitive to moisture due to the hydrolysis of the residual P−Cl bonds. For this reason *co*substituent polymers were synthesized in order to ensure the replacement of all or most of the chlorine atoms (see later).

However, the reason for the limited reactivity of amines **3** and **4** with $(NPCl_2)_n$ is of some interest, since the related primary amine, $H_2N(CH_2)_3SiMe_2OSiMe_3$, used in previous studies[24] was capable of complete chlorine replacement. The reactions of amine nucleophiles in general with poly(dichlorophosphazene) are known to be sensitive to steric retardation if the reactant amine, or the side groups already present, are bulky.[25,26] For example, poly(dichlorophosphazene) reacts completely with primary amines such as ethylamine, *N*-propylamine, and aniline, but sterically hindered primary amines (isopropylamine, isobutylamine) yield only partly substituted polymers. The behavior of secondary amines is similar. Dimethylamine replaces all the chlorine atoms in poly(dichlorophosphazene). Diethylamine, which is more sterically hindered, will react with only approximately 50% of the available P−Cl bonds.[27] In the present work, the presence of the *N*-methyl unit in the [(*N*-methylamino)propyl]siloxane side groups may provide enough steric bulk to interfere with the reactions of the incoming amines.

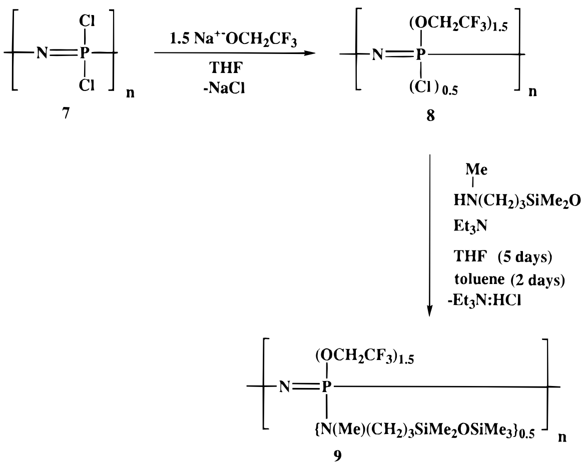
For these reasons it was necessary to design, synthesize, and study polyphosphazenes with both the second-

Table 2. ^{31}P, ^{1}H, and ^{13}C NMR Characterization Data for Polymers 9−20

	^{31}P NMR		^{1}H NMR[a]		^{13}C NMR	
polymer	signal	δ (ppm)	signal	δ (ppm)	signal	δ (ppm)
9	$\mathrm{NP(TFE)_2}$[b]	−11.4	$\mathrm{OC}\mathit{H}_2\mathrm{CF}_3$	4.2 (2H)	$\mathrm{O}\mathit{C}\mathrm{H_2CF_3}$	62.7
	NP(TFE)[N(Me)R]	−1.1	$\mathrm{N}(\mathit{Me})$	2.6	$\mathrm{OCH_2}\mathit{C}\mathrm{F_3}$	124.3
	$\mathrm{NP[N(Me)R]_2}$	5.9	$\mathrm{NC}\mathit{H}_2$	3.0	$\mathrm{N}(\mathit{Me})$	33.2
			$\mathrm{NCH_2C}\mathit{H}_2$	1.5 (2H)	$\mathrm{N}\mathit{C}\mathrm{H_2}$	52.5
			$\mathrm{NCH_2CH_2C}\mathit{H}_2$	0.4 (2H)	$\mathrm{NCH_2}\mathit{C}\mathrm{H_2}$	21.6
			$\mathrm{Si}\mathit{Me}_2\mathrm{OSi}\mathit{Me}_3$	0.0 (15H)	$\mathrm{NCH_2CH_2}\mathit{C}\mathrm{H_2}$	15.2
					$\mathrm{Si}\mathit{Me}_2\mathrm{OSi}\mathit{Me}_3$	1.7, 1.0, −0.1
10	$\mathrm{NP(TFE)_2}$	−12.0	$\mathrm{OC}\mathit{H}_2\mathrm{CF}_3$	4.2	$\mathrm{O}\mathit{C}\mathrm{H_2CF_3}$	62.5
	NP(TFE)[N(Me)R]	−1.0	$\mathrm{N}(\mathit{Me})$	2.6	$\mathrm{OCH_2}\mathit{C}\mathrm{F_3}$	123.5
			$\mathrm{NC}\mathit{H}_2$	2.9	$\mathrm{N}(\mathit{Me})$	33.4
			$\mathrm{NCH_2C}\mathit{H}_2$	1.5	$\mathrm{N}\mathit{C}\mathrm{H_2}$	52.5
			$\mathrm{NCH_2CH_2C}\mathit{H}_2$	0.4	$\mathrm{NCH_2}\mathit{C}\mathrm{H_2}$	22.0
			$\mathrm{Si}\mathit{Me}_2\mathrm{OSi}\mathit{Me}_2\mathrm{OSi}\mathit{Me}_3$	0.0	$\mathrm{NCH_2CH_2}\mathit{C}\mathrm{H_2}$	15.7
					$\mathrm{Si}\mathit{Me}_2\mathrm{OSi}\mathit{Me}_2\mathrm{OSi}\mathit{Me}_3$	0.2, 0.1, 0.0
11	$\mathrm{NP(TFE)_2}$	−12.9	$\mathrm{OC}\mathit{H}_2\mathrm{CF}_3$	4.2	$\mathrm{O}\mathit{C}\mathrm{H_2CF_3}$	62.4
	NP(TFE)[N(Me)R]	−3.9	$\mathrm{N}(\mathit{Me})$	2.7	$\mathrm{OCH_2}\mathit{C}\mathrm{F_3}$	123.7
	$\mathrm{NP[N(Me)R]_2}$	2.4	$\mathrm{NC}\mathit{H}_2$	3.0	$\mathrm{N}(\mathit{Me})$	33.5
			$\mathrm{NCH_2C}\mathit{H}_2$	1.5	$\mathrm{N}\mathit{C}\mathrm{H_2}$	53.0
			$\mathrm{NCH_2CH_2C}\mathit{H}_2$	0.4	$\mathrm{NCH_2}\mathit{C}\mathrm{H_2}$	21.7
			$\mathrm{Si}\mathit{Me}_2\mathrm{OSi}\mathit{Me}_3$	0.1	$\mathrm{NCH_2CH_2}\mathit{C}\mathrm{H_2}$	15.3
					$\mathrm{Si}\mathit{Me}_2\mathrm{OSi}\mathit{Me}_3$	1.8, 1.0, 0.1
12	$\mathrm{NP(TFE)_2}$	−12.5	$\mathrm{OC}\mathit{H}_2\mathrm{CF}_3$	4.2 (2H)	$\mathrm{O}\mathit{C}\mathrm{H_2CF_3}$	62.1
	NP(TFE)[N(Me)R]	−1.5	$\mathrm{N}(\mathit{Me})$	2.6	$\mathrm{OCH_2}\mathit{C}\mathrm{F_3}$	123.0
	$\mathrm{NP[N(Me)R]_2}$	5.2	$\mathrm{NC}\mathit{H}_2$	3.0	$\mathrm{N}(\mathit{Me})$	33.2
			$\mathrm{NCH_2C}\mathit{H}_2$	1.5	$\mathrm{N}\mathit{C}\mathrm{H_2}$	52.6
			$\mathrm{NCH_2CH_2C}\mathit{H}_2$	0.4	$\mathrm{NCH_2}\mathit{C}\mathrm{H_2}$	21.6
			$\mathrm{Si}\mathit{Me}_2\mathrm{OSi}\mathit{Me}_2\mathrm{OSi}\mathit{Me}_3$	0.1 (21H)	$\mathrm{NCH_2CH_2}\mathit{C}\mathrm{H_2}$	15.1
					$\mathrm{Si}\mathit{Me}_2\mathrm{OSi}\mathit{Me}_2\mathrm{OSi}\mathit{Me}_3$	1.6, 1.0, −0.2
13	$\mathrm{NP(OPhMe)_2}$	−21.7	$\mathrm{O}\mathit{Ph}$	6.6−7.1	$\mathrm{O}\mathit{Ph}$	150.0, 131.8, 129.1, 121.1
	NP(OPhMe)[N(Me)R]	−7.6	$\mathrm{OPh}\mathit{Me}$	2.2	$\mathrm{OPh}\mathit{Me}$	21.3
			$\mathrm{N}(\mathit{Me})$	2.5	$\mathrm{N}(\mathit{Me})$	33.5
			$\mathrm{NC}\mathit{H}_2$	2.8	$\mathrm{N}\mathit{C}\mathrm{H_2}$	52.5
			$\mathrm{NCH_2C}\mathit{H}_2$	2.3	$\mathrm{NCH_2}\mathit{C}\mathrm{H_2}$	22.9
			$\mathrm{NCH_2CH_2C}\mathit{H}_2$	1.0	$\mathrm{NCH_2CH_2}\mathit{C}\mathrm{H_2}$	18.7
			$\mathrm{Si}\mathit{Me}_2\mathrm{OSi}\mathit{Me}_3$	0.0	$\mathrm{Si}\mathit{Me}_2\mathrm{OSi}\mathit{Me}_3$	1.9, 1.0, 0.1
14	$\mathrm{NP(OPhMe)_2}$	−20.9	$\mathrm{O}\mathit{Ph}$	6.6−7.1	$\mathrm{O}\mathit{Ph}$	148.6, 130.9 129.1, 121.1
	NP(OPhMe)[N(Me)R]	−7.7	$\mathrm{OPh}\mathit{Me}$	2.1	$\mathrm{OPh}\mathit{Me}$	20.6
	$\mathrm{NP[N(Me)R]_2}$	3.5	$\mathrm{N}(\mathit{Me})$	2.4	$\mathrm{N}(\mathit{Me})$	34.2
			$\mathrm{NC}\mathit{H}_2$	2.8	$\mathrm{N}\mathit{C}\mathrm{H_2}$	52.0
			$\mathrm{NCH_2C}\mathit{H}_2$	2.3	$\mathrm{NCH_2}\mathit{C}\mathrm{H_2}$	21.2
			$\mathrm{NCH_2CH_2C}\mathit{H}_2$	1.0	$\mathrm{NCH_2CH_2}\mathit{C}\mathrm{H_2}$	11.0
			$\mathrm{Si}\mathit{Me}_2\mathrm{OSi}\mathit{Me}_2\mathrm{OSi}\mathit{Me}_3$	0.0	$\mathrm{Si}\mathit{Me}_2\mathrm{OSi}\mathit{Me}_2\mathrm{OSi}\mathit{Me}_3$	1.8, 1.2, 1.0 to −0.1
15	$\mathrm{NP(OPhMe)_2}$	−21.9	$\mathrm{O}\mathit{Ph}$	6.9−7.1	$\mathrm{O}\mathit{Ph}$	150.6, 131.5, 129.1, 121.2
	NP(OPhMe)[N(Me)R]	−8.3	$\mathrm{OPh}\mathit{Me}$	2.2	$\mathrm{OPh}\mathit{Me}$	20.7
	$\mathrm{NP[N(Me)R]_2}$	3.0	$\mathrm{N}(\mathit{Me})$	2.5	$\mathrm{N}(\mathit{Me})$	33.7
			$\mathrm{NC}\mathit{H}_2$	2.9	$\mathrm{N}\mathit{C}\mathrm{H_2}$	52.5
			$\mathrm{NCH_2C}\mathit{H}_2$	1.4	$\mathrm{NCH_2}\mathit{C}\mathrm{H_2}$	21.4
			$\mathrm{NCH_2CH_2C}\mathit{H}_2$	1.1	$\mathrm{NCH_2CH_2}\mathit{C}\mathrm{H_2}$	15.0
			$\mathrm{Si}\mathit{Me}_2\mathrm{OSi}\mathit{Me}_3$	0.0	$\mathrm{Si}\mathit{Me}_2\mathrm{OSi}\mathit{Me}_3$	2.0, 1.0 −0.2
16	$\mathrm{NP(OPhMe)_2}$	−22.1	$\mathrm{O}\mathit{Ph}$	7.3−6.8 (4H)	$\mathrm{O}\mathit{Ph}$	151.1, 131.3, 129.0, 121.2
	NP(OPhMe)[N(Me)R]	−8.9	$\mathrm{OPh}\mathit{Me}$	2.2	$\mathrm{OPh}\mathit{Me}$	20.7
	$\mathrm{NP[N(Me)R]_2}$	2.0	$\mathrm{N}(\mathit{Me})$	2.5	$\mathrm{N}(\mathit{Me})$	33.8
			$\mathrm{NC}\mathit{H}_2$	2.9	$\mathrm{N}\mathit{C}\mathrm{H_2}$	52.7
			$\mathrm{NCH_2C}\mathit{H}_2$	1.6	$\mathrm{NCH_2}\mathit{C}\mathrm{H_2}$	21.4
			$\mathrm{NCH_2CH_2C}\mathit{H}_2$	1.1	$\mathrm{NCH_2CH_2}\mathit{C}\mathrm{H_2}$	14.9
			$\mathrm{Si}\mathit{Me}_2\mathrm{OSi}\mathit{Me}_2\mathrm{OSi}\mathit{Me}_3$	0.0 (21H)	$\mathrm{Si}\mathit{Me}_2\mathrm{OSi}\mathit{Me}_2\mathrm{OSi}\mathit{Me}_3$	1.8, 1.2, 0.1
17	$\mathrm{NP(MEE)_2}$[c]	−8.5	MEE	4.1−3.3	MEE	71.9, 70.7, 70.2, 63.2, 58.9
	NP(MEE)[N(Me)R]	−3.0	$\mathrm{N}(\mathit{Me})$	2.6 (3H)	$\mathrm{N}(\mathit{Me})$	33.8
			$\mathrm{NC}\mathit{H}_2$	3.0 (2H)	$\mathrm{N}\mathit{C}\mathrm{H_2}$	52.6
			$\mathrm{NCH_2C}\mathit{H}_2$	1.4 (2H)	$\mathrm{NCH_2}\mathit{C}\mathrm{H_2}$	21.8
			$\mathrm{NCH_2CH_2C}\mathit{H}_2$	0.4 (2H)	$\mathrm{NCH_2CH_2}\mathit{C}\mathrm{H_2}$	15.5
			$\mathrm{Si}\mathit{Me}_2\mathrm{OSi}\mathit{Me}_3$	0.1	$\mathrm{Si}\mathit{Me}_2\mathrm{OSi}\mathit{Me}_3$	2.0, 0.4
18	$\mathrm{NP(MEE)_2}$	−7.5	MEE	4.1−3.3	MEE	71.9, 70.5, 70.2, 64.9, 58.8
	NP(MEE)[N(Me)R]	−3.8	$\mathrm{N}(\mathit{Me})$	2.6	$\mathrm{N}(\mathit{Me})$	33.9
			$\mathrm{NC}\mathit{H}_2$	3.0	$\mathrm{N}\mathit{C}\mathrm{H_2}$	52.7
			$\mathrm{NCH_2C}\mathit{H}_2$	1.4	$\mathrm{NCH_2}\mathit{C}\mathrm{H_2}$	21.8
			$\mathrm{NCH_2CH_2C}\mathit{H}_2$	0.4	$\mathrm{NCH_2CH_2}\mathit{C}\mathrm{H_2}$	15.4
			$\mathrm{Si}\mathit{Me}_2\mathrm{OSi}\mathit{Me}_2\mathrm{OSi}\mathit{Me}_3$	0.1	$\mathrm{Si}\mathit{Me}_2\mathrm{OSi}\mathit{Me}_2\mathrm{OSi}\mathit{Me}_3$	1.8, 1.1, 0.3
19	$\mathrm{NP(MEE)_2}$	−7.6	MEE	4.1−3.3 (11H)	MEE	71.4, 70.3, 69.4, 65.0, 58.1
	NP(MEE)[N(Me)R]	−4.5	$\mathrm{N}(\mathit{Me})$	2.6	$\mathrm{N}(\mathit{Me})$	34.0
			$\mathrm{NC}\mathit{H}_2$	3.0	$\mathrm{N}\mathit{C}\mathrm{H_2}$	52.1
			$\mathrm{NCH_2C}\mathit{H}_2$	1.4	$\mathrm{NCH_2}\mathit{C}\mathrm{H_2}$	22.0
			$\mathrm{NCH_2CH_2C}\mathit{H}_2$	0.4	$\mathrm{NCH_2CH_2}\mathit{C}\mathrm{H_2}$	15.1
			$\mathrm{Si}\mathit{Me}_2\mathrm{OSi}\mathit{Me}_3$	0.1 (15H)	$\mathrm{Si}\mathit{Me}_2\mathrm{OSi}\mathit{Me}_3$	2.0, 1.0, 0.5
20	$\mathrm{NP(MEE)_2}$	−8.0	MEE	4.1−3.2	MEE	72.0, 70.6, 70.3, 65.0, 58.8
	NP(MEE)[N(Me)R]	−4.3	$\mathrm{N}(\mathit{Me})$	2.6 (3H)	$\mathrm{N}(\mathit{Me})$	32.4
			$\mathrm{NC}\mathit{H}_2$	2.9 (2H)	$\mathrm{N}\mathit{C}\mathrm{H_2}$	50.8
			$\mathrm{NCH_2C}\mathit{H}_2$	1.4 (2H)	$\mathrm{NCH_2}\mathit{C}\mathrm{H_2}$	20.5
			$\mathrm{NCH_2CH_2C}\mathit{H}_2$	0.4 (2H)	$\mathrm{NCH_2CH_2}\mathit{C}\mathrm{H_2}$	15.4
			$\mathrm{Si}\mathit{Me}_2\mathrm{OSi}\mathit{Me}_2\mathrm{OSi}\mathit{Me}_3$	0.0 (21H)	$\mathrm{Si}\mathit{Me}_2\mathrm{OSi}\mathit{Me}_2\mathrm{OSi}\mathit{Me}_3$	1.8, 1.3, 1.0, 0.3

[a] All NMR data were recorded for solutions in $\mathrm{CDCl_3}$. [b] TFE = $-\mathrm{OCH_2CF_3}$. [c] MEE = $-\mathrm{OCH_2CH_2OCH_2CH_2OCH_3}$.

Scheme 2



ary aminosiloxy side groups and another type of side group as a cosubstituent. In each case, the cosubstituent was introduced first. A typical polymer synthesis sequence is depicted in Scheme 2. Poly(dichlorophosphazene) (**7**) was allowed to react with a stoichiometric deficiency of sodium trifluoroethoxide. The resultant polymer (**8**) was then allowed to interact with an excess of [(*N*-methylamino)propyl]pentamethyldisiloxane in the presence of triethylamine as a hydrogen chloride acceptor, to give polymer **9**. Cosubstituent polymers with *p*-methylphenoxy and (methoxyethoxy)ethoxy side groups were obtained in a similar manner. The polymers were characterized by ^{31}P, ^{1}H, and ^{13}C NMR, DSC, GPC, and elemental analysis techniques. The results are shown in Tables 2−4. In addition, two polymers were examined by DMA methods.

Provided the cosubstituent groups used in this synthesis protocol were alkoxy units, this strategy resulted in the replacement of essentially all of the chlorine atoms along the polymer chain. For example, cosubstituent polymers with 50% (methoxyethoxy)ethoxy side groups (**20**) or 50% trifluoroethoxy units (**12**) had 0.36 and 0.078% remaining chlorine, respectively. For the latter, the electron-withdrawing nature of the trifluoroethoxy group also assists in halogen replacement by sensitizing the remaining P−Cl bonds to nucleophilic attack. The remaining chlorine atoms in these polymers were sufficiently shielded that the polymers were not sensitive to water.

However, the use of aryloxy cosubstituent groups made it more difficult to achieve 100% replacement of the chlorine atoms. For example, polymers **15** and **16**, which have a 50% loading of the bulky *p*-methylphenoxy substituents, contained approximately 3% of unreacted chlorine, which corresponds to 19% of the side units. Nevertheless, these chlorine atoms also were sterically shielded and the polymers were stable to moisture.

Glass Transition Temperatures. (a) General Observations. The glass transition temperatures (T_g's) were determined by differential scanning calorimetry and are listed in Table 4. The interpretation of these data is based on three concepts. First, the phosphazene backbone is a highly flexible platform for the side groups. Second, this molecular flexibility is retained if the side groups are flexible, but steric interference between bulky side groups will inhibit backbone torsion and will raise the T_g. Third, any dissimilarity between the sizes and shapes of the side groups will generate free volume that will facilitate polymer motion and lower the T_g. Conversely, similarities in side group

Table 3. GPC and Elemental Analyses for Polyphosphazenes 9−20

				elemental anal. (%)	
polymer	M_n	M_w		calc	found
9	7.3×10^5	1.1×10^6	C	29.73	30.78
			H	4.99	5.57
			N	6.94	6.66
			Cl	0.00	<0.5
10[a]	4.1×10^5	1.3×10^6	C	32.68	33.60
			H	6.28	6.13
			N	6.29	6.78
			Cl	0.00	0.87
11	1.6×10^5	4.9×10^5	C	36.42	34.96
			H	7.23	7.45
			N	7.73	6.67
			Cl	0.00	1.84
12	4.1×10^5	9.8×10^5	C	35.73	33.15
			H	7.39	6.81
			N	6.41	5.63
			Cl	0.00	0.078
13	5.2×10^5	1.5×10^6	C	53.90	51.69
			H	7.96	7.64
			N	7.27	5.89
			Cl	0.00	0.74
14	4.3×10^5	1.2×10^6	C	51.62	49.97
			H	7.84	7.55
			N	6.13	5.32
			Cl	0.00	0.53
15	6.4×10^5	1.1×10^6	C	51.83	48.92
			H	8.43	8.21
			N	7.56	7.28
			Cl	0.00	2.56
16	7.0×10^5	1.1×10^6	C	48.59	46.89
			H	8.39	7.92
			N	6.30	6.35
			Cl	0.00	2.94
17	5.7×10^4	1.0×10^5	C	43.26	43.93
			H	8.63	9.04
			N	6.31	6.27
			Cl	0.00	0.12
18	3.5×10^4	7.1×10^4	C	42.20	41.14
			H	8.58	8.75
			N	5.68	5.48
			Cl	0.00	<0.5
19	7.6×10^3	1.1×10^5	C	43.87	41.21
			H	9.21	8.73
			N	7.31	6.78
			Cl	0.00	0.36
20	7.1×10^3	1.1×10^5	C	42.05	39.71
			H	9.05	8.64
			N	6.13	5.15
			Cl	0.00	0.40

[a] Actual polymer composition: $[NP(OCH_2CF_3)_{1.3}\{N(Me)(CH_2)_3SiMe_2OSiMe_2OSiMe_3\}_{0.7}]_n$.

Table 4. Phosphazene Polymer Glass Transition Temperatures

compound	T_g (°C)
$[NP(OCH_2CF_3)_2]_n$ (**21**)	−63
$[NP(OCH_2CF_3)_{1.5}\{(CH_3)N(CH_2)_3SiMe_2OSiMe_3\}_{0.5}]_n$ (**9**)	−53
$[NP(OCH_2CF_3)_{1.5}\{(CH_3)N(CH_2)_3SiMe_2OSiMe_2OSiMe_3\}_{0.5}]_n$(**10**)	−71
$[NP(OCH_2CF_3)_{1.0}\{(CH_3)N(CH_2)_3SiMe_2OSiMe_3\}_{1.0}]_n$ (**11**)	−56
$[NP(OCH_2CF_3)_{1.0}\{(CH_3)N(CH_2)_3SiMe_2OSiMe_2OSiMe_3\}_{1.0}]_n$ (**12**)	−72
$[NP(OCH_2CF_3)_{1.5}(NH(CH_2)_3SiMe_2OSiMe_3)_{0.5}]_n$[a] (**22**)	−70
$[NP(OC_6H_4CH_3)_2]_n$ (**23**)	−4
$[NP(OC_6H_4CH_3)_{1.5}\{(CH_3)N(CH_2)_3SiMe_2OSiMe_3\}_{0.5}]_n$ (**13**)	−22
$[NP(OC_6H_4CH_3)_{1.5}\{(CH_3)N(CH_2)_3SiMe_2OSiMe_2OSiMe_3\}_{0.5}]_n$ (**14**)	−39
$[NP(OC_6H_4CH_3)_{1.0}\{(CH_3)N(CH_2)_3SiMe_2OSiMe_3\}_{1.0}]_n$ (**15**)	−35
$[NP(OC_6H_4CH_3)_{1.0}\{(CH_3)N(CH_2)_3SiMe_2OSiMe_2OSiMe_3\}_{1.0}]_n$ (**16**)	−49
$[NP(MEE)_2]_n$ (**24**)	−84
$[NP(MEE)_{1.5}\{(CH_3)N(CH_2)_3SiMe_2OSiMe_3\}_{0.5}]_n$ (**17**)	−82
$[NP(MEE)_{1.5}\{(CH_3)N(CH_2)_3SiMe_2OSiMe_2OSiMe_3\}_{0.5}]_n$ (**18**)	−80
$[NP(MEE)_{1.0}\{(CH_3)N(CH_2)_3SiMe_2OSiMe_3\}_{1.0}]_n$ (**19**)	−75
$[NP(MEE)_{1.0}\{(CH_3)N(CH_2)_3SiMe_2OSiMe_2OSiMe_3\}_{1.0}]_n$ (**20**)	−83
$[NP(MEE)_{1.5}(NH(CH_2)_3SiMe_2OSiMe_3)_{0.5}]_n$[a] (**25**)	−78

$MEE = -OCH_2CH_2OCH_2CH_2OCH_3$

[a] Taken from ref 24.

shapes and dimensions may allow side group stacking or efficient packing that will raise the T_g and perhaps lead to microcrystallinity.[28] The T_g's of the new polymers were well below room temperature and ranged from −83 to −22 °C. These values are indicative of a high degree of torsional mobility in the polymer backbone. The highest glass transition temperatures were obtained when the polymers contained *p*-methylphenoxy cosubstituents. This is attributed to the steric hindrance of the methylphenoxy groups which raises the energy barrier to torsional motions of the phosphazene backbone. The lowest T_g values were obtained with the highly flexible (methoxyethoxy)ethoxy cosubstituents.

(b) Trifluoroethoxy/[(Methylamino)propyl]siloxane Cosubstituent Polymers (9−12). The glass transition temperature of poly[bis(trifluoroethoxy)phosphazene] (**21**) is −63 °C. Incorporation of 25% of the pentamethyldisiloxane side group (polymer **9**) raised the T_g to −53 °C. Incorporation of 25% of the heptamethyltrisiloxane unit lowered the T_g to −71 °C. This decrease may reflect an increase in free volume generated by the longer side group. The glass transition temperature of polymer **11**, with 50% incorporation of $-N(Me)(CH_2)_3SiMe_2OSiMe_3$ side groups, was similar to that of polymer **9** (−56 °C). The T_g of polymer **12**, with 50% loading of the trisiloxane-containing side group was approximately the same as that of polymer **10**, −72 °C. It appears that, in this mixed-substituent system, increasing the organosiloxane side group loading from 25 to 50% does not greatly affect the T_g. However, at the same percent loading, the longer trisiloxane segments lowered the T_g by 16−18 degrees compared to the disiloxane segments. Polymer **22**, with primary (aminopropyl)disiloxane side groups, was synthesized previously in our program and has a T_g of −70 °C.[24] This glass transition temperature is similar to that of the longer secondary (aminopropyl)trisiloxane polymer at the same side group loading.

(c) *p*-Methylphenoxy/[(Methylamino)propyl]siloxane Cosubstituent Polymers (13−16). Polymer **23**, poly[bis(*p*-methylphenoxy)phosphazene], has a T_g of −4 °C. The incorporation of 25% of the pentamethyldisiloxane side group lowered the T_g to −22 °C (polymer **13**). The analogous loading of the longer heptamethyltrisiloxane side group resulted in a polymer with a T_g of −39 °C. This decrease in the T_g compared to the case of polymer **13** may again be explained by an increase in free volume generated by the incorporation of a second substituent. Polymers **15** and **16**, with 50% of the aminoorganosiloxane side groups, had T_g values of −35 and −49 °C, respectively. All the methylphenoxy/[(methylamino)propyl]siloxane cosubstituent polymers have glass transition temperatures that are lower than that of the single substituent polymer **23**. This may be due to the ability of the (aminopropyl)siloxane side groups to disrupt aryloxy group packing and this would lower the glass transition temperature. Alternatively, and more likely, it may reflect the influence of the unreacted chlorine atoms present in these polymers, a consequence of the severe steric hindrance to replacements of the last ∼20% of the halogen atoms during the synthesis process. As with the trifluoroethoxy cosubstituent polymers, the longer heptamethyltrisiloxane side groups generated lower T_g's than did the corresponding pentamethyldisiloxane-containing polymers. However, unlike the first system, increased incorporation of (aminopropyl)siloxane side groups caused further decreases in the glass transition temperature. Polymers **15** and **16** had T_g values that were 13 and 10 degrees lower, respectively, than their 25% loaded analogues. But in both cases the influence of the residual chlorine on the T_g complicates the interpretation.

(d) (Methoxyethoxy)ethoxy/[(Methylamino)propyl]siloxane Cosubstituent Polymers (17−20). Poly[bis[(methoxyethoxy)ethoxy]phosphazene] (**24**) has a T_g of −84 °C. A 25% incorporation of the pentamethyldisiloxane side group in polymer **17** does not significantly change the T_g, which is −82 °C. The analogous heptamethyltrisiloxane polymer, **18**, has a T_g of −80 °C. Thus, a 25% loading of the more sterically bulky siloxane cosubstituents does not appear to hinder the torsional mobility of the polymer backbone. Polymer **19**, with 50% loading of $N(Me)(CH_2)_3SiMe_2OSiMe_3$ side groups, has a T_g of −75 °C, whereas the analogous polymer with the heptamethyltrisiloxane side groups has a T_g of −83 °C. The 10 degree increase in glass transition temperature for **19** is surprising given the low T_g values for polymers **17**, **18**, and **20**. It is possible that for **20**, the increase in steric hindrance near the backbone at 50% incorporation of the aminosiloxane side group is offset by an increase in the free volume generated by the trisiloxane segment. Polymer **19**, with only a disiloxane unit, would have less free volume and an increased T_g. Polymer **25**, which contains primary amino side groups, has a T_g of −78 °C[24] and is closer in value to polymer **18**, with the longer, trisiloxane units.

(e) Conclusions Regarding T_g's. Overall, several trends in the glass transition temperatures may be seen. (1) For all three cosubstituent systems, the longer heptamethyltrisiloxane side group generates a lower T_g than does the shorter pentamethyldisiloxane side group at equivalent loadings. As mentioned above, this may be due to free volume effects. (2) There appears to be a tradeoff between the effects of steric bulk in the secondary amines and the increasing free volume caused by the length of the siloxane portion of the side group. For example, the trifluoroethoxy cosubstituent polymers **9** and **11**, with pentamethyldisiloxane segments, actually have T_g values that are higher than that of the single substituent polymer $[NP(OCH_2CF_3)_2]_n$. However, increases in the length of the siloxane units to the heptamethyltrisiloxane segment cause the T_g values to fall below that of polymer **21**. (3) The presence of siloxane side groups has an influence on the T_g that is highly dependent on the nature of the cosubstituent. For example, the replacement of fluoroalkoxy or aryloxy units in poly[bis(trifluoroethoxy)phosphazene] and poly[bis(*p*-methylphenoxy)phosphazene] by siloxane side groups can lower the T_g. For example, polymer **16** has a T_g that is 45 °C lower than the single substituent polymer **23**. The (aminopropyl)siloxane side groups assist in disrupting side group associations and may generate more free volume. However, in the case of **16**, the interpretation is complicated by the presence of ∼19% chloro side units and the unknown influence of these units on the T_g. In the case of a highly flexible side group, such as (methoxyethoxy)ethoxy units, the T_g is unchanged or increased. The (methoxyethoxy)ethoxy substituent has little effect on the torsional mobility of the phosphazene backbone, as evidenced by the low T_g (−84 °C) of $[NP(OCH_2CH_2OCH_2CH_2OCH_3)_2]_n$. A secondary amine linkage would introduce a greater amount of steric hindrance, which could restrict backbone motion and elevate the glass transition temperature.

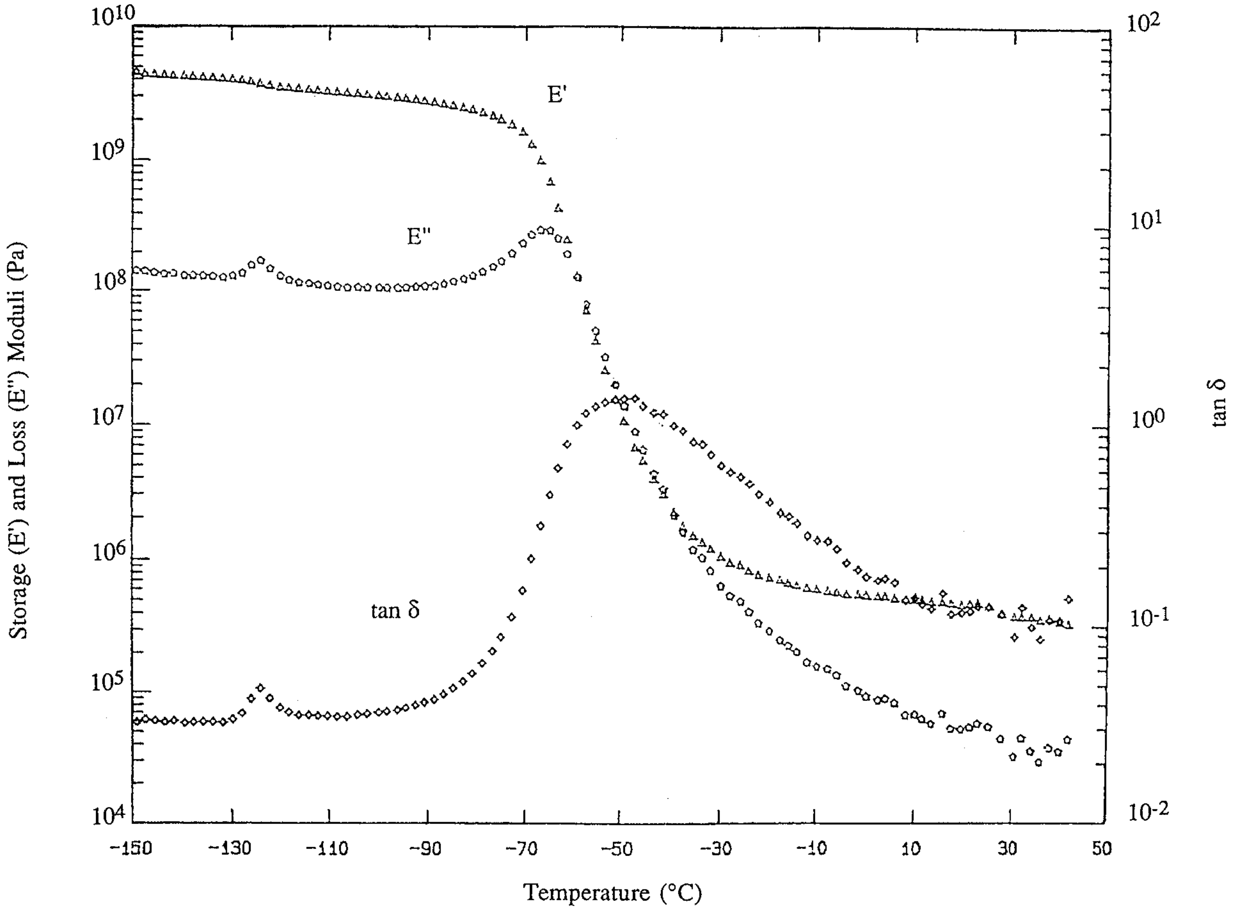


Figure 1. *E'*, *E"*, and tan *δ* versus temperature for polymer **10**.

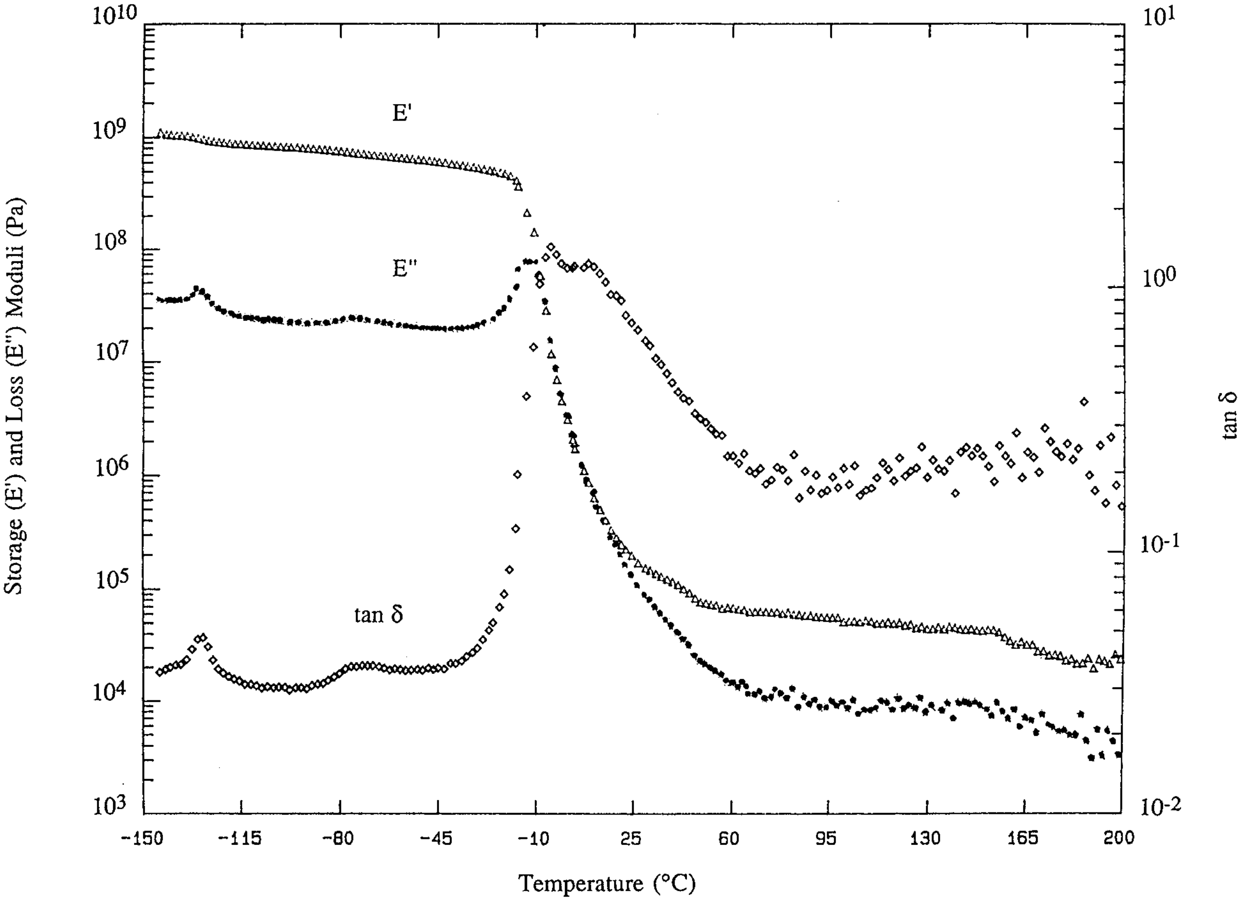


Figure 2. *E'*, *E"*, and tan *δ* versus temperature for polymer **13**.

Table 5. Reaction Conditions for Poly(aminoorganosiloxy)phosphazene Syntheses[a]

polymer	amt of $[NPCl_2]_n$ (mol)	amt of NaOR (mol)	solvent (reaction time) (days)	amt of HN(ME)R′ (mol)	Et_3N (mol)	reacn time (days)	
						THF	toluene
9	0.0172	0.0259	THF (2)	**3** (0.0182)	0.144	5	2
10	0.0086	0.0129	THF (2)	**4** (0.0086)	0.086	2	
11	0.0086	0.0086	THF (1)	**3** (0.0173)	0.072	2	4
12	0.0129	0.0155	THF (3)	**4** (0.0259)	0.259	5	6
13	0.0086	0.0129	dioxane (2)	**3** (0.0086)	0.034	4	
14	0.0086	0.0129	dioxane (2)	**4** (0.0086)	0.034	4	
15	0.0179	0.0190	dioxane (2)	**3** (0.0350)	0.172	5	
16	0.0172	0.0190	dioxane (2)	**4** (0.0320)	0.172	6	
17	0.0259	0.0407	THF (1)	**3** (0.0258)	0.103	2	4
18	0.0099	0.0149	THF (1)	**4** (0.0099)	0.717	3	4
19	0.0086	0.0095	THF (2)	**3** (0.0170)	0.170	5	4
20	0.0086	0.0095	THF (2)	**4** (0.0160)	0.170	5	4

[a] R = CH_2CF_3, p-$C_6H_4CH_3$, or $CH_2CH_2OCH_2CH_2OCH_3$. R′ = $SiMe_2OSiMe_3$ or $SiMe_2OSiMe_2OSiMe_3$.

Dynamic Mechanical Analysis. Polymers are viscoelastic materials. Elastic materials have the capacity to store mechanical energy, while viscous liquids have a capacity to dissipate energy. Thus, when a polymer is deformed, part of the energy is stored as potential energy and part is dissipated as heat. At the molecular level this is due to the many types of responses of a coiled polymer chain to applied stress. These responses include widening of bond angles, chain conformational rearrangement, uncoiling, and movement of molecules in relation to each other.

The properties of polymers **10** and **13** were investigated by dynamic mechanical analysis (DMA). The analyses were performed at a frequency of 10 Hz over a temperature range of −150 to +50 or +200 °C. The results are shown in Figures 1 and 2, where E' (storage modulus), E'' (loss modulus), and tan δ (loss tangent) are plotted against temperature. As shown in Figure 1, the storage modulus for polymer **10** remains nearly constant at temperatures from −150 to approximately −75 °C. There is a rapid decrease in the storage modulus and a peak in the loss modulus centered at −67 °C which corresponds to the glass transition temperature. Polymer **13** showed similar behavior, with the maximum in the loss modulus occurring at −10 °C (Figure 2). A secondary transition occurred at −124 and −129 °C for polymers **10** and **13**, respectively, that was not detected by DSC experiments. These transitions may be due to the local motions of the siloxane side groups since this is the temperature range associated with the T_g of poly(dimethylsiloxane) homopolymer or block copolymers. Although these transitions were not detected by DSC in the current study or for other polyphosphazenes that bear short linear siloxane substituents,[23,24] transitions in this temperature range have been detected by DSC for polyphosphazenes that bear branched siloxane side groups or long siloxane grafts.[22a,24]

Conclusions

A number of methylsiloxane-containing polyphosphazenes have been synthesized. The glass transition temperatures of these secondary aminosiloxane polymers are between −83 and −22 °C. No evidence was found for the rigidity or brittleness that was reported in the case of similar polyphosphazenes that bear primary aminosiloxane side groups,[24] and this is attributed to the absence of hydrogen bonding between side groups in the new materials. Polymers **9**−**20** are soft, flexible materials, which may be appropriate for low-temperature elastomer applications or for membranes. Thus, the presence or absence of hydrogen bonding near the polymer backbone has a profound influence on the polymer properties.

Experimental Section

Materials. Hexachlorocyclotriphosphazene (Ethyl Corp./Nippon Fine Chemical) was purified by recrystallization from heptane and by vacuum sublimation at 50 °C (0.05 mmHg). Poly(dichlorophosphazene) was prepared as described previously.[26] Sodium hydride (60% dispersion in mineral oil, Aldrich) and sodium (Aldrich) were used as received. Toluene, dioxane (anhydrous, Aldrich), and tetrahydrofuran (Omnisolv) were dried over sodium benzophenone ketyl and were distilled under a nitrogen atmosphere. N-Methylallylamine (Aldrich) was distilled and stored over 4 Å molecular sieves before use. 2-(2-Methoxyethoxy)ethanol (Aldrich) was purified by vacuum distillation and was stored over 4 Å molecular sieves. 2,2,2-Trifluoroethanol (Halocarbon) was dried and distilled from anhydrous calcium sulfate and stored over 4 Å molecular sieves. p-Methylphenol (Aldrich) was purified by vacuum sublimation. Triethylamine (Baker) was dried and distilled from calcium hydride into the reaction flask. Trimethylsilyl chloride (Aldrich) was purified by distillation and stored over 4 Å molecular sieves. Ethanol (Aaper Alcohol and Chemical Co., absolute) was used as received. Pentamethyldisiloxane (Petrarch) and 1,1,3,3,5,5,5-heptamethyltrisiloxane (Petrarch) were stored over 4 Å molecular sieves before use. Divinyltetramethyldisiloxane platinum complex [DVDS:Pt] (Huls America) was used as received. All glassware was dried overnight in an oven or flame dried under vacuum before use. All reactions were performed using standard Schlenk techniques utilizing an atmosphere of dry argon.

Equipment. ^{31}P NMR spectra were obtained with the use of a Bruker WM-360 spectrometer operated at 146 MHz. The chemical shifts are relative to 85% H_3PO_4 at 0 ppm with positive shift values downfield from the reference. The ^1H and ^{13}C NMR chemical shifts were recorded with a Bruker WM-360 NMR spectrometer operated at 360 and 90.27 MHz, respectively. ^1H and ^{13}C NMR are referenced to internal $CDCl_3$. Elemental analyses were obtained by Galbraith Laboratories, Knoxville, TN. Polymer molecular weights were estimated using a Hewlett-Packard HP1090 gel permeation chromatograph equipped with an HP-1037A refractive index detector and a polymer Laboratories PL gel 10 μm column. The samples were eluted with a 0.1% by weight solution of tetra-n-butylammonium bromide in THF. The GPC column was calibrated with polystyrene standards (Waters) and with fractionated samples of poly[bis(trifluoroethoxy)phosphazene] provided by Drs. R. Singler and B. Hagnauer of the U.S. Army Materials Technology Laboratories, Watertown, MA. Glass transition temperatures were obtained by differential scanning calorimetry with the use of a Perkin-Elmer DSC-7 unit controlled by a PE7500 computer. Heating rates of 10−25 °C/min and a sample size of 15−35 mg were used. Dynamic mechanical analyses were performed using a Rheometric solid analyzer (RSA-II). The temperature was increased at a rate of 2 °C/min, and the storage and loss moduli were measured at a frequency of 10 Hz.

Synthesis of Side Group Reagents. Synthesis of $(CH_3)_3SiN(Me)CH_2CH{=}CH_2$. Triethylamine (39.96 g, 0.208 mol) and trimethylsilyl chloride (30.8 g, 0.28 mol) in THF (250 mL) were placed in a 500 mL three-neck flask equipped with a condenser, a large stir bar, and an air inlet. The *N*-methylallylamine (10.0 g, 0.139 mol) was added slowly from an addition funnel. The reaction mixture was heated at reflux for 48 h. The mixture was then filtered through an airless frit, and the collected $Et_3N{:}HCl$ was washed with THF (150 mL). The filtrate was concentrated under vacuum. The resultant liquid was distilled under argon to give the desired product as a clear, colorless liquid (bp = 115 −120 °C, 60% yield). CI-MS: calc MI = 143, found M^+ = 143.2. ^{1}H NMR ($CDCl_3$): (*Me*)$_3$Si 0.1 ppm; (*Me*)N 2.4 ppm; NC*H*$_2$ 3.3 ppm; C*H*=CH$_2$ 5.7 ppm; CH=C*H*$_2$ 5.1 ppm. ^{13}C NMR ($CDCl_3$): (*Me*)$_3$Si −0.9 ppm; (*Me*)N 34.1 ppm; N*C*H$_2$ 53.1 ppm; *C*H=CH$_2$ 137.7 ppm; CH=*C*H$_2$ 114.8 ppm. EA [found (calc)]: C, 57.73 (58.62); H, 11.81 (11.96); N, 9.08 (9.77).

Synthesis of $HN(Me)(CH_2)_2SiMe_2OSiMe_3$ (3). The [3-(*N*-methylamino)propyl]heptamethyltrisiloxane was prepared by the hydrosilylation reaction between *N*-methyltrimethylallylamine and pentamethyldisiloxane in the presence of a platinum catalyst.[24,29] $(CH_3)_3SiN(Me)CH_2CH{=}CH_2$ (4.0 g, 27.9 mmol), two drops of DVDS:Pt, and THF (50 mL) were placed in a 100 mL three-necked flask equipped with a condenser and addition flask. The pentamethyldisiloxane (4.9 g, 25.1 mmol) in THF (15 mL) was added slowly from the addition funnel. The reaction mixture was heated to reflux for 48 h. Absolute ethanol (15 mL) was added and the solution was heated for 12 h. The solution was concentrated by rotary evaporation and the product was distilled under vacuum (bp = 33−35 °C at 10 μmHg, 70% yield). CI-MS: calc MI = 219, found MH^+ = 220. EA [found (calc)]: C, 48.97 (49.25); H, 11.54 (11.48); N, 6.09 (6.38).

Synthesis of $HN(Me)(CH_2)_3SiMe_2OSiMe_2OSiMe_3$ (4). Compound **4** was prepared in a manner similar to that for **3**.[24,29] $(CH_3)_3SiN(Me)CH_2CH{=}CH_2$ (12.0 g, 0.083 mol), 6 drops of DVDS:Pt, and THF (50 mL) were placed in a 100 mL three-necked flask equipped with a condenser and addition funnel. 1,1,3,3,5,5,5-Heptamethyltrisiloxane (19.6 g, 0.088 mol) in THF (15 mL) was added slowly from the addition funnel. The reaction was heated to reflux for 48 h. Absolute ethanol (15 mL) was added, and the solution was heated for 8 h. The solution was concentrated by rotary evaporator, and the product was distilled under vacuum (bp = 40−50 °C at 20 μmHg, yield = 80%). CI-MS: calc MI = 293, found MH^+ = 294. EA [found (calc)]: C, 44.90 (45.00); H, 10.65 (10.64); N, 4.38 (4.77).

Synthesis of Cyclic Trimers. Synthesis of $N_3P_3(OPh)_5Cl$ (5). The synthesis of compound **5** followed the literature procedure.[21,24]

Synthesis of $N_3P_3(OPh)_5[N(Me)(CH_2)_3SiMe_2OSiMe_2OSiMe_3]$ (6). $N_3P_3(OPh)_5Cl$ (1.0 g, 0.0016 mol) and triethylamine (0.726 g, 0.0072 mol) were placed in a three-necked flask with toluene (50 mL). Compound **4** (0.51 g, 0.0017 mol) was injected by syringe, and the reaction mixture was heated to reflux for 5 days. The reaction mixture was filtered, and the solvent was removed by rotary evaporation to yield an oil.

The oil was purified by column chromatography using hexane/diethyl ether (3/1) as the eluent and silica gel as the stationary phase. Yield, >80%. FAB-MS: calc MI = 892, found MH^+ = 893.

General Preparation of High Molecular Weight Polymers. The following general synthetic procedure was used for the preparation of polymers **10**−**21**. The details for each polymer reaction are listed in Table 5. A stoichiometric deficiency of NaOR (R = CH_2CF_3, $CH_2CH_2OCH_2CH_2OCH_3$, or *p*-$PhCH_3$) in THF was added slowly to a solution of $[NPCl_2]_n$ in THF. The reaction mixture was heated at 67 °C for 8−12 h and was then allowed to cool to room temperature. An excess of freshly distilled triethylamine was added to the reaction mixture and the (aminopropyl)siloxane was added by syringe to the flask. The reaction mixture was heated to reflux for 3−4 days. The THF was removed under vacuum and an equivalent amount of toluene and additional triethylamine were added to the reaction flask. The reaction mixture was heated to reflux for 3 more days. The polymers were purified by dialysis against H_2O (3 days), EtOH (3 days), and THF (3 days). After dialysis, the polymer solutions were filtered and the solvent was removed by rotary evaporation. Typical yields were in the range of 65% or higher.

Acknowledgment. We thank the U.S. Army Research Office and Eastman Kodak Co. for support of this work and Drs. John J. Fitzgerald and Wayne T. Ferrar for the DMA analyses.

References and Notes

(1) Allcock, H. R. *Adv. Mater.* **1994**, *6*, 106.
(2) Noll, W. *The Chemistry and Technology of Silicones*; Academic Press: New York, 1968.
(3) Voronkov, M. *The Siloxane Bond*; Plenum Press: New York, 1975.
(4) Mark, E. J.; Allcock, H. R.; West, R. *Inorganic Polymers*; Prentice-Hall, Inc.: Englewood Cliffs, NJ, 1992.
(5) Charrier, J. M. *Polymeric Materials and Processing: Plastics, Elastomers, and Composites*; Oxford University Press: New York, 1990.
(6) Zhivukhin, S. M.; Tolstoguzov, V. B.; Ivanov, A. I. *Russ. J. Inorg. Chem.* **1962**, *7* (9), 1134 (Engl. Transl.).
(7) Kireev, V. V.; Kolesnikov, G. S.; Raigorodskii, I. M. *Russ. Chem. Rev.* **1969**, *38* (8), 667 (Engl. Transl.).
(8) Beloglazova, T. N.; Kireyev, V. V.; Kolesnikov, H. S.; Raigorodskii, I. M. *Polym. Sci. USSR* **1971**, *A13* (7), 1828 (Engl. Transl.).
(9) Volkova, L. M.; Pisarenko, V. V.; Voichenko, N. M.; Andrianov, K. A.; Kabachnik, M. I. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1972**, *3*, 470 (Engl. Transl.).
(10) Kireev, V. V.; Kovyazin, V. A.; Kopylov, V. M.; Zaitseva, M. G.; Mitropul'skaya, G. I. *J. Gen. Chem. USSR* **1984**, *54* (8), 1692 (Engl. Transl.).
(11) Allcock, H. R.; Brennan, D. J.; Allen, R. W. *Macromolecules* **1985**, *18*, 139.
(12) Allcock, H. R.; Brennan, D. J.; Graaskamp, J. M.; Parvez, M. *Organometallics* **1986**, *5*, 2434.
(13) van de Grampel, J. C.; Jekel, A. P.; Puyenbroek, R.; Arling, T. J.; Paber, M. C.; Fransen, W.; Meetsma, A.; Wubbels, J. H. *Phosphorus, Sulfur Silicon* **1993**, *76*, 215.
(14) Ovchinnikov, Yu. E.; Shklover, V. E.; Struchkov, Yu. T.; Remizova, A. A.; Kopylov, V. M.; Konyazin, V. A.; Kireyev, V. V. *Z. Anorg. Allg. Chem.* **1985**, *523*, 14.
(15) Coggio, W. D. Doctoral Thesis, The Pennsylvania State University, 1991.
(16) Allcock, H. R.; Kuharcik, S. E. *J. Inorg. Organomet. Polym.* **1995**, *5* (4), 307−342.
(17) van de Grampel, J. C.; van de Grampel, R. D.; Hendriks, R. H. J.; Jekel, A. P.; Meetsma, A.; Veldman, E. G. M.; Uwbbels, J. H. *Phosphorus, Sulfur Silicon* **1994**, *93*−94, 273.
(18) Visscher, K. B. Doctoral Thesis, The Pennsylvania State University, 1992.
(19) Allcock, H. R.; Brennan, D. J.; Graaskamp, J. M. *Macromolecules* **1988**, *21*, 1.
(20) Puyenbroek, R.; Jekel, A. P.; van de Grampel, J. C. *J. Inorg. Organomet. Polym.* **1991**, *1*, 105.
(21) Allcock, H. R.; Coggio, W. D.; Archibald, R. S.; Brennan, D. J. *Macromolecules* **1989**, *22*, 3571.
(22) (a) Wisian-Neilson, P.; Islam, M. S. *Macromolecules* **1989**, *22*, 2026. (b) Wisian-Neilson, P.; Islam, M. S.; Schaefer, M. A. *Phosphorus, Sulfur Silicon* **1989**, *41*, 135. (c) Wisian-Neilson, P.; Schaefer, M. A.; Islam M. S. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1989**, *30*, 185.
(23) Allcock, H. R.; Smith, D. E.; Kim, Y. B.; Fitzgerald, J. J. *Macromolecules* **1994**, *27*, 5206.
(24) Allcock, H. R.; Coggio, W. D. *Macromolecules* **1990**, *23*, 1626.
(25) Allcock, H. R. *Phosphorus-Nitrogen Compounds*; Academic Press: New York, 1972.
(26) Allcock, H. R.; Kugel, R. L. *Inorg. Chem.* **1966**, *5*, 1716.
(27) Allcock, H. R.; Cook, W. J.; Mack, D. P. *Inorg. Chem.* **1972**, *11*, 2584.
(28) Allcock, H. R.; Lampe, F. W. *Contemporary Polymer Chemistry*, 2nd ed.; Prentice-Hall: Englewood Cliffs, NJ, 1990.
(29) Bachrach, A.; Zilkha, A. *Eur. Polym. J.* **1984**, *20*, 493.

MA951618+