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Surface Studies of Poly(organophosphazenes) Containing Dimethylsiloxane Grafts

Harry R. Allcock* and Dawn E. Smith

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

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Poly(organophosphazenes) containing dimethylsiloxane grafts were synthesized by carrying out hydrosilylation reactions on polymer precursors that contained unsaturated side groups. The surface properties of the siloxane-containing polymers were studied by contact-angle measurements and X-ray photoelectron spectroscopy. A cosubstituent poly(organophosphazene) containing both trifluoroethoxy side groups and grafted dimethylsiloxane side groups was found to have a surface rich in $-CF_3$ groups. A poly(organophosphazene) with siloxane grafts but phenoxy groups as the second substituent showed surface enrichment of the siloxane species. Surface-specific hydrosilylation reactions were detected between an allyl-functional polymer and heptamethyltrisiloxane dissolved in nonsolvents for the polymer. Polymer films showed the presence of silicon to depths of 25–60 μm as measured by energy-dispersive X-ray spectroscopy.

Introduction

A growing need exists for new polymer systems with predetermined surface properties. For example, the biocompatibility of a material is dependent on the nature of its surface and the interaction of that surface with living tissues.[1,2] Platelet adhesion and blood coagulation are influenced both by the surface characteristics of a material and by the adsorption of serum protein on the surface. Adhesion is another property which is strongly surface determined.[3,4] The fundamental problem in polymer surface science is that a material with the required surface properties may not necessarily possess appropriate bulk properties and vice versa. A solution to this dilemma is to select a polymer with the correct combination of bulk properties and then develop methods to modify its surface.

Surface modification is not a new concept. Mechanical roughening, etching, and flame treatment have been used historically to alter the adhesive properties of a variety of materials, and surface coatings have long been used to improve the surface properties of a polymeric material. Recent work[5-11] has involved controlled chemical reactions carried out on the surface region or at the surface monolayer in order to functionalize and graft chemical species to that surface while, at the same time, leaving the bulk of the material unchanged.

Thus the ability to choose a polymer with desired bulk properties and to tailor its surface chemistry to suit a particular application has widespread consequences. The polyphosphazene family (**1**, Chart 1) is particularly suited to this approach. The macromolecular substitution route commonly used in poly(organophosphazene) synthesis[12,13] allows control of the side-group ratios, and this in turn influences the bulk and surface properties. Solubility, crystallinity, and mechanical properties may be varied within wide limits. In surface modification procedures, the high chemical stability of the P–N backbone often allows more aggressive chemical reactions to be carried out than with most polymers, with a lower likelihood of chain cleavage. Previous surface reactions of polyphosphazenes carried out in our program have included sulfonation,[14] hydrolysis,[15] oxidation,[16] and nucleophilic substitutions.[17] Poly(organophosphazenes) have also been used as immobilization substrates for the covalent linkage of the enzymes glucose-6-phosphate dehydrogenase and trypsin.[18]

Considerable interest exists in the preparation and examination of polymers which contain both organophosphazene and organosilyl units. A number of different synthesis routes have been investigated.[19-29]

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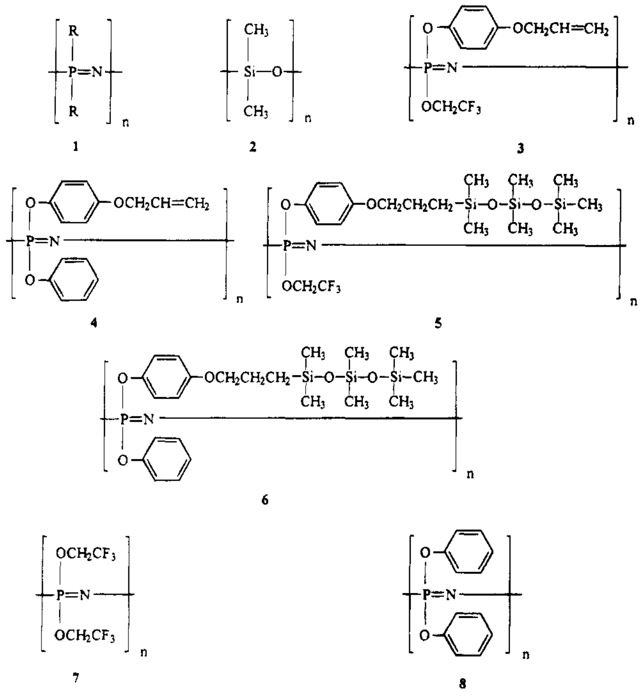
Table 1. Polymer Compositions and Glass Transition Temperatures

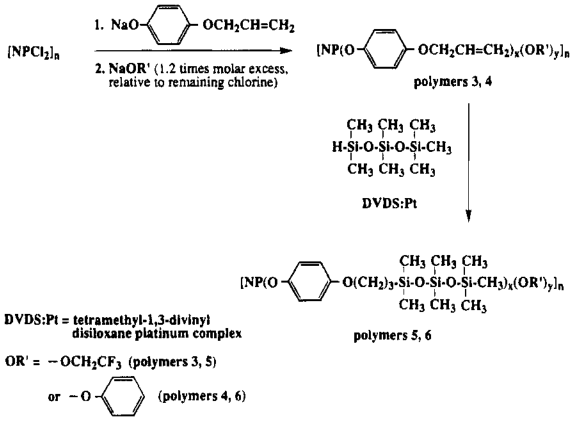
polymer	polymer structure	T_g (°C)[a]
5	$[NP(OCH_2CF_3)_{1.46}(OC_6H_4O\{CH_2\}_3SiMe_2OSiMe_2OSiMe_3)_{0.54}]_n$	−62
6	$[NP(OC_6H_5)_{1.60}(OC_6H_4(CH_2)_3SiMe_2OSiMe_2OSiMe_3)_{0.40}]_n$	−17
7	$[NP(OCH_2CF_3)_2]_n$	−63
8	$[NP(OC_6H_5)_2]_n$	−8

[a] Glass transition temperatures were determined by DSC at a heating rate of 20 °C/min.

Chart 1



Scheme 1



Possible properties and uses for these materials include: low-temperature elastomers,[19,20] thermally stable or flame-retardant materials,[21,22] and membranes with improved gas permeability.[23] In this paper the focus is on the surface properties of poly(organophosphazenes) that contain siloxane grafts, and the surface-specific reactions of poly(organophosphazenes) via the hydrosilylation of unsaturated sites.

Results and Discussion

Surface Studies of Polymers Containing Siloxane Grafts. The bulk properties of poly(organophosphazenes) that contain dimethylsiloxane grafts were described in an earlier publication.[29] Here, the surface properties are of interest. Blends and copolymers of poly(dimethylsiloxane) (**2**) with organic polymers such as poly(methyl methacrylate), poly(vinyl alcohol), and polysulfones have surfaces which are siloxane-rich, a consequence of the preferential migration to the polymer−air interface of the low surface energy, highly flexible dimethylsiloxane units.[30−33] The phase separation in block copolymers is determined by factors such as the copolymer composition, the flexibility of the block chain, and the interfacial tension between the copolymer chains.[34] Surface migration of siloxane species is particularly important in applications where adhesion is to be minimized, since poly(dimethylsiloxane) generally forms very low intermolecular adhesive forces with other materials.

Polyphosphazenes with 4-(allyloxy)phenoxy side groups and either trifluoroethoxy (**3**) or phenoxy (**4**) cosubstituent groups were prepared. The allyl units were allowed to react with heptamethyltrisiloxane in the presence of a platinum catalyst to give polymers with grafted dimethylsiloxane (**5** and **6**), as shown in Scheme 1. The single-substituent polymers poly[bis(trifluoroethoxy)phosphazene] (**7**) and poly[bis(phenoxy)phosphazene] (**8**) were prepared for comparison. The compositions of the polymers used in the study are shown in Table 1. Polymer films were made by spin-casting solutions in THF onto glass slides. The surface properties of the polymers were then studied by contact angle measurements and by X-ray photoelectron spectroscopy (XPS). Contact angle measurements were obtained using a series of hydrocarbons and other organic liquids of known surface tension. These values were used to calculate the critical surface tension of wetting γ_c, which is a useful tool for the comparison of different surfaces and may aid the identification of the chemical groups present at a material surface. XPS data were collected at a takeoff angle of 35°, which corresponded to a penetration of approximately 50 Å into the polymer film. The results are shown in Tables 2 and 3 and Figure 1.

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Table 2. Contact-Angle Data[a]

	contact angle in degrees (cosine in parentheses)			
γ_l (mN/m)	polyer **5**	polymer **6**	polymer **7**	polymer **8**
18.4	29 (0.88)	*c*	26 (0.90)	*c*
20.3	36 (0.81)	*c*	38 (0.78)	*c*
21.8	42 (0.75)	*c*	41 (0.75)	*c*
23.0	47 (0.68)	*c*	47 (0.69)	*c*
23.9	52 (0.61)	*c*	53 (0.60)	*b*
25.4	57 (0.54)	36 (0.81)	57 (0.54)	*b*
26.7	60 (0.50)	33 (0.84)	60 (0.50)	*b*
27.0	63 (0.46)	37 (0.80)	63 (0.46)	*b*
27.6	63 (0.45)	37 (0.80)	63 (0.45)	*b*
28.1	64 (0.44)	28 (0.88)	66 (0.41)	*b*
32.1		22[d] (0.93)		*b*
36.0		30 (0.87)		*b*
39.8		85 (0.80)		*b*
44.6		50 (0.64)		31[d] (0.86)
50.8		82 (0.14)		40 (0.77)
58.2		102 (−0.21)		70 (0.34)
63.4		113 (−0.39)		75 (0.27)
73.1		120[c] (−0.50)		92 (−0.04)

[a] The liquids used in this study, in order of increasing surface tension, were hexane, heptane, octane, nonane, decane, dodecane, tetradecane, pentadecane, hexadecane, heptadecane, styrene, hexachloro-1,3-butadiene, acetophenone, 1-bromonaphthalene, diiodomethane, formamide, glycerol, and water. Surface tension values were obtained from published data.[37,38] [b] These liquids caused swelling of the polymer surface. Contact angle data did not fit the Zisman plot. [c] These liquids spread across the polymer surface. [d] These values are approximate due to variations in the measured contact angle.

Table 3. Surface Composition of Polymer Films by XPS Analysis[a]

	composition in atomic percentages		
element	polymer **5**	polymer **6**	polymer **7**
carbon	29.1 (46.2)	52.8 (71.4)	25.1 (28.6)
oxygen	16.7 (15.4)	24.4 (14.3)	13.1 (14.3)
nitrogen	5.1 (4.8)	0.5 (4.5)	5.9 (7.1)
phosphorus	5.5 (4.8)	0.8 (4.5)	6.9 (7.1)
silicon	5.1 (5.8)	21.5 (5.4)	0.0 (0.0)
fluorine	38.4 (23.1)	0.0 (0.0)	48.6 (42.9)
total	99.9 (100.1)	100.0 (100.1)	99.6[b] (100.0)

[a] Theoretical atomic percentages, shown in brackets, were calculated by assuming an even distribution of all elements, excluding hydrogen which was not detected. [b] The remaining 0.4% was detected as sodium.

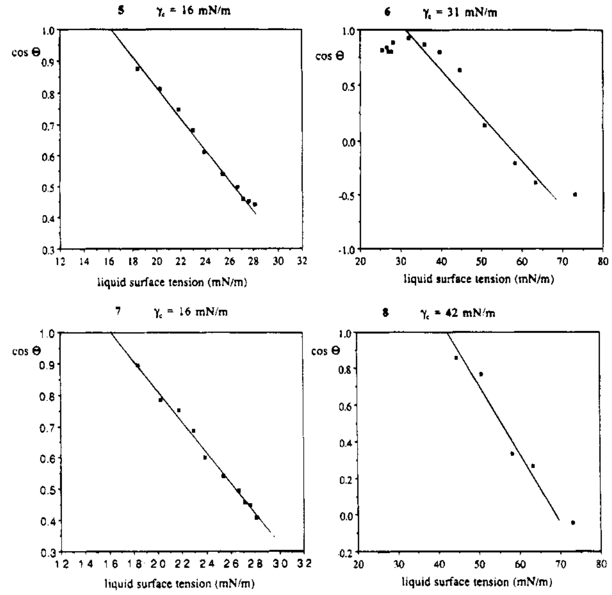

Figure 1. Zisman plots for polymers **5**−**8**. γ_c values were determined by extrapolation to cos $\theta = 1$.

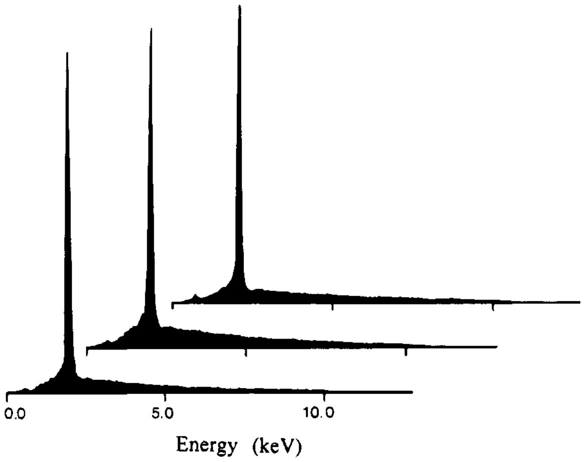

Figure 2. X-ray spectra of reference samples **e**, **f**, and **h**. Only phosphorus was detected at significant levels.

Poly[bis(trifluoroethoxy)phosphazene] (**7**) was found to have a critical surface tension of approximately 16 mN/m. The critical surface tension is a conveniently determined experimental parameter which is closely related to the surface energy. It is affected by the interactions of the atoms and molecules which make up the surface region. Low surface energies are a direct result of low intermolecular forces.[35] The weakest interactions are London dispersion forces which are associated with aliphatic hydrocarbons and fluorocarbons. Among polymers, some of the lowest surface energy values result from surfaces of closely packed methyl groups (e.g., poly(dimethylsiloxane), γ_c = 24 mN/m[36] or aliphatic fluorocarbon pendant groups (e.g., poly(tetrafluoroethylene), γ_c = 18−19 mN/m and poly(hexafluoropropylene), γ_c = 16 mN/m[35,36]).

Poly[bis(trifluoroethoxy)phosphazene] has a glass transition temperature of −63 °C. If the glass transition temperature of a polymer reflects its surface mobility as well as its bulk mobility, then this polymer should be sufficiently mobile at room temperature to allow the surface-active $-CF_3$ unit to be presented to the surface. The experimentally determined critical surface tension value of 16 mN/m is similar to that of other fluoroalkyl polymers, and this strongly suggests that $-CF_3$ groups do dominate at the surface. XPS data, on the other hand, show only a slight enrichment of fluorine over the theoretical bulk content. However, the XPS analysis depth of about 50 Å is perhaps too great to demonstrate the difference between surface and bulk compositions for this polymer, which has side groups with a much smaller volume than the polymers which are discussed below. If the $-CF_3$ groups of poly[bis(trifluoroethoxy)phosphazene] are oriented toward the surface, with the $-CH_2O-$ segments and the phosphazene backbone buried beneath, then the "surface region" might extend to a depth of about 5 Å and not the approximately 50 Å which was actually sampled. XPS analysis of the top

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50 Å would therefore include too much of the bulk sample, with its random composition, for adequate characterization.

The contact angle values for polymer **5** were very similar to those of poly[bis(trifluoroethoxy)phosphazene] (**7**). Both polymers had γ_c values of approximately 16–17 mN/m. This suggests that the surface atomic composition of polymer **5** is very similar to that of poly[bis(trifluoroethoxy)phosphazene], even though the polymer contains a significant proportion of dimethylsiloxane units. Surface fluorine contents, determined by XPS, were higher than the theoretical composition. Carbon contents were lower, which is also consistent with a fluoroalkyl-rich surface, since the siloxane graft segment is richer in carbon than is the trifluoroethoxy segment. Taken together, the data from both surface techniques suggest that polymer **5** rearranges into a conformation with $-CF_3$ units pointed toward the surface and the dimethylsiloxane segment buried more deeply in the bulk of the material. The driving force for polymer rearrangement is the minimization of the surface energy.

Polymer **6** contains no trifluoroethoxy substituents. Here 80 mol % of the side groups were phenoxy units and the remaining 20 mol % contained siloxane grafts. (The volume ratio of dimethylsiloxane is somewhat higher than 20% since this grafted segment is larger than the phenoxy group.) Of the two types of side group, the siloxane-containing unit has a higher surface activity than the aromatic phenoxy group. Therefore it is not surprising that polymer **6** showed evidence of migration of the siloxane segments to the air interface. The XPS data showed the surface of **6** to be very low in nitrogen and phosphorus, while silicon was present at a much higher level than the theoretical value. This suggests that the P–N backbone is buried while the siloxane segments are oriented toward the surface. Contact angle data tend to support this interpretation. The critical surface tension of polymer **6** was calculated as 31 mN/m, which is much lower than that of the single substituent poly[bis(phenoxy)phosphazene], which was calculated to be 42 mN/m. For comparison, literature sources quote γ_c for PDMS as 24 mN/m.[36]

In the case of polymer **5**, the preferential orientation toward the surface of those segments with lower surface energy led to surface enrichment of the trifluoroethoxy groups, while polymer **6** showed surface enrichment of the dimethylsiloxane graft. This is an interesting result, which demonstrates the relative surface-active natures of the three types of substituents: trifluoroethoxy, dimethylsiloxane, and phenoxy. Therefore, it is likely that the surface properties of multiple-substituent polyphosphazene materials will be affected most significantly by the side group with the lowest surface energy, at least for those polymers which have the freedom to rearrange at the molecular level. The behavior of the surfaces of high-T_g polyphosphazenes with surface-active substituents would be of considerable interest in order to assess the effect of polymer mobility on surface rearrangement.

Contact-angle data provide a convenient and useful way for characterization of the surface of a material, but problems can exist in the interpretation of the results. This is particularly true with multiple-component systems such as copolymers and cosubstituent polymers. Contact-angle data values may vary as the polymer molecules take up different orientations in contact with different liquids at the surface. Contact angles are changed when the polymer surface is swelled by (or is dissolving in) the liquid being tested. In this work, the contact angles of hydrocarbon liquids on poly[bis(trifluoroethoxy)phosphazene] (**7**) and polymer **5** were steady and reproducible and gave good Zisman plots. However, in the determination of γ_c for polymer **6** and poly[bis(phenoxy)phosphazene] (**8**), the contact angle data were not as reliable. Higher surface tension liquids were needed for the assessment, and many liquids showed interactions with the polymer surfaces. The experimentally determined γ_c values for these polymers may not be as accurate as those obtained for the other two, and as such the data offer only partial support for the proposed behavior.

Table 4. Surface Treatment of Polymer 3

sample	reaction medium	catalyst	reaction time	silicon analysis
a	hexane	Pt	30 min	no Si detected
b	hexane	Pt	2 h	no Si detected
c	hexane	Pt	6 h	Si detected at low levels
d	hexane	Pt	24 h	Si detected to a depth of 60 μm
e	hexane	none	2 h	no Si detected
f	hexane	none	24 h	no Si detected
g	2-propanol	Pt	24 h	Si detected to a depth of 30 μm
h	2-propanol	none	24 h	no Si detected

Surface-Specific Modification of Polymers Containing Unsaturated Side Groups. The allyl-functional polymer $[NP(OCH_2CF_3)_{1.46}(OC_6H_4OCH_2CH{=}CH_2)_{0.54}]_n$ (**3**) underwent a surface-specific hydrosilylation reaction under certain experimental conditions. Films of the polymer were immersed in a solution of heptamethyltrisiloxane in hexane, in the presence of a platinum catalyst. The exposure time was varied. The process was repeated using 2-propanol as a solvent, instead of hexane. Both liquids are solvents for the siloxane reagent but nonsolvents for the polymer. The reaction was monitored by silicon analysis of the modified polymer, after a thorough washing process. Polymer cross sections were examined by SEM with energy-dispersive X-ray spectroscopic analysis. The reaction conditions and analysis results are shown in Table 4.

It was important in this study to prepare and analyze suitable reference samples, to confirm that unreacted siloxane species were removed before analysis. Reference polymer films were exposed to heptamethyltrisiloxane solutions without the platinum catalyst. In the absence of the catalyst, no reaction was expected (and none was detected). Reference samples **e** and **f** (hexane), and **h** (2-propanol) did not show any significant increase in silicon content over the background values. Since silicon was not detected in the reference samples, it seems reasonable to assume that the silicon detected in the surface regions of **d** and **g** resulted from siloxane grafting reactions instead of just mixing.

Analysis of a point in the surface region of sample **d** showed a significant silicon content. A point in the central interior region of the sample had a silicon level comparable to the background value. Thus, it was possible to generate a profile map which not only showed a significant increase in Si content at both

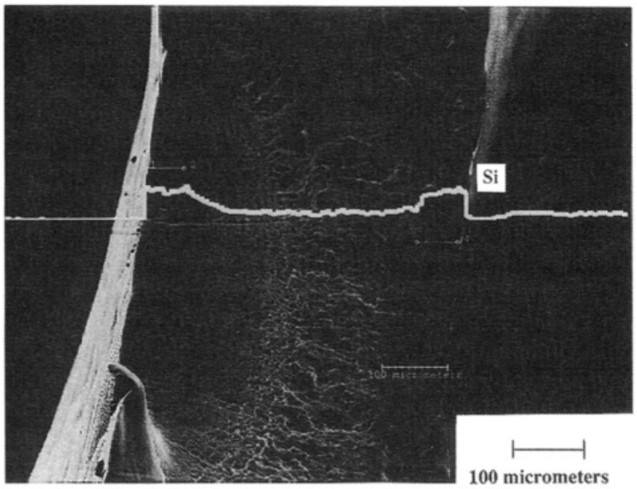

Figure 3. Cross section of sample **d**. The sample surface is visible as a light region toward the left of photomicrograph. The silicon line profile analysis of the cross section shows increased Si levels to a depth approximately 60 μm at both surfaces. The X-ray spectrum obtained in the surface region showed both silicon and phosphorus.

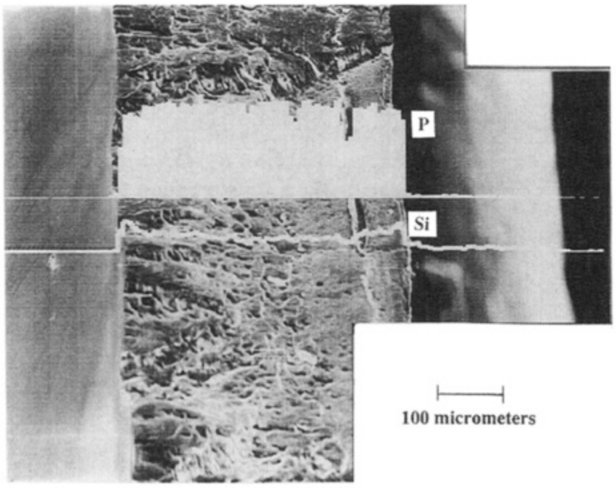

Figure 4. Cross section of sample **g**, showing silicon and phosphorus line profile analyses. Phosphorus levels did not vary significantly across the sample cross section. Silicon levels were increased in both upper and lower surface regions.

surfaces but also allowed the reaction depth to be measured. Sample **d**, which was treated for 24 h in a hexane solution of heptamethyltrisiloxane, showed a penetration depth of 35−60 μm. Sample **g**, treated for 24 h in a 2-propanol solution, showed significant surface enrichment of silicon to a depth of only 25−30 μm. Analysis profiles and X-ray elemental analysis count rate spectra are shown in Figures 2−4. The differing behavior in the presence of two different solvents (nonpolar hexane and polar 2-propanol) means that the degree of swelling of the polymer samples by the two solvents almost certainly differed. The modification of sample **g** can be considered more surface specific than that of sample **d** in the sense that the surface reaction of **d** was detected at a greater depth after the 24-h exposure time. However, careful examination of Figures 3 and 4 shows that the surface:bulk silicon ratio of sample **g** is much lower than that of **d**. In fact, the amount of silicon detected at the surface of **g** was only about twice that of the bulk value, which suggests that the relative amount of unsaturated groups that reacted with heptamethyltrisiloxane is quite low. This experiment was designed to monitor the depth of modification rather than the extent of reaction. However, the efficiency of the surface reaction under different experimental conditions clearly needs to be addressed in future work.

Experimental Section

Instrumentation. NMR spectra were obtained using a Bruker WP-360 MHz NMR spectrometer, with ^{31}P chemical shifts referenced to aqueous phosphoric acid.

Differential scanning calorimetry was carried out using Perkin-Elmer DSC-7 equipment. Samples (10−15 mg) were heated within an atmosphere of dry nitrogen in aluminum pans, with an empty aluminum pan as reference. The heating rate was 20 °C/min.

Electron microscopy was performed at the Electron Microscope facility for the Life Sciences in the Biotechnology Institute at the Pennsylvania State University. Energy-dispersive X-ray spectroscopy was carried out using a PGT IMIX version 7 X-ray analyzer attached to a JEOL JSM 5400 scanning electron microscope. Polymer films were fractured after dipping in liquid nitrogen. Smooth fracture surfaces were obtained. The film pieces were mounted edge-on onto aluminum stubs using conducting adhesive and were coated with carbon using a BAL-TEC SCD 050 sputter coater. Samples were scanned using an accelerating voltage of 20 kV at an angle of 30°.

Starting Materials. Poly(dichlorophosphazene) was synthesized by the thermal ring-opening polymerization of hexachlorocyclotriphosphazene at 250 °C.[30] 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 reaction were carried out under a stream of dry argon using standard Schlenk techniques.

Heptamethyltrisiloxane (Petrarch) was distilled and stored under dry argon. Tetramethyl-1,3-divinyldisiloxane−platinum complex (Petrarch) was used as received. 4-(Allyloxy)phenol was prepared by the reaction of hydroquinone with allyl bromide, as described previously.[29]

Synthesis of Polymers. Polymers with varying ratios of allyl functional side groups and either trifluoroethoxy or phenoxy cosubstituent groups were prepared by the nucleophilic replacement of chlorine in poly(dichlorophosphazene) by the sodium alkoxide and/or aryl oxide. The reaction conditions and purification procedures have been described in earlier work.[29] Polymers with unsaturated side groups were synthesized, purified, and modified by hydrosilylation reactions (Scheme 1). ^{1}H NMR assignments for the unsaturated substituent groups were: δ 7.7−6.6 (broad d, Ph), δ 6.0 (s, $-$CH=), δ 5.3 (d, =CH$_2$), δ 4.2 (s, $-$OCH$_2$). Protons assigned to trifluoroethoxy and phenoxy substituents were detected at δ 4.6−4.0 and δ 7.1−6.8 respectively. ^{1}H NMR assignments for the siloxane-containing substituent groups were δ 7.7−6.6 (br d, Ph), δ 3.9 (s, $-$OCH$_2$), δ 1.9 (s, $-$CH$_2-$), δ 0.7 (s, $-$CH$_2$Si), δ 0.1 (broad m, SiCH$_3$).

Surface-Specific Hydrosilylation Reactions. A 2.0 g sample of purified polymer **3**, $[NP(OCH_2CF_3)_{1.46}(OC_6H_4OCH_2CH{=}CH_2)_{0.54}]_n$, was dissolved in 10 mL of THF. The viscous solution was cast onto a Teflon sheet-coated mold. The film was allowed to dry for 3 days in a THF-enriched atmosphere and for a further 8 h under vacuum. The free-standing polymer film was cut into strips of approximate dimensions 10 mm × 20 mm × 400 μm. These films were exposed to heptamethyltrisiloxane dissolved in liquids which were nonsolvents for the polymer. The aim was to obtain surface-specific modification of the unsaturated polymer samples. Several different sets of reaction conditions were chosen. Six polymer films were immersed in a solution containing 3.5 g of heptamethyltrisiloxane and 100 mL of hexane, for varying periods of time both with and without the addition of 20 mg of tetramethyl-1,3-divinyldisiloxane platinum complex. The same process was repeated, substituting 100 mL of 2-propanol for hexane. All samples were agitated vigorously during the treatment using a mechanical shaker. After the specified length of time the samples were removed from the siloxane solutions and an extensive washing process was carried out. Each sample was washed a total of 12 times with either hexane or 2-propanol (the liquid corresponding to the reaction medium) with vigorous agitation (eight times), sonication (twice), and soaking periods of 16 h each (twice). Extensive washing was necessary to ensure that any unreacted, entrapped heptamethyltrisiloxane was removed since analysis for silicon would not differentiate between reacted and unreacted heptamethyltrisiloxane. The evacuation of samples within the SEM chamber would also help to remove any unreacted siloxane.

Surface Analysis. Smooth polymer films were obtained by spin casting THF solutions onto clean glass microscope slides at a speed of 2000 rpm. Contact angle measurements were obtained using a traveling microscope fitted with a Rame-Hart goniometer eyepiece. The contact-angle liquids (Aldrich) were all distilled under dry argon gas immediately before use, except for glycerol, which was used as received. Liquid drops were placed by means of a Gilmont syringe and a 24-gauge flat-tipped needle, inside an environmental chamber saturated with the vapor of the liquid in use. Contact angles were reported as the average of measurements taken from both sides of 10 liquid drops, where measurements were taken within 15 s of application. Values of the critical surface tension of wetting, γ_c were obtained by extrapolation of surface tension to $\cos \theta = 1$ for the plot of $\cos \theta$ against liquid surface tension.

X-ray photoelectron spectroscopy (XPS) was carried out at the Eastman Kodak Company, Rochester, NY. The takeoff angle was 35°, giving an approximate analysis depth of 50 Å into the polymer matrix. XPS detects electrons which are ejected from atoms near the surface of the material being analyzed. Electrons which are produced from deep within the sample are much less likely to reach the detector unscattered, although they may contribute to the background level at a lower kinetic energy value. The number of electrons which reach the detector decreases exponentially with depth. The signal is also dependent upon the angle of electron emission, the kinetic energy of the electron and the material through which it travels. Although XPS can provide extremely useful quantitative results, it is always necessary to consider possible sources of error. In the case of this work, the value of 50 Å for the surface penetration was simply an estimate which has shown to be reasonably accurate for many polymeric materials. The assumption was made that penetration was approximately the same for each of the three samples analyzed. However, the three polyphosphazene samples were of different elemental composition and therefore the exact analysis depth may have differed.[40]

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