Characterization of Bis-(phenoxy)phosphazene Polymers Using Radio Frequency Glow Discharge Mass Spectrometry

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ABSTRACT: A radio frequency glow discharge mass spectrometry (rf-GDMS) source is evaluated for future applications in the "fingerprint" characterization of polyphosphazene membranes. The rf-GDMS spectra of a series of bis(phenoxy)phosphazene polymers contain ions that originate from both the phosphazene backbone and the phenoxy moiety, resulting in signature ions of the polymer family. "Fingerprint" ions from the substituted R-group on the phenoxy moiety of the different derivatives allows the individual polymers to be distinguished from one another. The ability of the rf-GDMS source to characterize these materials directly in the solid state will be useful for the continued application of these polymers as separation membranes. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 76: 954–961, 2000

INTRODUCTION

Synthetic polymers, copolymers, and blends are presently used for a wide variety of membrane applications.[1,2] The vast majority of practical developments has occurred across the spectrum of organic polymers, including hydro- and fluorocarbon systems. One particularly interesting and versatile class of polymers, the polyphosphazenes, has an inorganic backbone structure consisting of alternating phosphorus and nitrogen atoms. These polymers are usually prepared by the thermal degradation of cyclic phosphazenes $(Cl_2PN)_3$ and $(Cl_2PN)_4$.[3,4] Because the chlorophosphazene polymer backbone is typically developed first, and chemical derivitization takes place in a later step, the number and type of polyphosphazene polymers are practically limitless.

The wide range of physical properties that can be generated through variations in the organic functional group has led to the use of the phosphazene polymers for numerous applications.[4–13] Some polyphosphazenes have high resistance to harsh chemical conditions and radiation, which leads to potential applications as membranes for environmental remediation and wastewater treatment. For example, Peterson and co-workers have observed polyphosphazene membranes to be effective for the separation of acidic gases from various waste streams in severe, chemically aggressive surroundings.[5] The application of these membranes has been extended to the separation of chlorinated hydrocarbons from water and air.[6] In addition, this class of polymers has a wide potential as biomaterials for the replacement of living tissue and as carriers for biologically active agents.[7–13] Finally, derivatized phosphazene polymers have begun to find use as structural materials. For example, a group of fluorinated phosphazene elastomers [poly(fluoroalkoxy-phosphazenes)] has been developed as a replacement for

fluorosilicones because of their ability to maintain damping and flexural integrity at temperatures down to −65°C.[13] With the growing number of new applications, there has developed an increased interest in understanding the interactions between the polymeric surfaces and their surrounding media.

As with the case of most polymer systems,[14,15] a large array of analytical methodologies have been employed to characterize the structure and reactions of polyphosphazene materials.[4] Particularly in the cases of film and membrane-form materials, differences in methods exist for "surface" and "bulk" characterization. When attempting to characterize the performance of membrane structures, such as those employed in chemical separations, sensitivity is a key issue. Of the surface sensitive analytical methods, such as Fourier transform infrared spectroscopy (FTIR) in the attenuated total reflectance mode, secondary ion mass spectrometry (SIMS), and X-ray photoelectron spectroscopy (XPS), only SIMS seems to have been applied for the surface characterization of phosphazene polymers.[16] SIMS has been applied for direct solids analysis of a number of polymers.[16–28] This is in contrast to the quickly evolving matrix-assisted laser desorption ionization (MALDI) method, which requires dissolution of the polymer sample and mixing with a specific photon-absorbing matrix species.[29–31] Only the direct analysis of solid polymers holds the potential for obtaining contaminant-free and depth-resolved mass spectra.

Secondary ion mass spectrometry employs ion/neutral particle bombardment to sputter the polymer into the gas phase, with the subsequent mass analysis of charged fragments. However, problems result when employing SIMS for the analysis of electrically insulating samples (such as many polymers). Under the influence of particle bombardment, the surface of a nonconducting material becomes charged such that both the acceleration of the primary ion beam and the energies and trajectories of the emitted secondary particles are affected. Overall, this leads to detrimental effects on the quality of secondary ion spectra and can completely degrade the analyte signal.[20] A variety of methods and techniques have been applied to reduce or compensate for this problem, including placement of a conductive mesh onto the surface,[21] primary beam modulation,[22] alternating bombardment of the surface with negative ions or neutral particles,[23] and simultaneous bombardment by electrons and positive primary

ions.[18,19,24–26] In any case, the use of charge compensation methods can make SIMS a powerful method for analysis of polymers. Although SIMS has matured with regard to polymer characterization, it is safe to say that it is not a "routine" tool at this point.[14,15]

Relevant to the work here, Groenewold and co-workers have employed static SIMS for the analysis of the same series of substituted bis-(phenoxy)phosphazene polymers.[16] Those researchers utilize a perrhenate (ReO_4^-) primary ion gun to sample the topmost layers (although no actual sampling depth is provided) of the polymer film samples efficiently. Pulsed secondary ion extraction is used to alleviate surface charging and allow almost simultaneous acquisition of anion and cation spectra.[20,27,28] In this approach, the polarity of the secondary ion extraction voltage is rapidly reversed to yield a balanced emission of positive and negative ions, resulting in a relatively neutral sample surface. The pulsed secondary ion extraction technique, when employed with SIMS, is noninvasive (i.e., no sample manipulation) and applicable to most materials, making it a viable method for the analysis of polymeric membranes.

Radio frequency glow discharge mass spectrometry (rf-GDMS) has recently been demonstrated by this laboratory to be a potentially powerful method for the bulk and depth-resolved analysis of polymeric materials and films.[32–35] In this technique, low-energy argon ions (~20–100 eV) produced in the negative glow region of the plasma sputter the polymer surface, resulting in the liberation of neutral fragment species. The secondary neutrals are then ionized in the negative glow region of the GD by collisions with either electrons or argon metastable atoms. This method is analogous to secondary neutral mass spectrometry,[36] except that the low pressure (~0.1 Torr) plasma inherently performs both the ablation and ionization steps. Unlike SIMS, the rf-GD plasma naturally supplies the charge compensation process needed for the analysis of nonconductive materials as the polarity of the potential applied to the sample surface alternates at a frequency of 13.56 MHz.[37]

Previous work from this laboratory has demonstrated the ability of the rf-GD source to produce mass spectra similar to static SIMS for both fluoro- and hydrocarbon polymeric materials (i.e., low mass fragments of backbone and side chain entities).[32,35] However, the rf-GDMS technique yields higher analyte beam currents (~10^{-9} A)

and shorter analysis times ($\sim$ 20 min) than static SIMS for the bulk analysis of these polymers. In addition, cryogenic cooling of polymer samples during rf-GDMS analysis increases the scope of applicability of this technique to thermally sensitive materials, such as polyethylene films.[33] The technique has also been shown to be very reproducible, with the use of internal referencing of characteristic fragments of fluoro- and hydrocarbon polymers yielding variations of <5% RSD for multiple analyses.[35] Finally, as with SIMS, the sputter ablation step permits the depth-resolved analysis of polymers, with typical sputtering rates of 0.1–1.0 μm/min and depth resolving powers on the order of 50 nm. Theore, the technique does not provide the level of absolute surface sensitivity or depth resolution realized in SIMS.

In the present study, we describe the use of a cryogenically cooled sample holder with an rf-GD mass spectrometry source for the analysis of polymeric membranes, specifically polyphosphazene derivatives. Three polyphosphazene membranes are characterized with the intention of determining fragmentation patterns within the series of polymers as well as prominent signature ions to differentiate structural variations in the side groups. The ability to distinguish completely the structures of these polymeric membrane materials, in the solid state, and in a rapid fashion will be useful in support of the application of these polymers as separation membranes.

EXPERIMENTAL

Instrumentation

The mass spectrometric measurements for each of the polymer samples were performed on a commercial quadrupole GDMS system (VG GloQuad, VG Elemental, Winsford, Cheshire, England). Several modifications were necessary for the coupling of a flat sample rf-GD ion source to this instrument. The construction of the flat-type sample holder and direct insertion probe (DIP) has been described in detail previously.[38,39] In brief, the original dc source interface was replaced with an interlock chamber faceplate equipped with a 12.5 mm compression fitting. The DIP was passed through the compression fitting and an 8 cm diameter flat sample holder assembly was mounted on the end of the DIP. Several modifications to the existing flat-type sample holder assembly were necessary to provide for additional cooling of poly-

mer samples.[33] In summary, a copper coolant block was placed behind the sample, which allowed for the passage of liquid nitrogen (LN$_2$) to cool the sample to temperatures of approximately -170°C.

Procedures.

A series of polyphosphazene derivatives supplied by the Idaho National Engineering Lab, Idaho Falls, ID, were examined by rf-GDMS. The poly-[bis(phenoxy)phosphazene] (PPOP) and poly-[bis(ethyl 4-carboxylatophenoxy)phosphazene] (EtO$_2$C-PPOP) were dissolved in a 5% w/v solution in tetrahydrofuran, and the poly[bis(4-methoxyphenoxy)phosphazene] (MeO-PPOP) was dispersed in 5% w/v solution in 1,4-dioxane. The samples for the rf-GDMS analysis were prepared by coating stainless steel targets (2.54 $\times$ 2.54 cm squares) with the polymer solutions and allowing the solvent to evaporate. The coated material was then soaked in hexane for 2 hours to remove contaminants. This is the same sample preparation procedure described by Groenewold and co-workers for their SIMS analyses.[16] The final films were uniform in thickness ($\sim$0.8 mm), corresponding to multiple layers on the surface of the target.

The discharge conditions for this study were held constant at a radio frequency power of 20 W and a discharge gas pressure of 0.1 mbar Ar. Radio frequency power was supplied by a 13.56-MHz generator and was impedance matched by an automatic matching network (Models RF-5s and AM-5, respectively, RF Power Products, Voorhees, NJ). The reported mass spectrometric data were acquired in the MASSCAL mode of the VG GloQuad system, wherein the spectra were recorded in the sequential fashion (4-242 Da, 12.5 pts/Da). The temporally resolved spectra data were acquired in the RUN (integrated peak hopping) mode. In this system, high ion currents ($>10^{-12}$ A), resulting from discharge gas and major fragment ions were measured on a Faraday plate detector; whereas, lower intensity signals were detected on an ion multiplier.

RESULTS AND DISCUSSION

The three derivatives of phenoxypolyphosphazene depicted in Figure 1 are the focus of this study. For all three polymers, the rf-GDMS spectra contain ions from both the P = N backbone and the pendant aromatic groups. Differences in
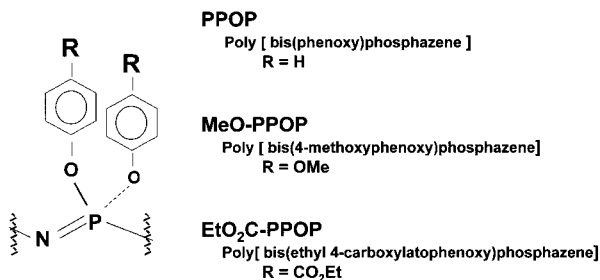
PPOP
Poly [bis(phenoxy)phosphazene]
R = H

MeO-PPOP
Poly [bis(4-methoxyphenoxy)phosphazene]
R = OMe

EtO$_2$C-PPOP
Poly[bis(ethyl 4-carboxylatophenoxy)phosphazene]
R = CO$_2$Et

Figure 1 Structures of bis-(phenoxy)phosphazene polymers investigated in these studies.

the mass spectra between the three derivatives originate from the subtle variations in the R-group on the pendant aromatic moieties. The most complex derivative, poly[bis(ethyl 4-carboxylatophenoxy)phosphazene] (EtO$_2$C-PPOP), clearly yields the most distinctive spectra from that of the simple hydrogen substituted PPOP. However, significant differences are also present for the second member of the substituted series (poly[bis(4-methoxyphenoxy)phosphazene] (MeO-PPOP).

Because the baseline for this polymer series is represented by the hydrogen substituted PPOP, its rf-GD mass spectrum is shown in Figure 2. All of the relevant information for the PPOP polymer is contained in the mass range of 4–160 Da, which is also the case for the other two derivatives. The higher current signals of the argon discharge gas as well as some background hydrocarbon (C$_2$H$_X$, where X > 2) and water-related species, were detected on a Faraday plate. Lower ion currents resultant from the N=P backbone and aromatic pendant group ions were detected with the ion multiplier.

Four distinct series of ions containing N, P, and O are observed in the rf-GDMS spectrum of each of the three polymers. These fragmentation series constitute a signature for the phosphazene polymers, because the ions originate from the phosphazene backbone. The proposed compositions of three of the series, which contain only N and P, are NH$_W$PH$_X^+$, NH$_W$PH$_X$NH$_Y^+$, and NH$_W$PH$_X$NH$_Y$-PH$_Z^+$, where both W and X are between 0 and 3, Y is from 0 to 2, and Z is either 3 or 4. The formation of saturated ion species is not unexpected, because sputtering of the polymers would yield some amount of free H atoms on the film surface and in the gas phase. In addition, the spectrum indicates that adventitious water, likely absorbed from the atmosphere, is being released from the film as well. Another signature ion fragmentation

series originates from the backbone of the phosphazene polymers and contains N and P, as well as O. This succession falls in the 130–132 Da range. The base structure for these fragments is suggested as NH$_W$P(OH)$_2$H$_X$NH$_Y$PH$_Z$ (where X and Y are either 0 or 1, and W and Z add to 6). Other compositions are possible for some of the ions; however, these are expected to be the most stable fragments.

The relative stability of the proposed structures is supported by the strengths of the respective P—N, P—O and C—O bonds as derived from infrared spectroscopy measurements.[40,41] Those data indicate, not surprisingly, that the respective single and double P—N bonds of the backbone are the strongest in the system; whereas, the respective pendant linkages (P—O and C—O) are much weaker. Groenewold and co-workers used these trends to explain the response of pendant fragments' signals in their SIMS analyses, which
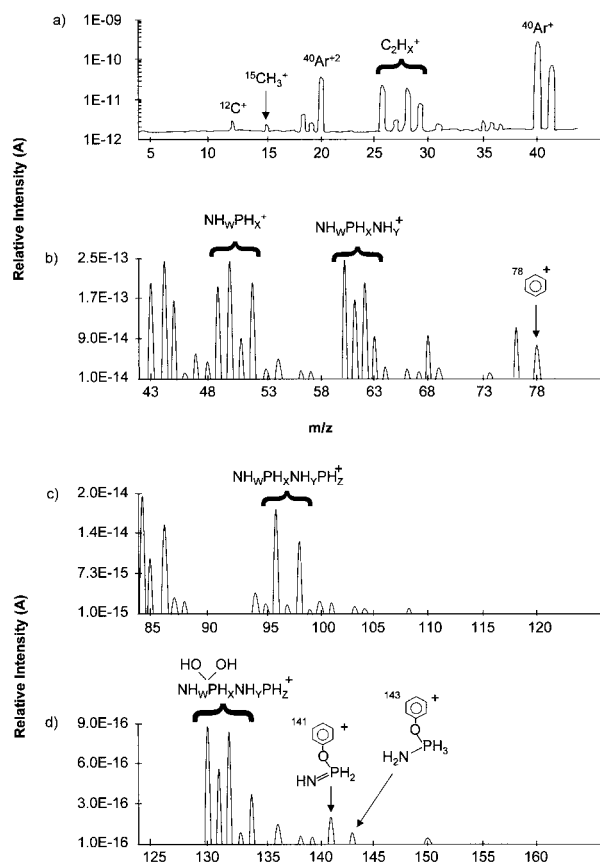

Figure 2 rf-GDMS mass spectrum of poly[bis-(phenoxy)phosphazene] sample. Note that signal intensity scale in a) is logarithmic, whereas, b–d) are in linear units of amps. rf power = 20 W, Ar pressure = 0.1 mbar.

decay far faster in the analysis cycle than back-bone species.[16] They reasoned that loosely bound pendant groups were more easily sputtered and most likely originated from the uppermost regions of the polymer films. The ion beam intensities for the proposed fragment compositions in the rf-GDMS spectrum of PPOP (Fig. 2) and the other derivatives seem to correlate very well with the bond strengths. For example, the lower mass N and P series has the greatest ion signal intensities, with the highest mass N and P arrangement having the lowest ion beam currents. Even less abundant ion signal intensities are found when there is a P—O bond, such as in the 130–132 Da series. Finally, another signature combination for the phosphazene polymers is derived from the phenoxy moiety and the phosphazene backbone at 141 and 143 Da. The ion beam currents for these ions are substantially less than the other characteristic ions of the phosphazene polymers, which could be related to the C—O bond being the weakest.

As described above, temporal variations among the various signature ions in the SIMS spectra of Groenewold are cited as being indicative of the physical location of particular chemical species in the polymer film (e.g., side groups located toward the film surface).[16] In actuality, all of the observed secondary ions showed a decay in intensity with sputtering time. Three possible mechanisms were suggested to explain the over-all behavior: (1) surface charging under ion bombardment, (2) surface contamination, and (3) diffusion within the polymer. Ratioing of characteristic ion intensities indicated that the decay was 2–4 times faster for pendant groups than backbone species, suggestive of their perential location at the film surface. Just as in the case with SIMS, sputtering in the rf-GD system effectively yields a depth profile of polymer constituents. By the same token, temporal trends can be indicative of contamination or other such effects as in SIMS. Figure 3 presents the temporal profiles for characteristic ions (identified in Fig. 2) for a film of the MeO-PPOP species. As can be seen, all of the fragment ion signals show a slight (<25%) decrease in intensity over the first 10–20 minutes of sputtering. There are no appreciable differences in the responses of backbone or pendant species. It is important to note that the sputtering rates for polymer films in rf-GDMS under these conditions are on the order of 0.1 μm/min, and so any surface segregation of the sort claimed by Groenewold et al. would not be apparent here. An additional
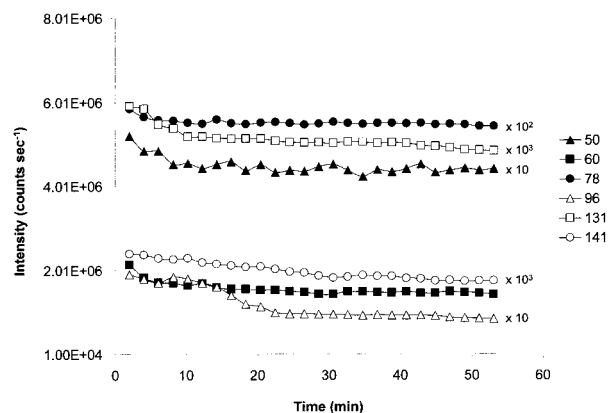

Figure 3 Temporal profile of characteristic ion fragments from the mass spectrum of a poly[bis-(4-methoxyphenoxy)phosphazene] sample. rf power = 20 W, Ar pressure = 0.1 mbar. Representative group assignments as in Figure 2.

point to note is the high level of temporal stability (<5 % RSD) once the plasma has reached a steady state. This is very important in the case of profiling layered polymer systems or where selective doping has occurred.[42] This is also an important trait for cases where high levels of sensitivity are required.

Previous studies of the use of rf-GDMS to characterize fluoro- and hydrocarbon polymers have illustrated a high level of reproducibility and the ability to differentiate between members in homologous series (e.g., polyethylenes) based on characteristic ion ratios.[35] For all of the phosphazene polymer samples, the rf-GDMS cation spectra yield a characteristic series, which develops a signature for this class of polymeric membranes. This signature includes ions originating from both the phosphazene backbone and the phenoxy moiety attached to the phosphazene backbone. Table I illustrates the trend between the three derivatives of the phosphazene polymers and the ion signal intensities for representative signature ion fragments of the various analogs obtained under the same discharge conditions. The similarity of the ion beam currents for each prominent fragment between the three derivatives is quite striking. The greatest discrepancy between the ion beam currents is found for the hydroxylated fragment ($^{132}N_2P_2H_7(OH)_2^+$), and even then the difference is fairly small when comparing separate samples studied on different days. Thus, the excellent reproducibility between the different derivatives, as well as sample-to-sample precision, of the phosphazene polymer family for the signa-

Table I   Ion Intensities (A) of Prominent Fragments of Phosphazene Polymers

	$^{50}NH_2PH_3^+$	$^{60}NPNH^+$	$^{96}NPHNHPH_4^+$	^{132}HO OH $\backslash$ $/$ $NH_2PNHPH_4^+$	$HN \diagup PH_2$
PPOP	2.3E-13	2.4E-13	1.8E-14	6.0E-16	2.0E-16
MeO-PPOP	2.5E-13	2.5E-13	1.8E-14	3.5E-16	3.0E-16
EtO$_2$C-PPOP	2.5E-13	2.5E-13	1.5E-14	6.0E-16	3.0E-16

ture ion signal intensities holds great promise for the rf-GDMS approach of polymer fingerprint analysis.

A signature of cation species for this polymer series is not present in the secondary ion mass spectrometry (SIMS) spectra for the three polymers,[16] where, with the exception of PPOP, the cation spectra of the other derivatives contain no ions originating from the polymer backbone. Although useful fragment ion information is obtained from the cation spectra generated by SIMS, most of the species in the spectra were nonspecific hydrocarbons. On the other hand, the SIMS anion spectra did yield ions originating from both the pendant aromatic moieties and the phosphazene backbone; however, the abundance of these signature fragments were not consistent from one derivative to another. For example, the most dominant characteristic anion species, phenoxide, of the PPOP and EtO$_2$-PPOP polymers was not even present in the SIMS anion spectrum of MeO-PPOP. Thus, it would be difficult to classify this series of polymeric membranes together based on the proportions of dominant ions.

Because a wide range of properties, and thus applications, can be affected by slight variations in the chemical structure of a polymer, it is not only essential to characterize a given class of polymers by an analytical technique, but also to distinguish subtle differences in a polymer series. The phosphazene polymers in this study are an excellent example of this scenario, because the polymer main chain is consistent and structural changes are only found in the aryl ether pendant groups. In addition to specific mass spectrometric differences among functionalized family members, selective chemistries might also be used to differentiate their identities. For example, Groenewold and co-workers found the polymer deriv-

ative, EtO$_2$-PPOP, to absorb tributyl phosphate (TBP) readily; however, the other polymer derivatives were incapable of producing a significant TBP SIMS signature.[43] By distinguishing the individual polymers by their surface chemistry, there may be an improved understanding of the solute/polymer interactions.

Chemical differences between the three phosphazene polymers originate from the pendant aromatic moieties. Figure 4 shows the respective signal responses for five prominent fragment ions generated by rf-GDMS for each of the three derivatives. In general, the PPOP polymer has the least abundant ion intensities for the monitored side-chain fragments; whereas, the most complex derivative, ETO$_2$C-PPOP, has the highest total current for pendant fragments, with the MeO-PPOP polymer registering somewhere in between the two ends of this series. In Figure 4, the 46 and 74 Da monitored ions are completely composed of
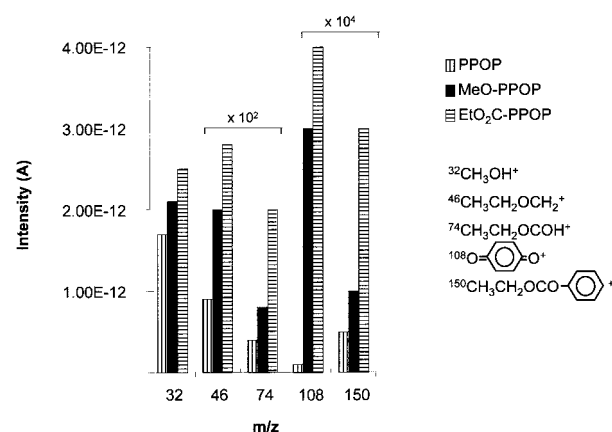

Figure 4 Ion signal intensities of prominent fragments for bis-(phenoxy)phosphazene polymer derivatives.

parts of the R-group of the ETO$_2$C-PPOP derivative; therefore, the intensities of these fragments are naturally highest for this species. Clustering and recombination of sputtered species and atoms is common in low-pressure plasmas,[44] resulting in the presence of ions of the same mass in the other two derivatives. This is also the case for the methanol ion monitored, where fragmentation and agglomeration occurs for the PPOP polymer. The final two distinguishing ions of the phosphazene polymers contain the aromatic group. The 108 Da species is drastically enhanced for the two species containing an O atom in the R-group, where very little is present for the PPOP derivative. This is also the case for the SIMS anion spectra of the three derivatives.[16] Although recombination and clustering play roles in the abundance of the prominent ions, the cumulative data of Figure 4 quite clearly point to the ability of the rf-GDMS to distinguish among this polymer series.

CONCLUSIONS

Previous laboratory studies have shown that radio frequency glow discharge mass spectrometry could be applied advantageously for the direct analysis of polymeric materials. Use of this technique permits direct analysis of polymeric membranes, specifically polyphosphazene derivatives. The surfaces of three polyphosphazene membranes were characterized, and fragmentation patterns within the family of polymers were identified. Prominent signature ions to differentiate the subtle variations in the side groups were also determined. The ability to distinguish completely these polymers as a class of polymeric membrane films, yet differentiate the derivatives among themselves will be useful for the application of these polymers as separation membranes.

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