A NEXAFS Examination of Unsaturation in Plasma Polymers of Allylamine and Propylamine

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Near edge X-ray absorption fine structure (NEXAFS) has been employed to provide insight into the chemical nature of nitrogen in deposits formed from plasmas of allylamine and propylamine. The nitrogen K-edge spectra of these materials unambiguously demonstrate the presence of significant quantities of sp or sp^2 hybridized nitrogen. This finding, in conjunction with carbon K-edge spectra, strongly indicates that there is a substantial level of dehydrogenation during the plasma polymerization process resulting in the formation of imine groups and, at high power, nitrile groups in addition to sp^3 hybridized amines. Comparison with standard polymers indicates that amide formation (following a few days exposure to atmosphere) is negligible. These findings suggest that the hydrolysis of aminated plasma polymers may be important in their long-term aging.

Introduction

The use of aminated surfaces in biotechnology is widespread. One route to the production of such surfaces is the plasma polymerization of organic amines, in particular, allylamine. It has been demonstrated that plasma polymerized allylamine may be employed to enhance the binding of negatively charged macromolecules, such as DNA,[1,2] to bind polysaccharides[3] and poly(ethylene glycol)[4] via imine (Schiff base) coupling, as a substrate for the culture of neuronal cells[5] and to enhance the sensitivity of antibody-based assays.[6,7] In these applications the allylamine plasma polymer is required either to have a high proportion of aliphatic amines (so that it becomes positively charged in aqueous media) or a high proportion of primary or secondary amines (for imine or enamine coupling). It is of additional importance in these applications that the plasma-polymerized allylamine is stable in the aqueous environment. In many respects these two requirements are antagonistic and attempts to increase the density of functional amine groups, by lowering the average power input, can lead to films which are soluble in aqueous media.[1]

The degree of functional retention in plasma polymers of allylamine is, in itself, somewhat difficult to determine. The commonly employed methods of X-ray photoelectron spectroscopy (XPS) and infrared spectroscopy (IR) do not easily distinguish between the different chemical species which may be present. This is a matter of some importance, because chemical groups which may be formed during plasma polymerization can severely impact upon the performance of the resulting surface, without such changes being detectable by XPS or IR. The binding energy of the N 1s peak (399.2 eV)[8] in XP spectra of allylamine plasma polymers effectively rules out the possibility of protonated amines, quaternary ammonium, or oxides of nitrogen (it should be noted that some oxygen is incorporated into plasma polymers on exposure to air). Chemical shifts within the C 1s envelope are difficult to extract informa-

tion from, although there is strong evidence of the presence of either iminic nitrogen or nitriles as well as amines[8,9] (C−N ~286 eV,[10] C=N estimated at ~286.5 eV,[8] C−C≡N ~286.4 and 286.7 eV[10]). IR spectra given in the literature[1,2,8,11] are all similar, showing N−H stretches at ~3300 cm^{-1}, aliphatic C−H stretches at ~2950 cm^{-1}, a nitrile (or possibly alkyne) stretch at ~2200 cm^{-1}, and a strong absorption at ~1670 cm^{-1}. This latter peak may contain contributions from imines, alkenes, amides, aromatic structures, and N−H bending vibrations. The nitrile absorption is quite weak and previously it has not been thought that this group was present in high concentrations;[8] however, it is worth noting that aliphatic nitriles absorb weakly,[12] and there may therefore be a significant presence of these groups. It is furthermore worth noting that there appears to be an increase in the intensity of the nitrile absorption with increased duty cycle (average power) in pulsed plasmas.[1]

Table 1 lists a number of possible environments for nitrogen which cannot be unambiguously eliminated on the basis of XPS and IR data. Excluded from the list are species such as hydrazines, azos, and azides which are highly reactive and unlikely to persist in the energetic plasma environment. The absence of aromatic and vinylic C−H stretches (~3010 cm^{-1}) in IR spectra of these materials means that aromatic amines, pyridines, and pyrroles are somewhat unlikely unless these species are highly substituted (i.e. part of a highly cross-linked environment). Comparison of the relative basicities and ability to undergo imine coupling suggests that the presence of any group except aliphatic amines is detrimental to the utility of the plasma polymer. Additionally the presence of significant unsaturation may give rise to fluorescence in the films, which would limit the application of these materials for a number of biochemical assays. Interestingly, all of these groups *except* the aliphatic amines would be expected to give strong and sharp features in near edge X-ray absorption fine structure (NEXAFS) spectroscopy due to the presence of local π bonding. Within this study we examine the potential role of NEXAFS in characterizing the nitrogen chemistry of amine-containing plasma polymers.

NEXAFS (also known as XANES: X-ray absorption near edge spectroscopy) spectra are obtained by monitoring the

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TABLE 1: Putative Nitrogen Containing Groups in Plasma Polymers of Aminated Monomers

Name	Structure	pK_b	Imine coupling
Aliphatic amine	-C-NR$_2$	4 to 5	Primary (imine) Secondary (enamine)
Aromatic amine	Ph-NR$_2$	~10	Primary (imine) Secondary (enamine)
Imine	-C=N-R	~10	No (Hydrolysis may give primary amine)
Enamine	C=C—N (C, C)	~10	No (Hydrolysis gives secondary amine)
Pyrrole	N-R	~14	No
Pyridine	N	~9	No
Nitrile	R-C≡N	NA	No
Amide	-CO-NR$_2$	NA	No

absorption of X-rays as a function of energy close to a core level excitation energy. Absorption is found to occur when the photon energy can promote the core electron to an unoccupied valence orbital. In this case, we are examining the carbon K edge (1s ~285 eV) and the nitrogen K edge (1s ~400 eV). Strong absorptions occur when the symmetry of the valence orbital is optimal, and sharp absorptions occur when the valence orbital energy corresponds to a bound state. In organic polymers these conditions are best met when there is a π* orbital associated with the atom (i.e. when it exhibits sp or sp^2 hybridization). A recent review has been published that provides carbon K edge NEXAFS spectra from a number of common polymers,[13] and nitrogen K edge spectra for some organic standards have been published as part of a study of carbonized polymers[14] and asphaltenes.[15] Studies by Castner et al. have illustrated the orientation of −(CF$_2$−CF$_2$)− chains in tetrafluoroethylene glow discharge films. The theme of investigating the retention and orientation of functional groups has until now been the main focus of NEXAFS studies on plasma polymers.[16,17]

Experimental Section

Plasma polymers of allylamine and propylamine were prepared on 1-cm^2 pieces of silver foil, which had been previously cleaned in a Bunsen flame. The apparatus for plasma polymerization comprised a 30 cm length glass reactor with stainless steel flanges and an external copper coil electrode.[9] The reactor was evacuated with a rotary pump with liquid nitrogen cold trap and the base pressure was approximately 10^{-3} mbar. For all plasma polymers studied here a flow rate of 4 cm^3 min^{-1} (STP) was used, which corresponded to a monomer pressure of 3 × 10^{-2} mbar. Depositions were carried out over 15 min, and additional samples made for XPS analysis.

XPS. XPS was performed on a VG CLAM2 spectrometer with a (nonmonochromated) Mg Kα source. Survey scans were taken at a pass energy of 100 eV and core level spectra at 20 eV. Elemental compositions for these films were calculated by using peak areas from the survey scans and experimentally derived sensitivity factors; in most instances small features due to the silver substrate were observed, indicating that the films were of the order of 10 nm thick. Core level spectra were fitted with Gaussian−Lorentzian curves according to a protocol described previously.[6]

Poly(isopropylacrylamide) (pIPAAm, synthesized in our laboratory), polyethyleneimine (pEI, Aldrich), polystyrene (Aldrich), and polyallylamine hydrochloride (pAAHC, Aldrich) were spin cast as thin films from appropriate solvents onto clean silver foil as standard materials for this investigation.

NEXAFS. NEXAFS experiments were performed on beamline BL1.1 of the Synchrotron Radiation Source (SRS) at Daresbury Laboratory. The SRS operated at 2 GeV with a ring current of between 100 and 250 mA. BL1.1 utilizes a dipole bending magnet and has three spherical grating monochromators; for this work we employed the low-energy Au grating with 1050 lines/mm and the exit slit (situated at 6.38 m from the monochromator) was set to a width of 0.4 mm. These settings give an energy resolution of better than 150 meV at a photon energy of 285 eV and better than 300 meV at 400 eV. Spectra were acquired under high vacuum (10^{-7} to 10^{-8} mbar) by using an end chamber equipped with sample manipulation, hemispherical electron energy analyzer, and partial yield detector (a channeltron mounted behind a biased mesh). XPS spectra were acquired at a photon energy of 600 eV to ensure that there was no contamination or any evidence of the silver substrate. It was found that the films were thin enough to obviate the need for charge compensation, yet thick enough that Ag 3d photoelectrons were undetectable at this photon energy. XPS spectra obtained in this manner were consistent with data obtained using the laboratory instrumentation described above. NEXAFS spectra were acquired by stepping the photon energy in a 40 eV range through the relevant K edge energy, typically starting 5 eV below the edge, with a step size of 0.1 eV. Absorption was monitored with electron yield detection. Three modes of detection were employed: total, partial, and Auger yields. The total electron yield (TEY) was monitored from the drain current from the sample. The partial electron yield (PEY) detector counts electrons that are emitted above a predefined energy, 220 eV for carbon K edge and 330 eV for nitrogen K edge. Auger electron yields (AEY) were obtained by using the hemispherical analyzer to monitor electron emission at the C KLL energy of 252 eV for carbon K edge and N KLL energy of 370 eV for nitrogen K edge. The three modes have different depth sensitivities which increase in the order AEY < PEY < TEY, so that differences between the spectra indicate a compositional variance with depth into the film. Figure 1 demonstrates that there is little qualitative difference between the three modes, and we select PEY for the remainder of the paper on the basis that AEY suffers from low counts (and hence some noise, evident in Figure 1) and there is some danger that with TEY a contribution from contaminants on the silver surface may appear.

Spectra were normalized to the X-ray flux, which was monitored from the I_0 foil. Photon energy calibration was performed by aligning the features in the I_0 traces to obtain a relative energy calibration of better than 0.1 eV between traces. The maximum energy difference between traces was found to be 0.5 eV, which is primarily due to changes in beam position during refills and the temperature of optics during each acquisition. The carbon K edge spectra were then calibrated to the sharp 1s−π* transition in polystyrene (spectrum not shown) which was set at 285.2 eV. This compares to values taken from

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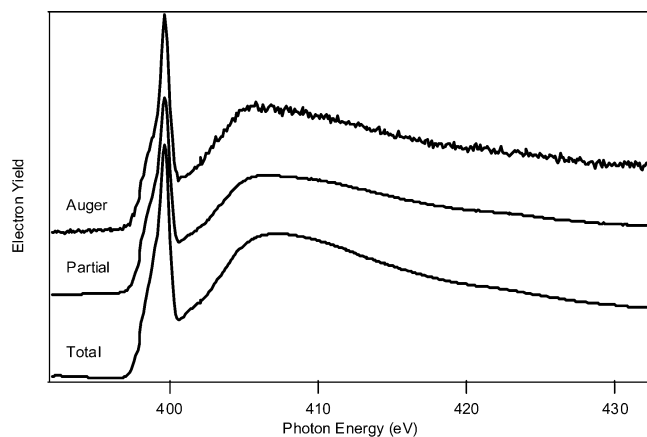
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Figure 1. Comparison of N K edge NEXAFS spectra obtained from a 5 W allylamine plasma polymer with Auger, partial, and total electron yields.

TABLE 2: Summary of XPS Results from Plasma Polymers Used in This Study[a]

monomer	power (W)	C (%)	N (%)	O (%)	HC (% C)	C−N (% C)	C=N (% C)	C=O (% C)
AA	2	73	22	5	60	12	22	6
AA	5	74	19	7	60	14	20	6
AA	20	80	14	6	61	12	22	5
PA	2	79	18	3	63	16	16	5
PA	3	80	18	2	63	17	16	4
PA	5	80	18	2	66	15	16	3
PA	20	78	20	2	60	14	24	2

[a] AA = allylamine, PA = propylamine. Atomic concentrations were obtained from survey scans and carbon environments from C 1s narrow scans. Note that the C=N peak may also include contributions from C−O and both carbons in the C−C≡N environments.

the literature of 285.2 eV[17] and 285.18 eV for poly(α-methyl styrene),[13] although a value of 284.7 eV has also been reported.[18] The mean energy offset was found to be 1.5 eV, which corresponds, through use of the grating equation for first-order diffraction (eq 1),[19] to an angular offset at the grating of 0.011°. For this beamline θ, which is half the angle between the entrance and exit slits, is 86°, d is the distance between lines on the grating, and β is the angle between the grating normal and the exit slit.

$$\lambda = 2d \cos\theta \sin(\theta + \beta) \qquad (1)$$

At the nitrogen K edge (400 eV) this angular offset corresponds to an energy shift of 2.9 eV, which was used to shift internally calibrated spectra for lack of a suitable reference material. Therefore the carbon K edge data presented here have absolute calibration to within 0.1 eV; however, the nitrogen K edge data, while internally consistent in energy calibration to within 0.1 eV, are not absolutely calibrated to the same accuracy.

Curve fitting was performed with use of Gaussian peaks and an error function to represent the edge step.[20] While this procedure does not produce perfect fits to the data because of the asymmetry of NEXAFS peaks, it does give a reasonable approximation for the sharp peaks below the edge step which are the features of importance in this study. The data had a constant background subtracted (taken as the signal at photon energies below any NEXAFS features) and multiplied by a factor so that the signal (with background removed) at photon energies higher than any distinct features (315 eV for carbon and 435 eV for nitrogen) was unity. In this manner a comparison of peak areas between datasets could be made, since an increase in a peak area should then correspond proportionally to an increase in the fraction of atoms in the environment associated with that peak.

Results

The elemental compositions and the chemical environment of carbon from the plasma polymers were obtained with XPS, and the results are summarized in Table 2. A typical peak fit of the C 1s envelope is provided in Figure 2, the limitations of which are discussed in the Introduction. It is notable that propylamine plasma polymers demonstrate negligible changes in elemental composition as the power is increased, whereas allylamine plasma polymers exhibit a marked decrease in nitrogen content. Also apparent is a generally higher oxygen incorporation into allylamine plasma polymers. The C 1s profiles of allylamine plasma polymers show almost no change with power, which is difficult to reconcile with the drop in nitrogen content. Similarly, polymers formed from propylamine at low
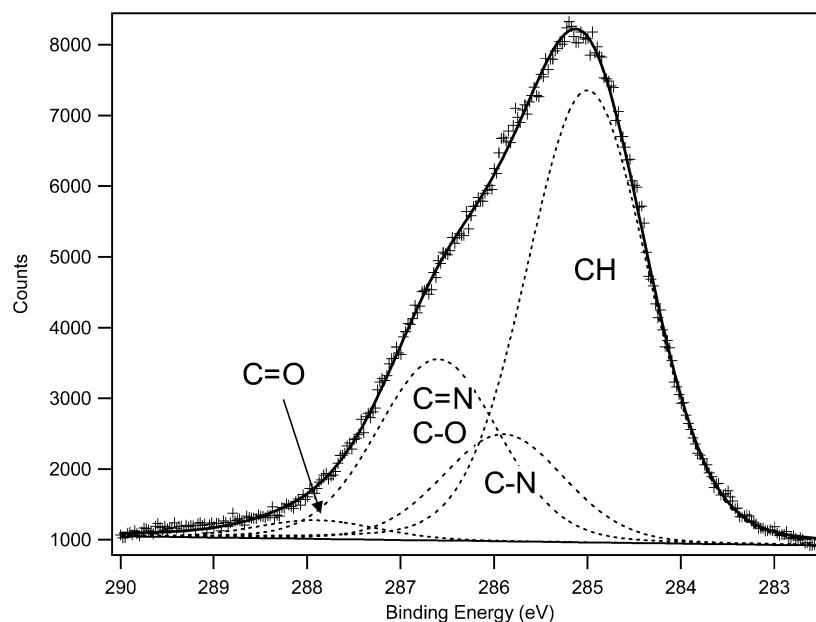

Figure 2. Example curve fit of the C 1s XPS spectrum for the 20 W propylamine plasma polymer.

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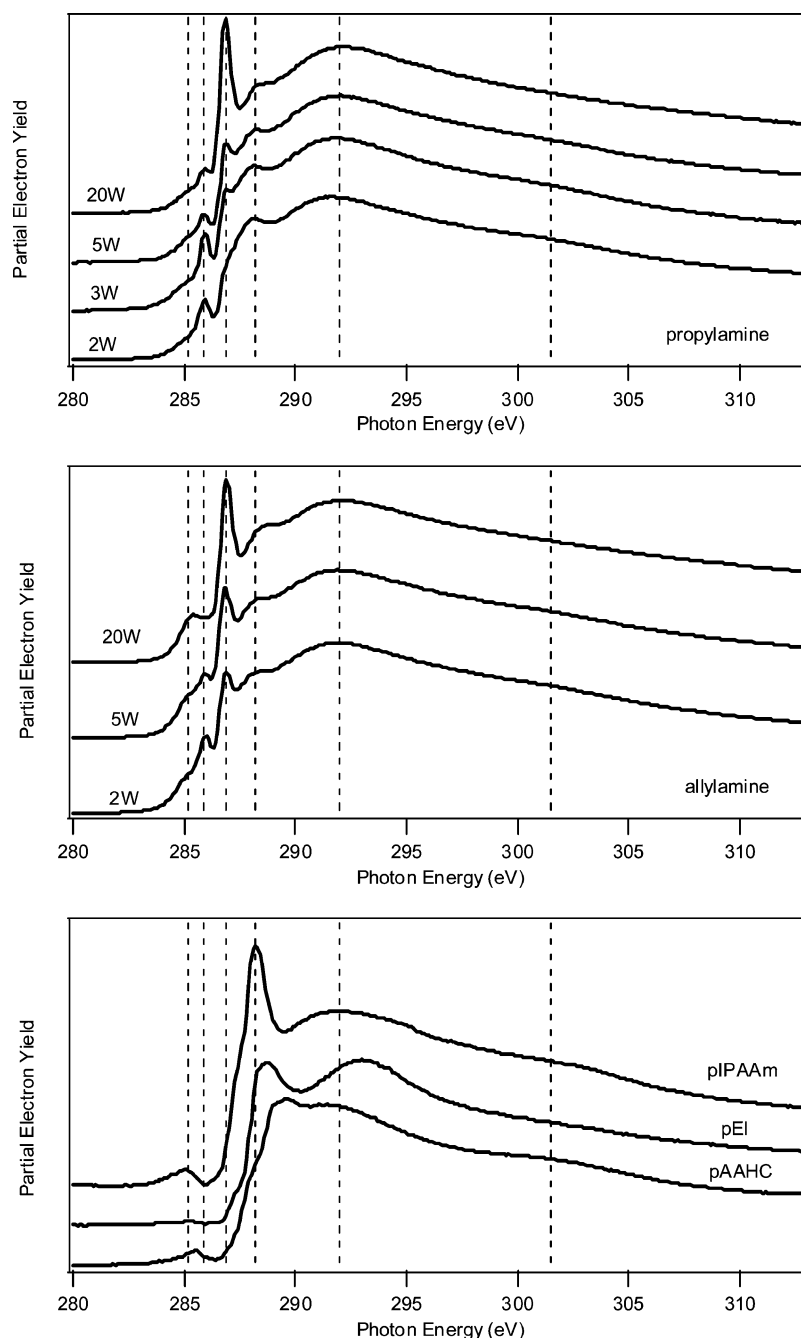
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Figure 3. Carbon K edge NEXAFS spectra of plasma-polymerized propylamine and allylamine and some nitrogen-containing polymers. Resonances found in plasma polymers are marked by dashed lines and overlaid on polymer spectra. All spectra are normalized in height to the step between the first and last data point. From lowest photon energy to highest, the dashed lines are at 285.2, 285.9, 286.9, 288.2, 292.0, and 301.5 eV.

TABLE 3: Carbon K Edge Resonances for Plasma Polymers, Speculative Assignments, and Intensities

position (eV)	assignment	allylamine	propylamine
285.2	aromatic or vinylic π^*	moderate	weak
285.9	C=N π^*	moderate to weak, decreases with power	weak
286.9	C≡N π^*	moderate to strong, increases with power	weak to strong, increases with power
288.2	C−H σ^*	moderate	moderate
292.0	C−C, C−N σ^*	strong	strong
301.5	C=C, C=N σ^*	weak to absent, decreases with power	weak to absent, decreases with power

powers show little power dependence, but have a different composition to allylamine plasma polymers. The 20 W propylamine plasma polymer has a similar C 1s profile to allylamine plasma polymers.

Figures 3 and 4 display the carbon and nitrogen K edge NEXAFS spectra respectively from all samples. The peaks that are apparent in the spectra are summarized in Tables 3 and 4

and indicated on the spectra by dashed vertical lines. In the carbon K edge spectra the lowest energy peak at 285.2 eV is typical of transitions to π^* orbitals for polymers containing phenyl groups and unconjugated double bonds.[13,18] More conjugated systems typically display multiple transitions with the first at a lower energy than 285 eV, thus it seems unlikely that highly conjugated moieties are present in anything but trace
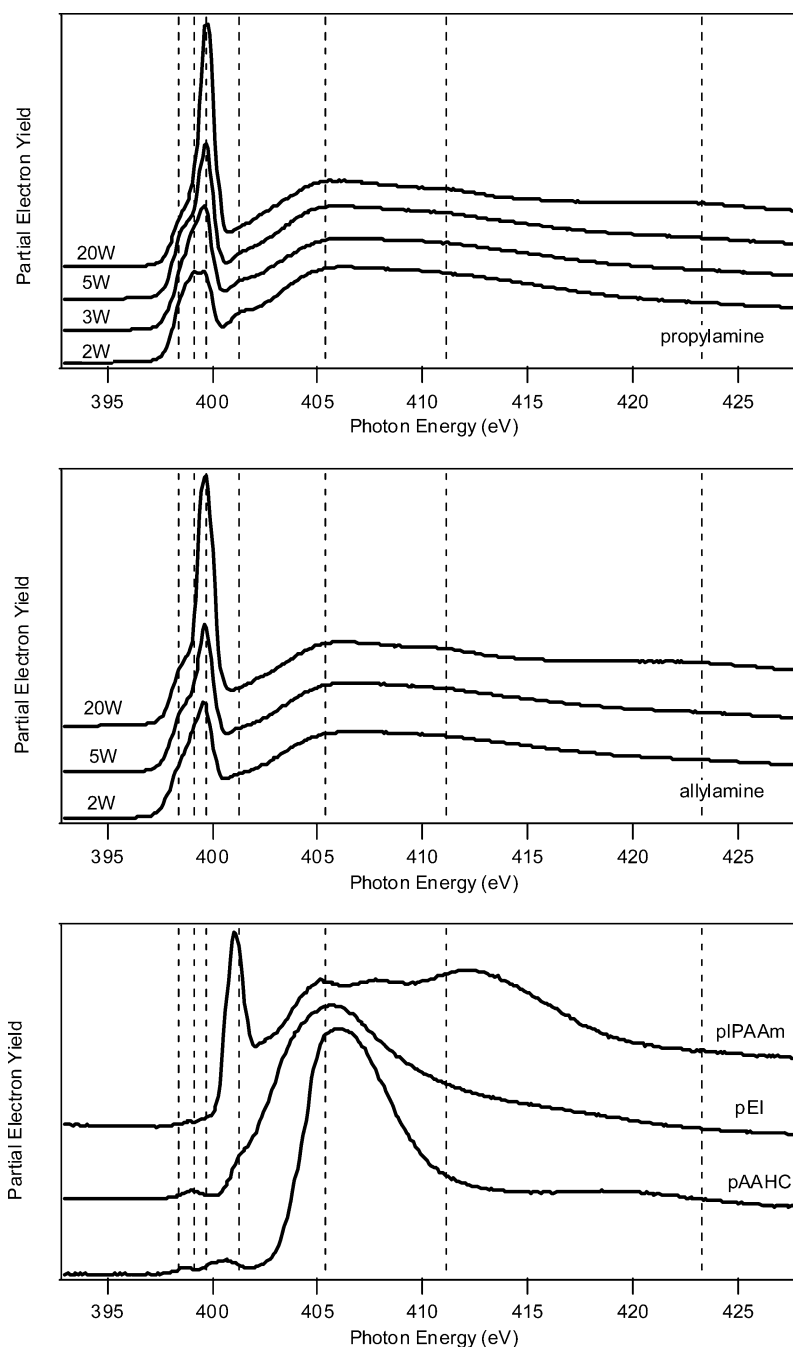
Figure 4. Nitrogen K edge NEXAFS spectra of plasma-polymerized propylamine and allylamine and some nitrogen-containing polymers. Resonances found in plasma polymers are marked by dashed lines and overlaid on polymer spectra. All spectra are normalized in height to the step between the first and last data point. From lowest photon energy to highest, the dashed lines are at 398.4, 399.1, 399.7, 401.3, 405.4, 411.1, and 423.3 eV.

TABLE 4: Nitrogen K Edge Resonances for Plasma Polymers, Speculative Assignments, and Intensities

position (eV)	assignment	allylamine	propylamine
398.4	aromatic π^*	moderate	moderate
399.1	imine π^*	weak	moderate to weak, decreases with power
399.7	N≡C π^*	moderate to strong, increases with power	moderate to strong, increases with power
401.3	N−H σ^*	very weak to absent, decreases with power	weak to absent, decreases with power
405.4	N−C σ^*	strong	strong
411.1	N=C σ^*	weak	weak
423.3	N≡C σ^*	absent to weak, increases with power	absent to weak, increases with power

quantities in these plasma polymers. Carbon atoms which have double bonds to electronegative atoms display similar sharp resonances, but with a shift that is analogous to the chemical shift in XPS, so polyvinylpyridine has resonances at 284.9 and 285.4 eV (the second being chemically shifted) and polyacrylonitrile has a single resonance at 286.6 eV.[13] Thus, the second

two resonances at 285.9 and 286.9 eV can be assigned to carbon nitrogen double and triple bonds, respectively, and judging from the 286.9 eV peak height for 20 W plasma polymers (twice the edge step measured at 315 eV) in comparison to acrylonitrile (eight times the edge step at 315 eV),[13] approximately 1 in 12 carbon atoms are in this environment. Note that none of these
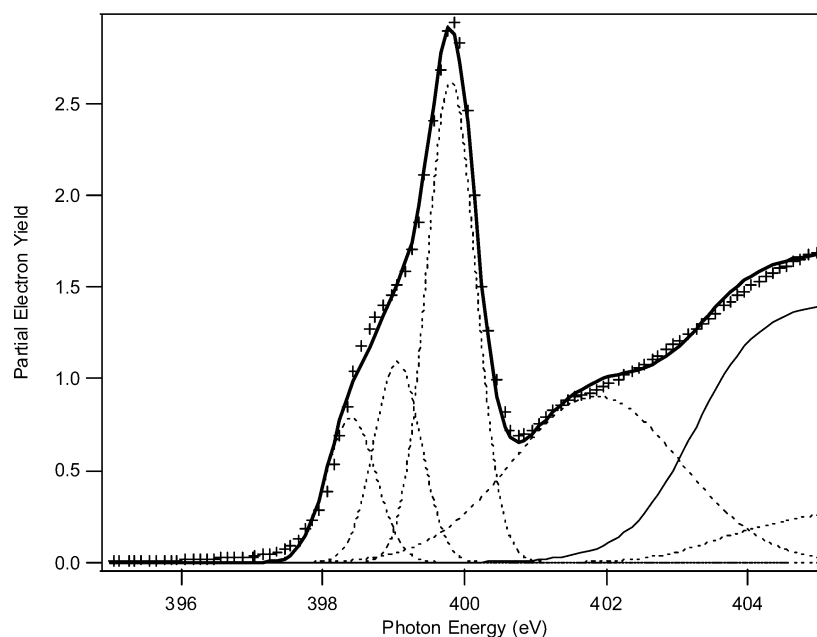
Figure 5. Example curve fit of the nitrogen K edge NEXAFS spectrum for the 5 W propylamine plasma polymer.

resonances correspond to amide groups, which are shifted to 288.2 eV (Nylon6),[13] as illustrated by the pIPAAm spectrum (288.2 eV), the only possibility of oxygen contribution is from carbonyl groups at 286.6 eV (polyvinylmethyl ketone).[13] We can thus discount anything but a trace presence of amide groups in these plasma polymers, although there is evidence to suggest that they may appear after aging for long periods.[21,22] Unsaturated polymers tend to display broad peaks at, or around 288 eV,[13] see also the pEI spectrum in Figure 3, and we associate the peaks at 288.2 and 292.0 eV with single bonds from unsaturated regions of the plasma polymer. The relative intensities and width of these two features would support this assignment. A very weak, broad peak is present at 301.5 eV and can be tentatively assign to a σ^* resonance associated with carbon−nitrogen double bonds, in a fashion similar to the association of the 302 eV resonance in PMMA with carbon−oxygen double bonds.[20]

In assigning the features present in the nitrogen K edge spectra we have been guided by the assignments in the carbon K edge. The three peaks associated with π^* resonances at 398.4, 399.1, and 399.7 eV respectively display the same trends as the three lowest energy peaks in the carbon K edge spectra. The peak at 399.7 eV is thus associated with the nitrile environment and is most intense in the high power plasma polymers. This is similar to the value of 399.5 eV[23] and 399.6 eV[24] found for nitrile-containing polyimides and multilayers of acrylonitrile, respectively. It is, however, somewhat different from the energy of 401.4 eV found for polyacrylonitrile;[14] however, the energy referencing in that particular work is obscure at best and almost certainly unreliable. We speculatively associate the peak at 399.1 eV with imines and that at 398.4 eV with aromatic amines, pyrroles, and pyridine species, which we broadly classify as "aromatic". Although there is some uncertainty in these assignments because, for example, conjugated nitriles can give rise to additional transitions at lower energies than the main peak at ~399.5 eV,[23,24] their presence at least indicates that there are conjugated structures associated with nitrogen atoms in the plasma polymer.

The weak peak at 401.3 eV and the strong peak at 405.4 eV are almost certainly associated with the aliphatic amine environment, as is evident from a comparison with the pEI spectrum.

Literature values for aliphatic amines[14] are once again somewhat different from ours due to the absence of absolute energy referencing in that previous work. Consistent with the carbon edge spectra, we find that amide groups are not significantly present, although the weak peak at 401.3 eV may contain some contribution from such groups. The pIPAAm spectrum demonstrates a strong peak at about this energy and other workers have obtained a resonant energy of 401.2 eV for amide groups.[25] The peaks at 411.1 and 423.3 eV may be associated with C−N double and triple bonds, respectively. It is notable that the nitrogen K edge spectra of the two 20 W plasma polymers are virtually indistinguishable.

Figure 5 shows an example of curve fitting the NEXAFS spectra of these polymers. While agreement between the data and the fit is not exact, due to the limitations of the procedure employed, these analyses are more than sufficient for extracting general trends in the intensity of the π^* resonances. The results of the fits are displayed in Figure 6, taking the 2 W propylamine plasma polymer as reference. The lowest energy resonance, associated with aromatic structures, shows no clear trend but there generally appears to be a higher intensity in the allylamine carbon K edge data than for propylamine perhaps indicating a higher degree of unsaturation in allylamine plasma polymers. The second resonance, associated with the imine environment, once again shows little change with increasing power, except in the case of the carbon K edge of the allylamine plasma polymer. Reduction in this peak intensity is due to a lower incorporation of nitrogen into the polymer at higher powers as shown in the XPS data (note that this would not be expected to affect the nitrogen K edge data, and in fact does not). The third resonance, associated with the nitrile environment, shows a marked increase in intensity with increasing power. For allylamine plasma polymers, the carbon K edge intensity increases less markedly than that for the nitrogen K edge intensity, once again a reflection of the lower incorporation of nitrogen into the plasma polymer. Also notable is the higher general level of nitrile concentration in allylamine plasma polymers in comparison to propylamine plasma polymers, particularly at low powers.
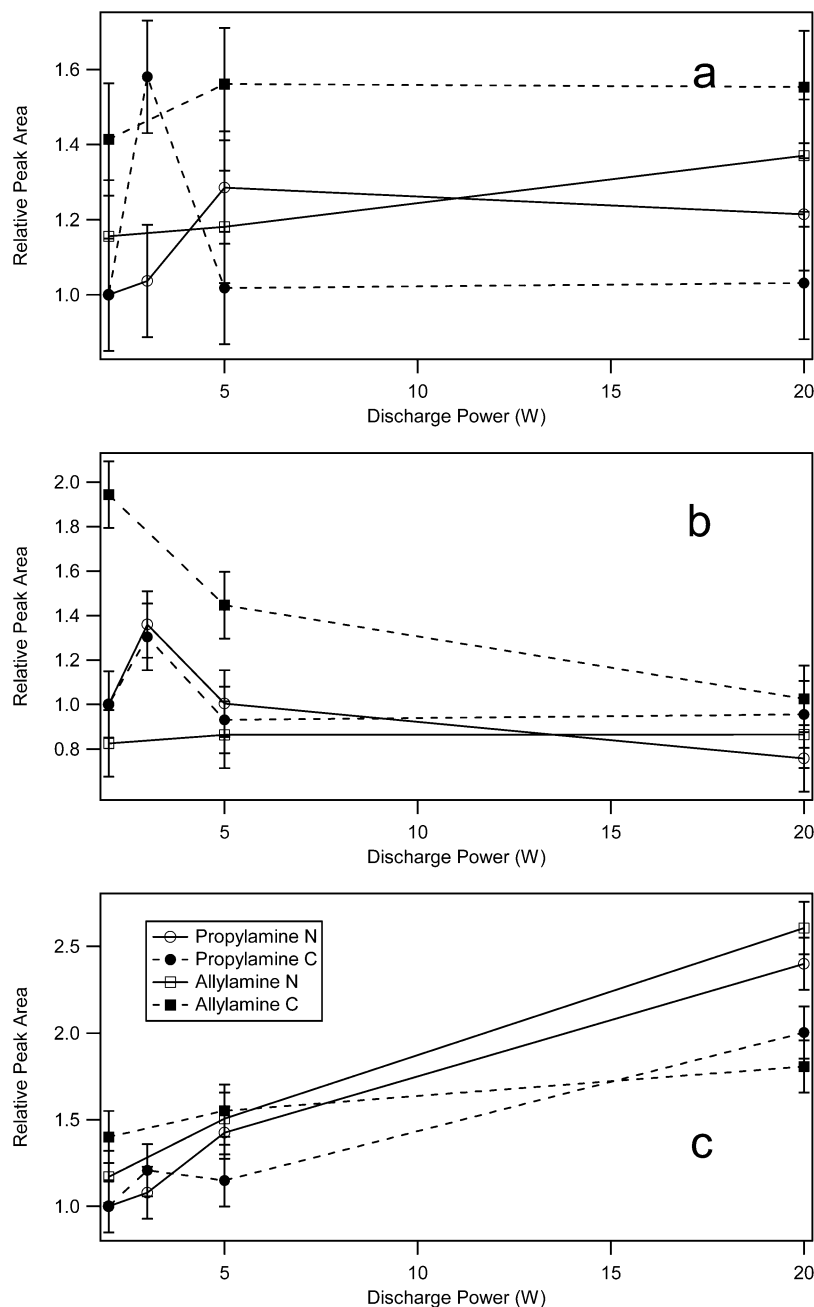
Figure 6. Results of NEXAFS curve fitting. Peak areas for the three π^* resonances are shown relative to areas found in the 2 W propylamine plasma polymers. Circles represent propylamine plasma polymers and squares allylamine plasma polymers. Filled symbols represent carbon K edge data and open symbols nitrogen K edge data. (a) Lowest energy resonance (285.2 eV for carbon, 398.4 eV for nitrogen), (b) intermediate energy resonance (285.9 eV for carbon, 399.1 eV for nitrogen), and (c) highest energy resonance, associated with the nitrile environment (286.9 eV for carbon, 399.7 eV for nitrogen). Error bars are estimated (± 0.15) from the typical deviations found from a number of repeat fits to the same data with different initial parameters.

Discussion

It is clear from the XP spectra of these plasma polymers that some chemical transformation of primary amine groups has occurred during plasma polymerization. The observation of a contribution at a binding energy of 286.6 eV indicates the formation of multiple bonds between carbon and nitrogen atoms. In most cases, the number of carbon atoms with multiple bonds to nitrogen appears to exceed the number with single bonds. In the standard interpretation of these spectra this would indicate a significant formation of imine groups. However, the transformation cannot simply be from a primary amine to an ammonia imine since there is a significant shortfall in nitrogen content within the polymers: As an example, the 3 W plasma

polymers would require an elemental composition of about 75% carbon and 25% nitrogen for consistency with this assumption. Therefore, a reasonable assertion is that secondary and tertiary amines and substituted imines are also present in these polymers,[8] the only possible exception being the 2 W allylamine polymer. The presence of secondary and tertiary amines suggests that the amine content of the plasma polymers is lower than indicated by XPS, as such groups contribute doubly or triply to the C−N environment, likewise substituted imines contribute once to the C=N environment and once to the C−N. This pessimistic analysis entirely discounts the possibility of nitrile groups in the plasma polymer. Each nitrile group contributes twice to the "C=N" environment due to a large β shift on the

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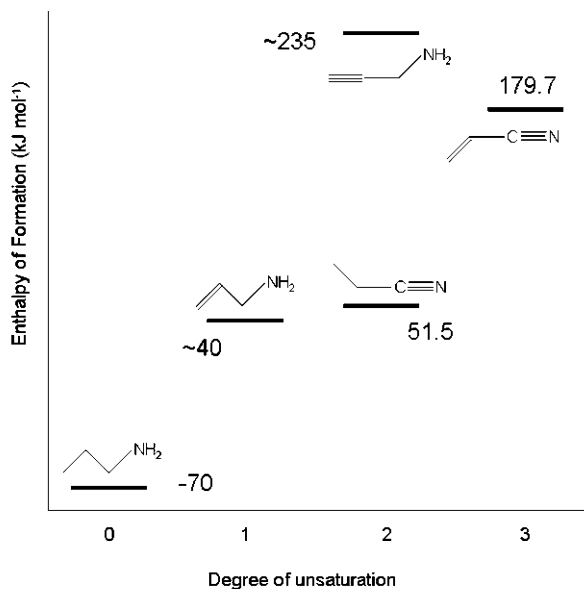*J. Phys. Chem. B, Vol. 108, No. 33, 2004* **12479**

Figure 7. Enthalpies of formation of gas-phase C_3H_xN compounds sourced from the NIST database (webbook.nist.gov), primary references given here: propylamine (ref 27), allylamine estimate from liquid (10 kJ mol^{-1}, ref 28), propanenitrile (ref 29), propargylamine estimate from liquid (206 kJ mol^{-1}, ref 30), propenenitrile (ref 29). Estimates of gas-phase enthalpies were obtained by adding ~30 kJ mol^{-1} to liquid enthalpies of formation (cf. 31.5 kJ mol^{-1} for propylamine, 36 kJ mol^{-1} for propanenitrile, and 33 kJ mol^{-1} for propenenitrile from the same references).

adjacent carbon atom that is similar in magnitude to the primary chemical shift. This additional contribution means that if nitrile groups were present, there could be higher concentrations of amine groups than previously thought.

The presence of nitrile groups, particularly in high power plasma polymers of allylamine and propylamine, is clearly shown in the NEXAFS data. These groups have been noted before in IR spectroscopy, but because of the weakness of the IR absorption have not been thought to be of importance. NEXAFS is rather sensitive to the presence of this functional group, so may overemphasize their presence. However, for 20 W plasma polymers the estimate of 1 in 12 carbon atoms in the nitrile environment is not insignificant and indicates that a quarter of the available amine groups have been lost by conversion to nitrile. This figure is consistent with XPS data, implying ~17% of the C 1s intensity at 286.6 eV binding energy is due to nitrile groups, which is less than the experimental values of over 20% in the "C≡N" environment.

The presence of these groups should not be a mystery if one considers the thermodynamics associated with unsaturated CHN compounds. The instability of primary and secondary enamines in comparison to imines (analogous to keto−enol tautomerism) suggests that it is energetically favorable to have carbon−nitrogen double bonds rather than carbon−carbon double bonds. The enthalpies of formation of various C_3H_xN compounds are schematically shown in Figure 7 and comparison between propanenitrile and propylargylamine clearly demonstrates the same trend for triple bonds. The enthalpies of formation increase with the degree of unsaturation as expected, but this does not mean that reaction to form unsaturated compounds is unfeasible. The entropy gain involved in producing hydrogen could more than counterbalance the enthalpy parameter, particularly at the low pressures employed during plasma polymerization (a reasonable estimate of $T\Delta S$ for the reaction with 0.01 mbar partial pressures would be 65 kJ mol^{-1}). Of particular interest is the similarity in formation enthalpy between allylamine and
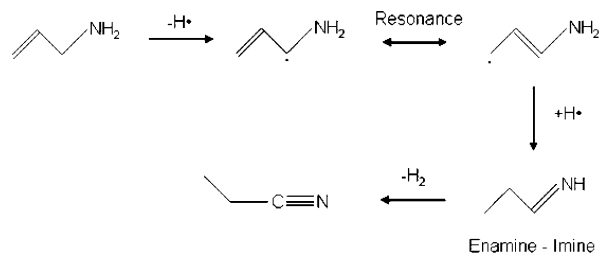

Figure 8. Suggested mechanism for the formation of nitriles from allylamine.

propanenitrile. The formation of propanenitrile from allylamine will almost certainly be spontaneous if a suitable reaction pathway is available.

The high-energy environment of a plasma makes available reaction pathways that would normally be inaccessible. A suggested gas-phase mechanism for the conversion is given in Figure 8, and similar reactions could occur in the plasma deposit following activation by, for example, ion bombardment. Note that this route involves an imine intermediate and there is a strong suggestion of the presence of imines in this NEXAFS and previous IR data. Furthermore, the amount of nitrogen present in imine environments from this NEXAFS study shows little power dependence, which may be taken as supporting evidence for its presence as an intermediate. The suggested mechanism would indicate that the formation of nitrile groups is favored by increasing the power of the plasma, or increasing the exposure time of amine groups to the high-energy environment. Experimentally, the increase in nitrile concentration with power is unambiguous; however, it is impossible to confirm that exposure time has any influence and a study of flow rate or pressure dependence would be required to verify this prediction.

The major differences between allylamine and propylamine plasma polymers are found to be a larger concentration of imine groups in propylamine at low powers and a larger concentration of C−C aromatic and double bond structures in allylamine plasma polymers. Both plasma polymers indicate that the formation mechanism is dominated by dehydrogenation and the concentration of unsaturation close to nitrogen atoms in the polymer, which may occur through the activation of reaction routes similar to that shown in Figure 8.

The findings of this study shed new light on the aging mechanisms of aminated plasma polymers. If there are significant concentrations of imines, these will eventually hydrolyze to produce carbonyls and either ammonia or primary amines. Nitrile groups hydrolyze to produce first primary amides and then carboxylic acids. The long-term incorporation of oxygen into aminated plasma polymers may thus be attributed to hydrolysis rather than, or in addition to, the free radical mechanisms originally proposed by Gengenbach et al.[21]

Although the presence of nitrile and imine groups may detract from the amine functionality of the plasma polymer it should be possible to reduce both groups to amines by using, for example, lithium aluminum hydride.[12] However, the findings also suggest that the plasma polymers may be used for a dual functionalization, using imine coupling chemistry. An initial coupling to the amines, followed by a reduction with lithium aluminum hydride would reduce the imines and enamines formed in the coupling reaction (this is a common stabilization step, usually performed with sodium borohydride) but also create fresh amine groups from the nitrile groups. These may then be employed in a second imine coupling reaction resulting in a surface with two different molecules attached.

While the presentation of NEXAFS in this paper has been semiquantitative, it may be possible to use the technique to quantify the individual components present in plasma polymers using appropriate reference spectra. Such an approach has been used previously, for example, in the analysis of two-component polymer blends by scanning transmission X-ray microscopy.[26] This would be a highly complicated operation for plasma polymers due to their generally highly random structures and the large numbers of different functional groups present.

Conclusions

We have demonstrated the utility of NEXAFS in the elucidation of chemical species in nitrogen-containing plasma polymers. NEXAFS is able to provide a sensitive probe of unsaturation in plasma polymers and therefore offers a useful complement to XPS that has a similar information depth, but is unable to unambiguously identify the nature of unsaturated chemical environments. The study of amine-containing plasma polymers has revealed new insights into the importance of dehydrogenation during the deposition process. In particular, the presence of nitrile groups in plasma deposits may be much more significant than previously supposed. We show that the nitrogen environments in plasma polymers of allylamine and propylamine are similar and at high powers there is little distinction between their respective NEXAFS spectra. Unsaturation in both plasma polymers increases with discharge power and is located mainly within carbon–nitrogen bonds. Although there is evidence for carbon–carbon bond unsaturation, this is only prominent for high-power allylamine plasma polymers. We have explained the preference for the location of unsaturation within carbon–nitrogen bonds by a simple thermochemical argument. These findings suggest a new interpretation of long-term aging effects for aminated plasma polymers in terms of hydration, and potential new applications for such materials.

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