Poly(organophosphazenes) Containing Allyl Side Groups: Cross-Linking and Modification by Hydrosilylation

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ABSTRACT: Poly(organophosphazenes) containing 4-(allyloxy)phenoxy and 4-[4′-(allyloxy)phenyl]phenoxy side groups were synthesized and modified by hydrosilylation reactions. A small-molecule model compound, pentaphenoxy[4-(allyloxy)phenoxy]cyclotriphosphazene, underwent platinum-catalyzed hydrosilylation reactions with heptamethyltrisiloxane and dimethylethoxysilane. The product of the second reaction, containing one dimethylethoxysilane group, underwent hydrolysis and self-condensation reactions in the presence of acid. Transposition of this chemistry to the high-polymer level was then accomplished. Thus, hydrosilylation of phosphazene high polymers with allylaryloxy side groups yielded poly(organophosphazenes) with dimethylsiloxane side group graft units. High siloxane loadings were obtained without evidence of Si–O or Si–C bond cleavage. A series of polymers with 4–100% grafting of dimethylsiloxane segments (corresponding to 6.5–56.2% dimethylsiloxane by weight) were synthesized and characterized by DSC, TGA, and GPC. Two polymers were further characterized by DMA. Glass transition temperatures of the siloxane-containing polymers ranged from −79 to +20 °C, according to the amount of siloxane grafting and the nature of the other groups attached directly to the phosphazene polymer backbone. The siloxane-containing polymers also showed a relaxation at approximately −120 °C. This combined with SAXS data suggested that the dimethylsiloxane side group may exist in microphase-separated domains. Cross-linking of polymers that contained unsaturated groups was achieved by ultraviolet irradiation and γ-irradiation. Poly(organophosphazenes) bearing 20 and 46 mol % dimethylethoxysilane groups cross-linked readily on exposure to atmospheric moisture.

Introduction

Poly(organophosphazenes) possess a wide spectrum of properties according to the nature of the side groups attached to the phosphorus–nitrogen backbone.[1] A common method for the preparation of poly(organophosphazenes) is by means of nucleophilic substitution reactions carried out on a poly(halophosphazene) macromolecular intermediate, itself synthesized by ring-opening polymerization of a halophosphazene cyclic trimer.[2–4] Treatment of the macromolecular intermediate with organic nucleophiles, such as amines or sodium salts of alcohols or phenols, results in halogen replacement by organic units. Polyphosphazenes prepared in this manner have organic substituents bound to phosphorus through oxygen or nitrogen links. This synthetic procedure is valuable in the sense that a wide variety of substituents and mixed substituents may be attached to the polymer backbone. However, this reaction has some limitations. For example, bulky side groups can retard the replacement of neighboring chlorine atoms.[5] Difunctional reagents, such as those which would yield side groups with pendent alcohol, aldehyde, or carboxylic acid functionalities, cannot normally be attached to the polymer by this method because of premature cross-linking.

Considerable interest exists in the preparation and examination of polymers which contain both organophosphazene and organosiloxane units.[6–18] The incorporation of siloxane units into a polyphosphazene could lower the surface energy, lower the glass transition temperature, and increase the gas permeability, properties that are of considerable technological importance.[19–21] Three synthetic routes to hybrid phosphazene–siloxane polymers have been explored in the past. In the first reaction route, organosilane or organosiloxane groups were linked to small-molecule cyclophosphazenes which were then subjected to ring-opening polymerization.[7,8,11] Only limited silane or siloxane loadings in the polymer could be obtained because of the polymerization-inhibiting effect of more than two organosiloxane substituents on the cyclotriphosphazene ring. Polymers prepared by this route were then treated with nucleophiles to replace the remaining chlorine atoms. Under some reaction conditions, C–Si bond cleavage resulted in a loss of the organosilicon component.[11] In the second reaction route, amines that contain siloxane groups were allowed to react with poly(dichlorophosphazene).[12] Aminosiloxanes replaced chlorine atoms to an extent that depended on their size and degree of branching. For example, complete replacement was achieved using the nucleophile $H_2N(CH_2)_3SiMe_2OSiMe_3$, but only 80–90% of the chlorine atoms were replaced by $H_2N(CH_2)_3Si(OSiMe_3)_3$. The resultant polymers are elastomers when the organosiloxane side groups comprised up to 25% of the side groups present and rigid amorphous materials at high aminosiloxane contents. The lack of flexibility of some of the polymers was believed to be the result of hydrogen bonding. A third reaction route allowed organosilane units to be attached to preformed poly(organophosphazenes) by substitution reactions. For example, phosphazene polymers that contained *p*-bromophenoxy groups were subjected to partial lithiation and then coupled to chlorosilanes to generate polymers containing silane and siloxane grafts.[15] Up to 80% of the bromine atoms were replaced by lithium. The total organosilicon substitution varied from 35 to 75%. Wisian-Neilson and co-workers[16,17] prepared graft copolymers by generating anionic sites on poly(alkyl/arylphosphazenes) and treating these with hexamethyltrisiloxane or tri-

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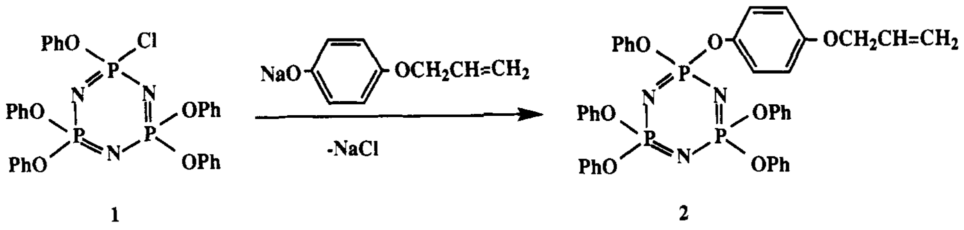
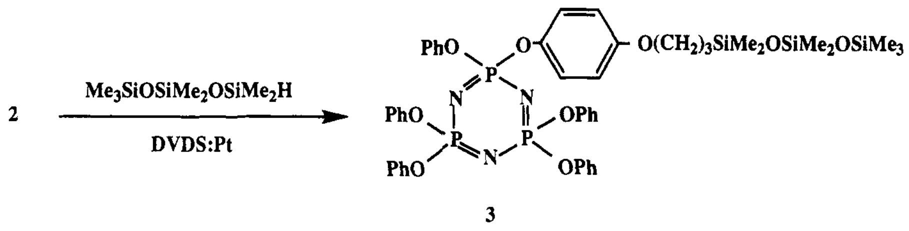
Scheme 1

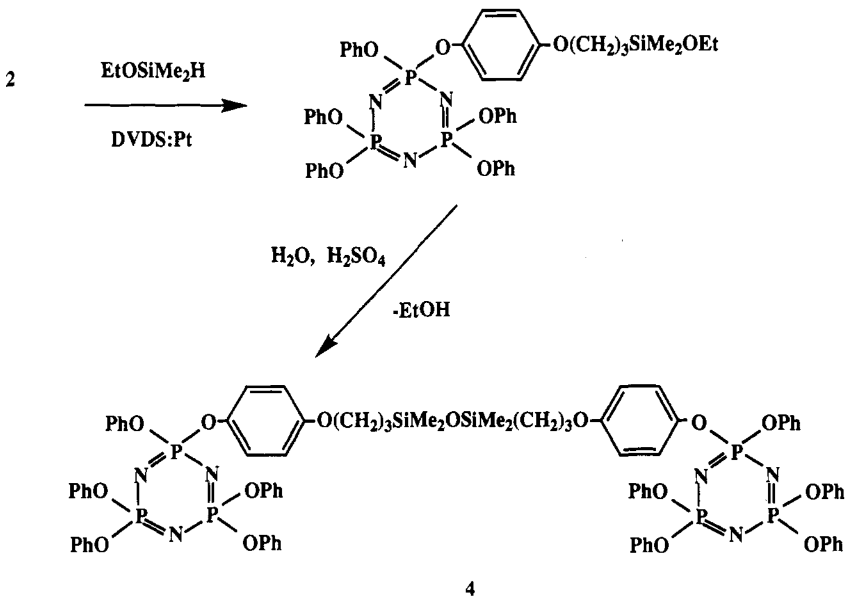


Scheme 2



(DVDS:Pt = tetramethyl-1,3-divinyldisiloxane platinum complex)

Scheme 3



DVDS:Pt = tetramethyl-1,3-divinyl disiloxane platinum complex

methylchlorosilane. In an alternative approach, van de Grampel and co-workers[18] obtained polysiloxanes that bore cyclophosphazene side units by hydrosilylation reactions between allyl-functional cyclophosphazenes and poly(methylhydrosiloxanes). Complex reaction routes have been used by Gleria and co-workers[22-25] to obtain polyphosphazenes with grafted side chains. Polyphosphazenes were first functionalized and then modified. For example, the exposure of poly[bis(4-isopropylphenoxy)phosphazene] to UV radiation resulted in the formation of hydroperoxides,[23,24] which decomposed to form radicals, followed by grafting of styrene to the polymer.[25]

In this paper the focus is on poly(organophosphazenes) that contain side group unsaturation and which may be used as precursors in the preparation of polymers with otherwise inaccessible structures. We discuss the preparation of polyphosphazenes that contain allyl side groups and the use of hydrosilylation reactions to prepare siloxane side unit polymers.

Results and Discussion

Small-Molecule Model Studies. Model reactions using small-molecule cyclic phosphazenes were carried out initially. The initial reaction protocol was for the preparation of allyl derivatives of cyclophosphazenes similar to those used by van de Grampel and co-workers.[18] In this work the approach was to graft short siloxane segments to allyl-functional cyclic phosphazenes, initially at the small-molecule level as a prelude to the preparation of high molecular weight polymers. Pentaphenoxy[4-(allyloxy)phenoxy]cyclotriphosphazene (2; prepared according to Scheme 1) was dissolved in chloroform and was allowed to react with heptamethyltrisiloxane and dimethylethoxysilane at room temperature in the presence of a platinum catalyst. The reactions were complete within 20 h, as determined by ^1H NMR spectroscopy. The reaction of 2 with heptamethyltrisiloxane yielded product 3 only (Scheme 2). The reaction product of 2 with dimethylethoxysilane was heated to reflux in aqueous

Scheme 4

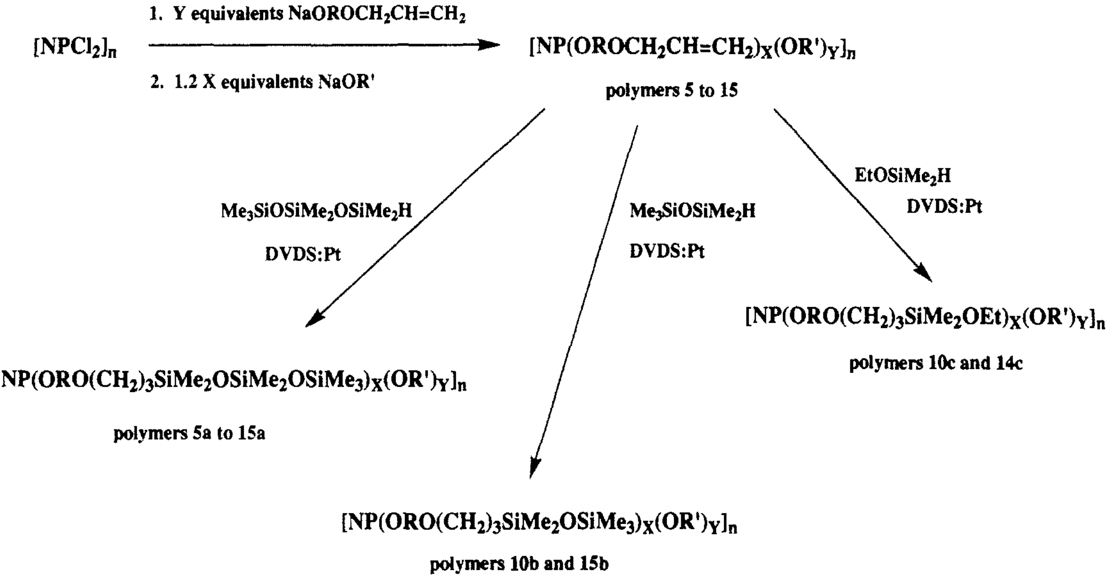


Table 1. Poly(organophosphazenes) Bearing Unsaturated Side Groups

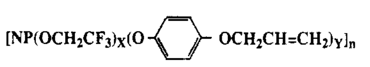
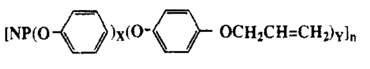
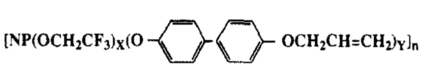
	Polymer	X	Y
	5	1.92	0.08
	6	1.85	0.15
	7	1.46	0.54
	8	1.30	0.70
	9	0.00	2.00
	10	1.60	0.40
	11	1.92	0.08
	12	1.81	0.19
	13	1.75	0.25
	14	1.08	0.92
	15	0.76	1.24

Table 2. Glass Transition Temperatures of Polyphosphazenes 5–15[a]

	mol % substituent groups (approx)				
polymer	A	B	C	D	T_g (°C)[b]
$[NP(OCH_2CF_3)_2]_n$	100				−63
5	96		4		−63
6	92		8		−61
7	73		27		−44
8[c]	65		35		
9			100		−9
$[NP(OC_6H_5)_2]_n$		100			−8
10		80	20		−10
11	96			4	−60
12	90			10	−58
13	87			13	−31
14[c]	54			46	
15[c]	38			62	

[a] A = trifluoroethoxy, B = phenoxy, C = 4-(allyloxy)phenoxy, and D = 4-[4′-(allyloxy)phenyl]phenoxy. [b] Glass transition temperatures measured by DSC at a heating rate of 20 °C/min. [c] Polymers 8, 14, and 15 did not show glass transitions by DSC analysis.

ethanol for 48 h in an attempt to hydrolyze the ethoxysilane group. No reaction was detected by TLC, but the addition of a trace amount of sulfuric acid induced a coupling reaction (Scheme 3) to form compound 4 in significant quantities. These model studies suggested that hydrosilylation reactions might be carried out on allyl-bearing high-polymeric organophosphazenes and that the dimethylethoxysilane group might be used as a hydrolytically sensitive cross-linking site.

Synthesis of High Polymers with Unsaturated Functionalities. The preparation of allyl-containing poly(organophosphazenes) via the reaction of sodium allylaryloxides with poly(dichlorophosphazenes) (Scheme 4) required the careful exclusion of oxygen and moisture and protection from light. Nucleophilic substitutions were carried out at 25 °C where possible to avoid thermal cross-linking through the allyl side groups. Where further reactions were to be performed, purifications were carried out without extensive drying of the unsaturated polymers, and the purified polymers were stored in solution under dry argon.

Physical Properties of Polymers with Allyl Side Units. The physical properties of the polymers depended on the side group ratios. Polymer compositions are listed in Table 1. While poly[bis(trifluoroethoxy)phosphazene] and poly(diphenoxyphosphazene) are both fibrous, microcrystalline (semicrystalline) polymers, polymers **5–8** and **10–15** with two types of side group were flexible and noncrystalline. Table 2 shows the glass transition temperatures of the allyl-containing polymers.

The effect of side groups on the glass transition temperatures of poly(organophosphazenes) has been studied.[19] The lowest T_g values (−60 to −100 °C) are for alkoxy and fluoroalkoxy derivatives in which low intermolecular interactions are combined with the flexibility of specific side groups. Increases in the length of fluoroalkoxy side groups, for example, tend to raise the T_g. Polymers with trifluoroethoxy, pentafluoropropoxy, and heptafluorobutoxy substituents have glass transitions at −66, −25, and 14 °C, respectively. Random copolymers in general have glass transitions at temperatures intermediate between those of the parent polymers.[19] Cosubstituent organophosphazene polymers which contain more than one type of side group can have lower glass transition temperatures than either of the single-substituent polymers, due to a loss of symmetry and packing efficiency and hence a greater free volume being available for chain movement.[19] A reduced level of crystallinity in the cosubstituent polymers is also found.[1]

In polymers **5–9** the glass transition temperatures increased within the range −63 to −9 °C with increasing incorporation of 4-(allyloxy)phenoxy side groups. The mixed-substituent polymer T_g's were intermediate between those of the two single-substituent polymers. All were soft and extensible at room temperature.

The glass transition temperatures of polymers **9** and **10** did not differ significantly from that of poly(diphenoxy-

Table 3. Effect of Cross-Linking on the Glass Transition Temperature of 10

treatment	T_g (°C)[a]	swelling ratio	gel fraction
un-cross-linked polymer	−10	N/A	N/A
0.2 Mrad γ-radiation[b]		20.8	0.75
0.5 Mrad γ-radiation[b]	−10	13.4	0.80
1.0 Mrad γ-radiation[b]	−9	8.5	0.83
2.0 Mrad γ-radiation[b]		6.5	0.85
5.0 Mrad γ-radiation[b]	−8	4.1	0.89
10.0 Mrad γ-radiation[b]		0.7	0.98
UV irradiation[c]	−8	6.9	0.71
UV irradiation, photoinitiator	−4	3.6	0.94

[a] Differential scanning calorimetry at a heating rate of 20 °C/min. [b] Cobalt-60 source, 160 krad/h. [c] 220–400 nm, 30 min exposure.

phosphazene) (−8 °C). In all three polymers, the influence of the rigid, bulky aromatic group predominates, and it limits free movement of the flexible P–N backbone. The allyloxy segments apparently do not exert a strong influence on chain motion. The 4-[4′-(allyloxy)phenyl]phenoxy group is bulkier and more rigid. Thus, the presence of this side group has a more significant effect on the properties of polymers **11–15**. Table 2 shows a higher T_g value for polymer **13** compared to the phenoxy analogues. Glass transitions were not detected by DSC for **14** or **15**. The difference in material properties was very pronounced. Polymer **13** was a tough, flexible polymer while **14** and **15** were hard, brittle materials at room temperature. The phenoxy analogues **5–9** were all soft and extensible.

Cross-Linking of Polymers with Unsaturated Units in the Side Chain. Poly(organophosphazene) elastomers with a small proportion of unsaturated side groups are produced commercially.[26] These polymers may be cross-linked by reaction of the unsaturated groups with peroxides. Commercial poly(fluoroalkoxyphosphazene) elastomers contain small amountsof $CH_2{=}CHCH_2O$ substituents[26] which allow cross-linking with peroxides such as α,α'-bis(*tert*-butylperoxy)diisopropylbenzene or dicumyl peroxide. These compounds can be processed using conventional elastomer processing equipment and have applications as low-temperature elastomers.

Poly(organophosphazenes) **7**, **10**, and **13** with 20–27 mol % 4-(allyloxy)phenoxy or 4-[4′-(allyloxy)phenyl]phenoxy side groups underwent cross-linking reactions at elevated temperatures (100–200 °C) or at ambient temperature when exposed to UV radiation or γ-radiation. Cross-linking did not affect the glass transition temperature of polymer **10** appreciably, except in the case of UV irradiation in the presence of photoinitiator. In this case the T_g was raised by 6 °C. Table 3 shows the effect of cross-linking on the glass transition temperature. The cross-linked polymers were insoluble but swellable in specific solvents such as THF and acetone. Swelling measurements were used to compare the degree of cross-linking of each polymer under different irradiation conditions. The thermally induced cross-linking reaction was not studied in detail.

Each of the polymers **7**, **10**, and **13** cross-linked photolytically without photoinitiator on exposure to UV radiation, but the use of benzophenone photoinitiator resulted in a higher degree of cross-linking (as indicated by a lower solvent uptake in the swollen gel, a higher gel fraction, and a T_g increase over the un-cross-linked polymer).

Swelling studies of γ-irradiated polymers indicated that the degree of cross-linking was closely related to the total radiation dose at exposures of 0.5–5.0 Mrad.

Table 4. Characterization Data for Polyphosphazenes 5a–15a[a]

polymer	mol % substituent groups (approx) A	B	E	F	T_g (°C)	M_w	M_w/M_n
$[NP(OCH_2CF_3)_2]_n$	100				−63	0.9×10^6	1.3
5a	96		4		−61[b]		
6a	92		8		60[b]	4.4×10^6	2.0
7a	73		27		−62	1.5×10^6	2.5
8a	65		35		−67		
9a			100		−79		
$[NP(OC_6H_5)_2]_n$		100			−8		
10a		80	20		−17	2.5×10^6	2.0
11a	96			4	−61	0.6×10^6	1.3
12a	90			10	−58		
13a	87			13	−38	3.4×10^6	2.8
14a	54			46		1.8×10^6	1.2
15a	38			62	20	3.4×10^6	1.2

[a] A = OCH_2CF_3, B = OC_6H_5, E = $OC_6H_4O(CH_2)_3SiOMe_2SiOMe_2SiMe_3$, and F = $OC_6H_4C_6H_4O(CH_2)_3SiOMe_2SiOMe_2SiMe_3$. [b] DMA carried out using an RSA-II rheometric tensile analyzer at 10 Hz and 2 °C/min heating rate measured the glass transition temperatures of **5a** and **6a** as approximately −45 °C. In addition, both polymers showed a small but definite transition at −120 (**5a**) and −128 °C (**6a**).

The Dimethylethoxysilane Group as a Cross-Linking Site. Complete hydrosilylation was achieved by reaction of polymers **10** and **14** with dimethylethoxysilane under the experimental conditions described. The product polymers were purified by precipitation into hexane. Precipitation of the product solutions into water resulted in cross-linking. The un-cross-linked polymers formed transparent films which cross-linked on drying in the atmosphere at 25 °C. Further cross-linking was achieved by heating the films to 140 °C. The swelling ratio of polymer **14c** decreased from 23 to 8 after heating at 140 °C for 10 min. The degree of swelling did not change for samples heated at this temperature for longer than 10 min. Polymers applied to glass substrates adhered well and could not be removed without tearing the polymers. This result suggests that the polymer may bond covalently to the glass surface by the formation of Si–O–Si linkages. Cross-linking occurred under much milder conditions than those required to obtain significant coupling of the small-molecule model compound. This is not surprising since reaction of only a small proportion of the ethoxysilane sites will cause cross-linking of these high molecular weight polymers. The dimethoxyethoxysilane group is therefore a potentially useful cross-linking site in thin-film or surface-coating applications which require mild curing conditions.

Siloxane-Containing Poly(organophosphazenes). Polyphosphazenes with siloxane-terminated side groups were obtained by hydrosilylation reactions at ambient temperatures, as illustrated in Scheme 4. Incomplete hydrosilylation resulted when the process was terminated before completion of the reaction or when a stoichiometric deficiency of siloxane was used. These polymers contained residual olefin groups which enabled cross-linking reactions to be carried out according to the methods described previously.

Fully hydrosilylated polymers **5a–15a** were generally softer and more extensible than their allyl-containing precursors. Characterization data for the polymers are shown in Tables 4 and 5. Polymers **9** and **9a**, which contained only one type of side group, had both a glass transition (−9 and −79 °C, respectively) and melting behavior (DSC endotherms at 47 and 60 °C) typical of semicrystalline polymers. A decrease in T_g from −9 (unsaturated polymer **9**) to −79 °C (siloxane-containing polymer **9a**) resulted from the introduction of short

Table 5. Elemental Analysis Results for Polyphosphazenes 5a–15a[a]

polymer	composition	calcd				found			
$[NP(OCH_2CF_3)_2]_n$	2.00 A	C 19.77	H 1.66	N 5.76	P 12.74	C 19.82	H 1.68	N 5.70	P 12.23
5a	1.92 A, 0.08 E	C 23.22	H 2.41	N 5.29	Si 2.55	C 23.20	H 2.19	N 5.07	Si 2.58
6a	1.85 A, 0.15 E	C 25.80	H 2.96	N 4.93	Si 4.45	C 26.27	H 3.06	N 5.07	Si 3.42, 3.88†
7a	1.46 A, 0.54 E	C 35.57	H 5.08	N 3.59	Si 11.66	C 35.84	H 5.08	N 3.63	Si 11.82
8a	1.30 A, 0.70 E	C 38.20	H 5.65	N 3.23	Si 13.60	C 38.73	H 4.97	N 3.55	Si 10.19
9a	2.00 E	C 48.75	H 7.93	N 1.78	Si 21.38	C 48.18	H 7.63	N 1.97	Si 17.87
$[NP(OC_6H_5)_2]_n$	2.00 B	C 62.34	H 4.36	N 6.06	P 13.40	C 60.25	H 4.35	N 5.88	P 13.95
10a	1.60 B, 0.40 E	C 58.33	H 5.80	N 4.48	Si 7.18	C 55.65	H 5.75	N 4.34	Si 6.58
11a	1.92 A, 0.08 F	C 24.82	H 2.47	N 5.17	Si 2.49	C 23.90	H 2.45	N 5.18	Si 2.04
12a	1.81 A, 0.19 F	C 30.29	H 3.35	N 4.53	Si 5.18	C 30.11	H 3.25	N 4.61	Si 4.92
13a	1.75 A, 0.25 F	C 32.73	H 3.74	N 4.24	Si 6.38	C 33.14	H 3.63	N 4.13	Si 3.96
14a	1.08 A, 0.92 F	C 47.71	H 6.14	N 2.48	Si 13.75	C 48.04	H 6.01	N 2.73	Si 9.68
15a	0.76 A, 1.24 F	C 51.21	H 6.70	N 2.07	Si 15.47	C 51.43	H 6.57	N 2.14	Si 11.43, 12.05†

[a] A = OCH_2CF_3, B = OC_6H_5, E = $OC_6H_4O(CH_2)_3SiOMe_2SiOMe_2SiMe_3$, and F = $OC_6H_4C_6H_4O(CH_2)_3SiOMe_2SiOMe_2SiMe_3$. Polymer compositions were confirmed by ^1H NMR spectrometry within approximately 5%. While carbon, hydrogen, and nitrogen analysis results agreed well with theoretical values, silicon analysis gave values which were mostly lower than those expected. Repeat analysis of two samples showed a small increase in the silicon content (†). The analysis was carried out using an open-vessel digestion technique. It was believed that some silicon-containing species were volatilized during analysis, which resulted in low values for silicon. This behavior is not surprising in view of the thermal degradation properties discussed in this paper. Although high silicon contents could be a sign of unsatisfactory purification (for example, incomplete removal of excess heptamethyltrisiloxane), such samples would also show deviant C, H, and N analysis results and unbalanced NMR characterization results. This was not the case.

Table 6. Glass Transition Temperatures of Polymers Prepared from 10

polymer	T_g (°C)
$[NP(OC_6H_5)_2]_n$	-8
10	-10
10a	-17
10b	-13
10c	-11

dimethylsiloxane grafts. The flexible siloxane grafts may allow the onset of chain motion at lower temperatures by increasing the free volume and minimizing intermolecular interactions. This trend is best illustrated by the polymers with high siloxane contents. As with the unsaturated polymers, the effect of the rigid phenylphenoxy segment in cosubstituent polymers **11a–15a** is to increase the glass transition temperature relative to that of poly[bis(trifluoroethoxy)phosphazene]. The properties of these siloxane-containing polymers are dependent not only on the siloxane content but also on the nature of the cosubstituent group (in this case, trifluoroethoxy or phenoxy) and of the spacer group between the siloxane segment and the phosphazene backbone. Siloxane-containing polymers could be prepared which were either highly extensible or rigid, durable materials by judicious choice of the cosubstituent spacer groups.

Weight-average molecular weights and polydispersity values (Table 4) were obtained by gel permeation chromatography referenced against polystyrene standards. The variation in molecular weights may result from slight differences in the chain length of the different batches of poly(dichlorophosphazene) from which the polymers were prepared. Moreover, differences in the purification techniques may have influenced the molecular weights of the purified polymers.

Table 6 shows the effect of the graft type on the resulting polymer properties. Polymer **10b**, prepared by hydrosilylation of **10** with pentamethyldisiloxane, had a higher T_g than **10a** which possessed longer siloxane grafts. Polymer **10c**, prepared from **10** and dimethylethoxysilane, followed by allowing the polymer to cross-link at room temperature, had a T_g approximately equal to that of **10** itself. This polymer was insoluble and showed recoverable extensibility at room temperature.

The physical properties of two phosphazene–siloxane cosubstituent polymers, **5a** and **6a**, were investigated further. Dynamic mechanical analysis (DMA) was carried out over the temperature range −150 to +60 °C at a frequency of 10 Hz. The single-substituent polymer poly[bis(trifluoroethoxy)phosphazene] was tested for comparison. The results are shown in Figures 1 and 2. The storage modulus of poly[bis(trifluoroethoxy)phosphazene],

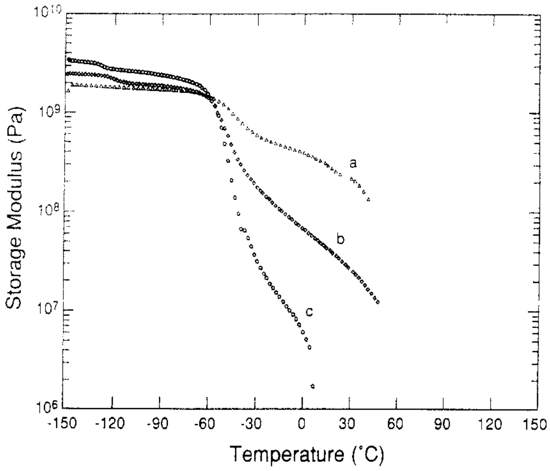


Figure 1. Dynamic storage moduli vs temperature for $[NP(OCH_2CF_3)_2]_n$ (a), polymer **5a** (b), and polymer **6a** (c). **5a** and **6a**, containing siloxane grafts, show reduced storage modulus values above the glass transition compared to poly[bis(trifluoroethoxy)phosphazene].

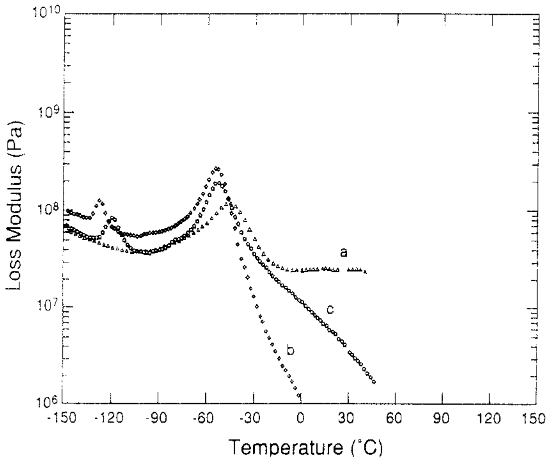


Figure 2. Dynamic loss moduli vs temperature for $[NP(OCH_2CF_3)_2]_n$ (a), polymer **5a** (b), and polymer **6a** (c).

a semicrystalline polymer, remained nearly constant at temperatures from −150 to −60 °C. Between −60 and −30 °C there was a decrease in the storage modulus and a peak in the loss modulus centered at −46 °C, corresponding to the glass transition of the polymer. DSC and DMA testing gave different values (−63 and −46 °C, respectively) for the glass transition temperature. This difference results from the measurement of two different properties, heat capacity and mechanical damping, which are affected slightly differently by the onset of polymer motion. As heating continued, a precipitous drop in the storage modulus was observed at a temperature of about 50 °C. This was presumably due to melting of the crystalline portions of the polymer.

DMA data of samples **5a** and **6a** are also shown in Figures 1 and 2. Both polymers showed a maximum in the loss modulus at approximately −45 °C. The glass transition occurred at about the same temperature in all three polymers studied. The introduction of dimethylsiloxane-containing side groups appeared to have virtually no effect on the glass transition. An additional feature was found. Both siloxane-containing polymers **5a** and **6a** showed an interesting relaxation at lower temperatures (−130 to −120 °C) which poly[bis(trifluoroethoxy)phosphazene] did not exhibit. The small peaks in loss moduli can be seen in Figure 2. This transition was not detected by DSC. Interestingly, the temperature range in which this peak was observed is often associated with the glass transition temperature of poly(dimethylsiloxane) homopolymers or block copolymers.

There are several possible reasons why this peak is detected by dynamic mechanical analysis and not by DSC. First, if the transition is due to local motions of the side group (so-called secondary relaxations), DSC would not be sensitive to this transition. More likely, the dimethylsiloxane segment might exist in a microphase-separated domain. At low concentrations the heat capacity change associated with this transition would be small and it is unlikely that it would be detected by DSC.

The extent to which the dimethylsiloxane segments can microphase-separate will depend on the polymer architecture. The siloxane segments are covalently attached to the P=N backbone through aryloxy units. These were originally linked to the backbone by the nucleophilic replacement of chlorine atoms. The addition of the nucleophile dropwise with rapid stirring should not allow the formation of a blocky structure, since the substitution is relatively slow (several days were required for full reaction at room temperature). Moreover, no reason existed to expect localized reactions for other reasons, such as inductive effects. Allcock and Kim[27] found that the reactions of trifluoroethoxide and phenoxide salts with poly(dichlorophosphazenes) resulted in the linkage of aryloxide groups to the chain in a random manner, with low percentages of geminal substitution. This was attributed to the bulkiness of the aryloxide nucleophile. Thus, it is proposed that the dimethylsiloxane segments are arrayed randomly along the polymer backbone and that phase separation on a large scale is limited by this arrangement. Only small-scale phase rearrangements would be possible, aided by the high backbone flexibility of this polymer. Thus, it appears that small siloxane domains may be formed.

Polymer **15a**, containing 40.6 wt % siloxane, was examined by transmission electron microscopy. The polymer appeared to be completely homogeneous at all magnifications up to 200 000 times. This evidence supports the view that large-scale phase separation does not occur. However, the technique probably cannot detect domains of 100 Å or less, and this result does not rule out the possibility of small domain formation.

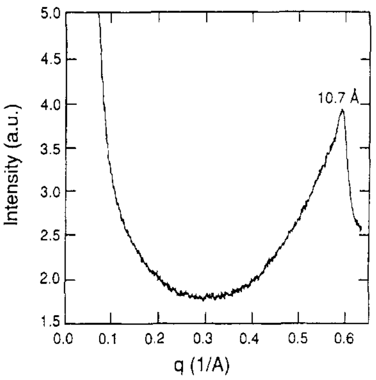


Figure 3. Small-angle X-ray scattering plot of polymer **5a**.

Small-angle X-ray scattering (SAXS) analysis was carried out in an attempt to detect the presence of small dimethylsiloxane domains. Figure 3 is a plot of intensity vs scattering angle for sample **5a**. A peak was detected at 10.7 Å which may correspond to a correlation distance between the polymer chains. Note that no low-angle peak was observed that could be correlated with interdomain spacing of phase-separated siloxane domains. However, an increase was detected in the intensity of the scattering at low angles. This can be attributed to inhomogeneities in the sample. Since the siloxane groups are present at low concentrations, a well-defined interparticle distance was not established. The excess scattering may be due to intraparticle interference of the dilute siloxane domains. Similar results have been obtained by Fitzgerald and coworkers in the case of polyimide-siloxane block copolymers at low concentrations of the siloxane block.[28]

The interesting morphology of these polymers is the subject of ongoing investigations.

Blends of Siloxane-Containing Polyphosphazenes with Poly(dimethylsiloxane). The 12 polymers reported here comprise dimethylsiloxane–organophosphazene cosubstituent systems containing 4–100% grafting of siloxane segments to the organic side groups of the polyphosphazene. This corresponded to 6.5–56.2% dimethylsiloxane by weight. Higher siloxane contents might be accessible by the preparation of blends (alloys) of these polymers with poly(dimethylsiloxane) (PDMS). Blending is one method used to obtain a material with specific properties from two or more component materials which alone do not have the desired characteristics. Polymer blends are mixtures which may show a range of miscibility at the molecular level depending on the types of intermolecular attractions that exist between the two components. A completely miscible two-component blend would show a single glass transition temperature (T_g), intermediate in value between the single-component transition temperatures and dependent on the ratio of the two components. A partially miscible blend generally shows two transitions characteristic of each of the two components.[29] The temperatures of the transitions are normally displaced from those of the pure components. The glass transitions of blends may occupy a broader temperature range than those of the single components, due to variations in composition throughout the blend.[29]

Four blends of PDMS and siloxane-containing polyphosphazenes were prepared and analyzed by differential scanning calorimetry (DSC). None showed any significant changes in the polymer transition temperatures following alloying. Figure 4 shows a DSC thermogram of a blend

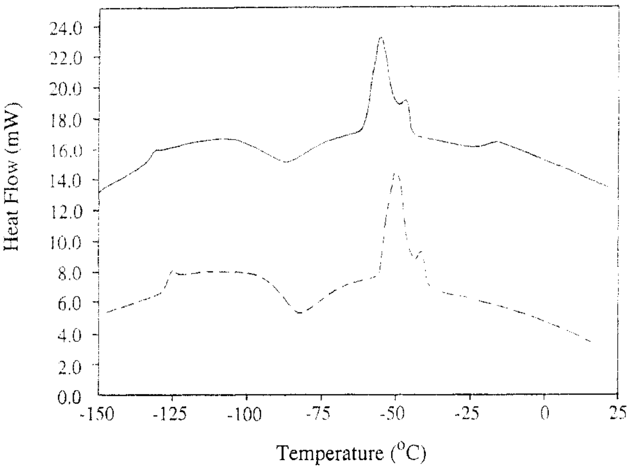


Figure 4. DSC thermogram of a 1:1 blend of PDMS with **10b**. The dashed line shows the thermal behavior of PDMS alone.

of PDMS with **10b** compared to that of PDMS alone. The poly(dimethylsiloxane) sample showed a glass transition at −126 °C. A broad exotherm (with a peak at −82 °C) preceded a broad, double endotherm (with a peak at −51 °C). These two transitions result from crystallization and melting behavior. In the blend of PDMS with polymer **10b**, two glass transitions were detected, at −128 and −16 °C, which were attributed to the independent transitions of the two components. The melting and crystallization behavior of PDMS was also observed. The other three blends showed similar behavior. The T_g values of the poly(organophosphazene) component in the blends containing **10a** and **10b** varied no more than 3 °C from those of the polymers alone. Polymers **15a** and **15b** did not show a glass transition alone or in the blends by differential scanning calorimetry. The poly(dimethylsiloxane) T_g was detected at −127 ± 1 °C in each of the four systems. Thus, even with high loadings of organosiloxane side groups, the polyphosphazenes are incompatible with the polysiloxanes.

PDMS has been combined with organic polymers in interpenetrating networks[30,31] but very little information exists in the literature relating to blends of unmodified PDMS with nonsiloxane polymers. Poly[bis(trifluoroethoxy)phosphazene] and poly(diphenoxyphosphazene) are immiscible with PDMS over a broad range of component concentrations.[32] Despite the presence of short dimethylsiloxane chains in **10a**, **10b**, **15a**, and **15b**, these cosubstituent polymers did not show miscibility or semimiscibility with PDMS. This evidence of incompatibility between the organophosphazene polymers and PDMS further supports the suggestion that polymers containing both substituents may microphase separate.

Thermal Stability. Pyrolysis studies were carried out to determine if the siloxane graft polymers showed high-temperature behavior that was different from that of other poly(organophosphazenes). The thermal behavior of several organophosphazene polymers has been studied,[33-38] particularly the equilibration of poly[bis(trifluoroethoxy)phosphazene] and poly(diphenoxyphosphazene). Both polymers undergo depolymerization to form small-molecule cyclic phosphazenes at elevated temperatures, with the cyclic species undergoing subsequent cross-linking reactions in the case of the diphenoxyphosphazene system.[35] Thermal degradation is generally thought to initiate by chain cleavage at "weak" points, such as P–Cl or P–OH sites along the phosphazene chain.[33,35] Unzipping by a thermal initiation chain transfer mechanism has been proposed.[36] Poly(aminophosphazenes) undergo side group condensation and cross-linking reactions rather than skeletal cleavage or depolymerization. The elimination of amines occurs at temperatures above 100–150 °C, and nonvolatile residues consisting of graphitic carbon and phosphorus nitride have been isolated.[35]

Table 7. Thermal Degradation of Selected Poly(organophosphazenes)

polymer	T_{max} (°C)[a]	residue[b] (wt %)
$[NP(OC_6H_5)_2]_n$	498	29
7	466	23
7a	495	22
9	517	50
9a	474	28
10	533	56
10a	468	50
$[NP(OCH_2CF_3)_2]_n$	469	4
12	491	1
12a	489	25

[a] Thermogravimetric analysis at 20 °C/min under nitrogen flow. [b] Polymer residue remaining at 800 °C.

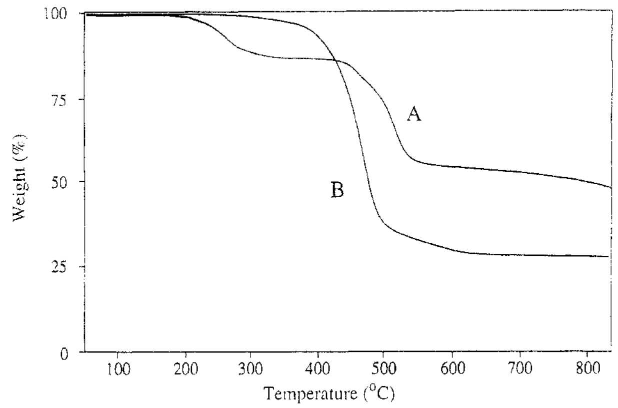


Figure 5. Thermogravimetric analysis of polymers **9** (A) and **9a** (B). Polymers containing unsaturated side groups typically showed two regions of weight loss, one below 300 °C and the other at temperatures above 400 °C.

The high-temperature behavior of the polymers prepared in the present work was studied by combining thermogravimetric analysis with electron impact (EI) mass spectrometric analysis of volatile degradation products. Thermogravimetric results are reported as T_{max}, the temperature at which the maximum rate of weight loss occurs, and in terms of the nonvolatile residue remaining at 800 °C (Table 7).

The thermogravimetric curves were generally of two types, examples of which are shown in Figure 5. The siloxane-containing polymers generally showed negligible weight loss below 300 °C, followed by one major region of weight loss at 400–500 °C. Polymers that contained unsaturated side groups showed two distinct regions of weight loss, one at 200–300 °C and the other at 450–550 °C. The weight loss at lower temperatures is believed to result from cleavage of allyl side groups since EI mass spectrometry provided evidence for fragments at 41 and 57 units which corresponded to the allyl groups or their decomposition products. These fragments were not detected for polymers that lacked unsaturated groups. Fragments of masses 28, 73, 147, and 221, attributed to siloxane fragments Si^+, $SiMe_3^+$, $SiMe_2OSiMe_3^+$, and $SiMe_2OSiMe_2OSiMe_3^+$, were detected over the temperature range 250–450 °C for polymers **9a** and **12a**. Evidence of chain unzipping and cyclization was obtained: polymers **12**, **12a**, and $[NP(OCH_2CF_3)_2]_n$ showed fragments of masses 729 ($N_3P_3(OCH_2CF_3)_6^+$) and 972 ($N_4P_4(OCH_2CF_3)_8^+$) in addition to 630 ($N_3P_3(OCH_2CF_3)_5^+$) and 873 ($N_4P_4(OCH_2CF_3)_7^+$).

Pyrolysis residues varied in weight from 1 to 56 wt %. These black, ceramic-like solids result from cross-linking reactions of either the polymer or the cyclic depolymerization products. Poly(diphenoxyphosphazene) is known to depolymerize and undergo subsequent cross-linking reactions with the evolution of phenol.[35] The suggested mechanism involves heterolytic cleavage of P–O linkages followed by electrophilic substitution of the phosphazenium cation on the phenyl ring of a second phosphazene molecule. This reaction is presumably also possible in each of the polymers tested here, since phenoxy and phenylphenoxy spacer groups connect the alkylsiloxanes or allyl groups to the phosphazene chain. In the case of poly(organophosphazenes) with unsaturated side groups, cross-linking had been found for samples heated at 100–200 °C. Cross-linking reactions at temperatures below which depolymerization occurs might be expected to increase the weight retention at high temperatures: polymers **7**, **9**, and **10** gave higher residual weights than their siloxane-containing counterparts. Polymers **12** and **12a** were the exceptions to this trend; **12** volatilized almost completely, unlike all other unsaturated polymers which were studied.

In summary, the results indicate that the thermal degradation consists of three main processes: cleavage of side groups, cross-linking reactions, and depolymerization. Side group cleavage was proposed to explain the mass spectrometric detection of fragments which were attributed to siloxane segments. The siloxane-containing polymers cross-linked at elevated temperatures, which may have been due in part to small amounts of residual unsaturation. Nonvolatile residues remaining after thermogravimetry at 800 °C are analogous to residues obtained from poly(aminophosphazenes) and poly[(aryloxy)phosphazenes] whose thermal degradation behavior has been studied.[35] Depolymerization, the typical decomposition process of poly(organophosphazenes), was confirmed by the detection of fragments attributed to cyclic phosphazene compounds.

The relative degree to which each of these three processes occurs depends on the ratio of the different side groups present, which is illustrated in Table 7.

Experimental Section

Instrumentation. NMR spectra were obtained with a Bruker WP 360 MHz NMR spectrometer, with ^{31}P chemical shifts referenced to aqueous phosphoric acid. IR spectra were obtained with a Perkin-Elmer 1710 FT-IR spectrometer. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

^{60}Co γ-irradiation experiments were carried out at the Breazeale Nuclear Reactor at The Pennsylvania State University. Dried bulk samples were irradiated under vacuum (approximately 0.05 mmHg) at a dose rate of 156 krad/h.

Ultraviolet irradiation experiments were carried out with a Hanovia 450 W mercury lamp. The lamp produced radiation in the range 220–400 nm. Polymers were dissolved in THF alone and in THF with benzophenone photoinitiator at 0.1 mol equiv relative to the unsaturated groups. Polymer films then were cast onto Teflon surfaces and were dried to give samples approximately 0.04 mm thick. Samples were placed 11 cm from the radiation source and were exposed for varying lengths of time: 20 min was found to be the optimum exposure time under these conditions. Swelling studies were carried out with the use of distilled THF. The initial dry weight, W_i, was first recorded. The swollen samples were then weighed and replaced in fresh solvent daily until constant weights W_s were obtained. The final dry weights W_d were obtained by repeated swelling and drying under vacuum until constant values were obtained. The gel fraction was calculated from W_d/W_i and the swelling ratio was calculated from $(W_s - W_d)/W_d$.

Differential scanning calorimetry was carried out using Perkin-Elmer DSC-7 equipment. Samples (10–15 mg) were examined within an atmosphere of dry nitrogen in aluminum pans, with an empty aluminum pan as reference. The heating rate was 20 °C/min. Thermal weight loss measurements were made using a Perkin-Elmer TGA-7 thermogravimetric analyzer equipped with a PE 7500 computer. Testing was carried out under a stream of dry nitrogen at a heating rate of 20 °C/min. Samples of 4–5 mg were analyzed. Analysis of pyrolysis products was performed using a Kratos MS 9/50 electron impact magnetic sector mass spectrometer (impact energy 70 eV) with an electron multiplier detector. The sample was heated in the range 120–500 °C using a Kinderman probe.

A Rheometrics solid analyzer (RSA-II) was used to carry out dynamic mechanical analysis (DMA). The temperature was increased at a rate of 2 °C/min, and both the storage modulus and the loss modulus were measured at a frequency of 10 Hz.

Gel permeation chromatography was conducted using a Hewlett-Packard 1090 liquid chromatograph with a refractive index detector. The columns were calibrated against 11 polystyrene standards (Polysciences) of molecular weights 4×10^3 to 3×10^6. Polymer solutions were prepared at concentrations of approximately 1% bulk weight using HPLC grade THF (Omnisolv).

Electron microscopy was carried out at the electron microscope facility for the Life Sciences in the Biotechnology Institute at The Pennsylvania State University. Transmission electron microscopy was performed using a JEOL 1200 EXII TEM microscope at an accelerating voltage of 80 kV. Polymer samples were infiltrated with ethanol, embedded in a low-viscosity epoxy resin, and sectioned with a diamond knife. Samples were examined unstained and stained with osmium tetraoxide.

Small-angle X-ray scattering measurements were obtained from poly(organophosphazene) films. The X-ray instrument has been described previously.[28]

Starting Materials. Poly(dichlorophosphazene) was synthesized by the thermal ring-opening polymerization of hexachlorocyclotriphosphazene at 250 °C.[2] Hexachlorocyclotriphosphazene (provided by Ethyl Corp.) was purified by two recrystallizations from hexane and two vacuum sublimations. Phenol (Aldrich) was dried by azeotropic removal of water by benzene and was further purified by vacuum sublimation. Poly(dichlorophosphazene), sodium, and sodium hydride were stored and handled in a nitrogen-filled glovebox. 2,2,2-Trifluoroethanol was treated with sodium carbonate and distilled before use. Tetrahydrofuran and dioxane were freshly distilled from sodium benzophenone ketyl. All reactions were carried out under a stream of dry argon using standard Schlenk techniques.

Heptamethyltrisiloxane, pentamethyldisiloxane, and dimethylethoxysilane (Petrarch) were distilled and stored under dry argon. Platinum divinyltetramethyldisiloxane complex (Petrarch) was used as received.

Synthesis of Compounds 1–4. Compound 1. Hexachlorocyclotriphosphazene (10 g, 28.7 mmol) was treated with 5 equiv of sodium phenoxide (prepared from reaction of 13.5 g (143.6 mmol) of phenol and 4 g (173.9 mmol) of sodium) in THF. After heating at reflux for 2 days, the solvent was evaporated under reduced pressure and the product was dissolved in methylene chloride and washed with distilled water. The pure product was obtained by column chromatography with a yield of 66%.

Compound 2. 4-(Allyloxy)phenol was prepared by the reaction of hydroquinone with allyl bromide. A mixture of hydroquinone (20 g, 181.2 mmol), allyl bromide (10 g, 82.6 mmol), potassium hydroxide (6 g, 107.1 mmol), and potassium iodide (1.5 g, 9 mmol) in approximately 200 mL of absolute ethanol was heated to reflux under a stream of argon for 4 days. The ethanol was evaporated under reduced pressure and the product was dissolved in methylene chloride. The product solution was washed with water and dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure to yield a dark brown liquid. The crude product was distilled to obtain a mixture of the diallyl ether and monoallyl ether. The final product was obtained by column chromatography. The yield was approximately 20%.

4-(Allyloxy)phenol (1.5 g, 10.0 mmol), dissolved in THF, was allowed to react with sodium (0.28 g, 12.2 mmol) at room temperature overnight. Compound 1 (3.4 g, 4.9 mmol) was added and the solution was heated to reflux overnight (Scheme 1). The solution was concentrated and dissolved in methylene chloride, and then washed with distilled water and 5% (w/v) NaOH aqueous solution. The product solution was dried over magnesium sulfate. *m/z* 749; ^{1}H NMR (200 MHz, $CDCl_3$) 7.05 (m, .25H), 6.8 (m, 4H), 6.1 (m, 1H), 4.4 (m, 2H).

Compound 3. One drop (about 10 mg) of platinum tetramethyl-1,3-divinyldisiloxane complex (Petrarch), **2** (0.42 g, 0.73 mmol), and heptamethyltrisiloxane (0.33 g, 1.48 mmol) were dissolved in 5 mL of $CDCl_3$ (Scheme 2). The progress of the reaction was monitored by ^{1}H NMR spectroscopy: no "unsaturated" protons were detected after 21 h at room temperature. Species **3** was purified by column chromatography.

Compound 4. One drop (about 10 mg) of platinum tetramethyl-1,3-divinyldisiloxane complex (Petrarch), **2** (0.8 g, 1.06 mmol), and dimethylethoxysilane (0.33 g, 3.2 mmol) were dissolved in 20 mL of $CDCl_3$. After 17 h no "unsaturated" protons were detected by ^{1}H NMR spectroscopy. $CDCl_3$ was evaporated under reduced pressure. Ethanol (20 mL) and distilled, deionized water (1 mL) were added and the solution was heated to reflux. No new products were detected by TLC for up to 48 h. One drop of concentrated sulfuric acid (Scheme 3) was added, and the mixture was maintained at reflux overnight to obtain a product mixture containing a significant amount of **4** as determined by TLC and confirmed by FAB MS (*m/z* 1615).

4-[4′-(Allyloxy)phenyl]phenol was prepared from the reaction of 4,4′-biphenol with allyl bromide. A mixture of 4,4′-biphenol (43 g, 231 mmol), allyl bromide (84 g, 694 mmol), potassium hydroxide (14.2 g, 254 mmol), and potassium iodide (3.9 g, 23.5 mmol) in approximately 500 mL of absolute ethanol was heated to reflux under argon for 2 days. The ethanol was evaporated under reduced pressure and the product mixture was dissolved in methylene chloride. The product solution was washed with water, dried, and recrystallized twice from ethanol. The final product was obtained by column chromatography.

Synthesis of Polymers. Polymers **5–15**, with varying ratios of allyl-functional side groups and either trifluoroethoxy or phenoxy cosubstituent groups, were prepared by the nucleophilic substitution of poly(dichlorophosphazene) by sodium alkoxides and aryloxides. Sodium salts of 4-(allyloxy)phenol and 4-[4′-(allyloxy)phenyl]phenol were prepared by allowing them to react with excess sodium hydride dispersion in THF solution at ambient temperature. The mixtures were filtered to remove unreacted sodium hydride. Sodium trifluoroethoxide was prepared by the reaction of trifluoroethanol in THF with excess sodium for 16 h. Sodium phenoxide was prepared by allowing phenol, in THF solution, to react with excess sodium for 16 h. To a solution of poly(dichlorophosphazene) in THF was slowly added a stoichiometrically calculated amount of either the sodium 4-(allyloxy)phenoxide or sodium 4-[4′-(allyloxy)phenyl]phenoxide. The reaction was allowed to proceed at ambient temperature (25 °C) and was monitored by ^{31}P NMR analysis. On completion of the reaction, a THF solution containing either sodium trifluoroethoxide or sodium phenoxide in a slight excess to that required was added. The reaction was monitored by ^{31}P NMR analysis and the solution was heated where necessary to obtain full chlorine replacement. The polymer was purified by precipitation from THF three times into water and once into hexane. Polymers were stored under dry argon. Cosubstituent compositions of polymers **5–15** are shown in Table 1. Polymer **9** was prepared by the nucleophilic displacement of chlorine atoms by one nucleophile (sodium 4-(allyloxy)phenoxide) only. This reaction required 2 weeks in refluxing THF with the addition of 0.1 mol of 15-crown-5 per P–Cl to achieve full substitution of the chlorine atoms by the bulkier aryloxy substituent groups. ^{1}H NMR assignments for the unsaturated substituent groups were δ 7.7–6.6 (broad d, Ph), 6.0 (s, CH=), 5.3 (d, $=CH_2$), and 4.2 (s, OCH_2). Protons assigned to trifluoroethoxy and phenoxy substituents were observed at δ 4.6–4.0 and 7.1–6.8, respectively.

Hydrosilylation of Polymers. Hydrosilylation reactions were performed on polymers with unsaturated alkyl side units according to the reaction shown in Scheme 4. A trace amount of platinum catalyst (about 10 mg) was added to an ethyl acetate (or chloroform) solution of ether pentamethyldisiloxane or heptamethyltrisiloxane, present as a 3 times molar excess relative to the calculated concentration of unsaturated groups. After 30 min of vigorous stirring, the siloxane solution was added to the allyl-containing polymer, itself dissolved in ethyl acetate (or chloroform). The reactions were monitored by ^{1}H NMR spectroscopy, with the disappearance of signals at 6.0 and 5.3 ppm indicating reaction of the allyl groups. The reactions reached completion after 1–3 days. The product solutions were filtered and dialyzed against THF. Polymers were obtained by drying and were purified by precipitation twice into ethanol (in the case of polymers with high siloxane content) or hexane (for polymers with low siloxane content). Polymers **5a–15a** were obtained by reaction of polymers **5–15** with heptamethyltrisiloxane. Polymers **10b** and **15b** were obtained by reaction of **10** and **15** with pentamethyldisiloxane. Residual chlorine (from incomplete substitution of P–Cl bonds) was found by elemental analysis to be less than 0.1%. ^{1}H NMR assignments for the siloxane-containing substituent groups were δ 7.7–6.6 (broad d, Ph), 3.9 (s, OCH_2), 1.9 (s, CH_2), 0.7 (s, CH_2Si), and 0.1 (broad m, $SiCH_3$). Elemental analysis results gave good agreement of carbon, hydrogen, and nitrogen with the theoretical values. Silicon contents determined experimentally using an open digestion method were consistently low. It was believed that this resulted from the unsuitability of this analysis technique, since other analysis results were consistent (Table 5).

Preparation and Cross-Linking of Polymers Containing Dimethylethoxysilane Groups. A trace amount of platinum catalyst (about 10 mg) was added to a stoichiometric equivalent of dimethylethoxysilane in ethyl acetate solution. After 30 min of vigorous stirring, the silane solution was added to the olefin-containing polymer, itself dissolved in ethyl acetate. The reaction was monitored by ^{1}H NMR spectroscopy. After 1 day of reaction, the mixture was filtered and the product was isolated by precipitation into hexane. Polymers **10c** and **14c** containing dimethylethoxysilane groups cross-linked readily on drying in the atmosphere at 25 °C. Cross-linked films were heated at 140 °C for varying lengths of time, and swelling studies were carried out to determine the effect of heating on cross-linking.

Preparation of Blends. Polymers **10a**, **10b**, **15a**, and **15b** (0.05 g) were dissolved in THF (6 mL). Each solution was stirred overnight with 0.05 g of PDMS (Petrarch PS041.2 trimethylsiloxy-terminated PDMS of molecular weight 9430) dissolved in 4 mL of THF. Films were obtained by solution casting and drying under vacuum. Films prepared from the blends were soft, flexible, and opaque. Miscibility was assessed by DSC.

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