

The Role of Ions in the Plasma Polymerization of Allylamine

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The radio-frequency-induced plasma polymerization of allylamine has been investigated in the plasma-gas phase by mass spectrometry and at the plasma–solid interface by means of an ion flux probe and a quartz mass balance. The surface chemistry of the deposits has been determined by X-ray photoelectron spectroscopy. The objective of this study was to unravel the mechanism(s) by which allylamine plasma polymers form. The results are compared with those obtained in an earlier investigation of the plasma polymerization of acrylic acid. In the plasma-gas phase, evidence is provided for reactions between cations and intact neutral monomers (allylamine). These oligomerization reactions were found to be relatively power-insensitive compared with those seen in plasmas of acrylic acid, as was the gas-phase concentration of the intact neutral monomer. At the polymer surface, ion fluxes were found to increase with plasma input power (P) from 6.6×10^{16} ions $\text{m}^{-2} \text{s}^{-1}$ at 1 W to 1.4×10^{18} ions $\text{m}^{-2} \text{s}^{-1}$ at 14 W. The ionic mass transport to the polymer surface (ion mass flux) was calculated by multiplying the measured ion flux by the average ion mass (determined by mass spectrometry). At $P = 1$ W, the ion mass flux was $11.7 \mu\text{m m}^{-2} \text{s}^{-1}$, and at 14 W, the ion mass flux was $226.6 \mu\text{m m}^{-2} \text{s}^{-1}$. These values differed from the total mass deposition rates measured by the quartz mass balance, which were 18.7 and $127.1 \mu\text{m m}^{-2} \text{s}^{-1}$, respectively. However, the relationship found between the ion mass flux, the mass deposition rate, and P was complex, and it is shown that, at very low P (< 1 W), the ion mass flux is sufficient to account for all of the deposit.

Introduction

It has long been known that radio frequency (RF) induced plasmas of volatile organic compounds can be used to deposit thin polymeric films onto a wide variety of substrates.^{1,2} These films, usually described as plasma polymers (pps), have numerous technological applications as protective and functional coatings. Films containing controlled concentrations of specified functional groups have great utility as they can alter the surface chemistry of the material that is coated. This is of significant value in many areas, including membranes (for filtration and separation), electronic devices, biomaterials, sensors, corrosion protection, and adhesion.^{1–4} Surfaces containing amines are of particular interest as biomedical coatings for the subsequent immobilization of polysaccharides.⁵ pps showing high functional group retention have been prepared by using continuous-wave plasmas produced with a low ratio of power (P) to monomer flow rate (ϕ).⁶ Such films have also been successfully prepared using pulsed plasmas where the ratio of RF “on” to “off” time is an important parameter in controlling the properties of the pp.^{1,7} Continuous-wave plasmas of allylamine are the subject of this study.

Plasmas are known to contain a range of species including ions, neutrals, radicals, electrons, excited species, and photons. Despite a vast literature in the area of plasma polymerization (e.g., refs 1, 2, and 8), the mechanisms involved remain poorly understood. Early workers in the field of plasma polymerization⁹

found that the rate of polymerization was dependent on the number of molecules adsorbed to the electrode in a dc discharge. They also found no polymer on the anode in a dc discharge and concluded that the positive ions formed in the negative glow by electron bombardment of the monomer molecules played a major role in polymer formation. More recently, however, the role of free radicals in plasma polymerization and the rather random nature of plasma-phase reactions have often been emphasized.⁸

At low P , there is sufficient evidence to suggest that specific reactions between ions and molecules take place in the plasma-gas phase, leading to the formation of oligomeric species.^{10–15} These reactions could contribute to the formation of the pp deposit. In general, no gas-phase neutral oligomers are detected. We have proposed that ion–molecule, rather than or possibly as well as, radical–radical or radical–neutral reactions play a significant role in the formation of the deposit. In the case of acrylic acid, direct correlations were found between the degree of cationic dimer and trimer formation in the plasma and functional group retention and P .¹³

There are problems associated with making direct ion flux measurements for depositing plasmas. An insulating layer is deposited on any probe in contact with the plasma, which can interfere with the operation of the probe. Recently, however, Braithwaite et al. described a novel electrostatic probe¹⁴ that allows ion flux measurements to be made even when the surface of the probe is coated with insulating material. This is achieved by using a pulsed RF bias.

Earlier work by the Sheffield group showed that pp's prepared from allylamine at low ratios of P to flow rate retained much

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of the nitrogen and some primary amine groups from the monomer.¹⁵ As P was increased to 15 W, the retention of nitrogen fell only slightly, but the concentrations of other functional groups, such as secondary and tertiary amines and imines, increased.

Direct measurements of the ion flux (onto a surface) as a function of P have been made for allylamine plasmas. These measurements were combined with mass spectral analysis of the plasma, allowing for a reasonable estimate of the charged mass (ion mass flux) being transported to the surface of the deposit to be made. This value was compared to the total mass deposited, measured directly using a quartz mass balance. In this way, an estimate of the potential contribution of ion bombardment to total mass deposition can be made. A similar study of acrylic acid plasmas has been reported,^{18,19} and these earlier results are compared with the data presented here for allylamine plasmas.

Experimental Section

The plasma apparatus consisted of a tubular glass reactor interfaced to a mass spectrometer (a quadrupole HAL EQP 500 model supplied by Hiden Analytical, Warrington, U.K.), which has been described in detail elsewhere.¹³ A rotary pump was used to evacuate the plasma reactor, and the lower pressure required in the mass spectrometer was achieved by means of a turbomolecular pump. The plasma was sustained by a RF generator (13.56 MHz) and amplifier coupled to the plasma via an externally wound copper coil. The power used was in the range 0.2–15 W. Measurement of the mass deposition rate was made using a quartz crystal mass balance (Leybold, Manchester, U.K.), which was inserted into the plasma region using a rigid support to ensure consistent positioning of the crystal. The active area of the crystal was 0.535 cm². In a separate series of experiments, to determine the relationship between P and the ion flux, an ion flux probe was placed in the plasma, close to where the quartz crystal had been. The probe was biased negatively by RF pulses and the transient current used to determine ion flux. The experimental parameters associated with the probe itself were chosen so that the potential across the space charge sheath changed at a very slow rate compared to the transit time of the ions crossing the sheath. The transit time has a square-root dependence on ion mass and plasma density.¹⁹ This ensures that the measured current is due to the particle fluxes only and not to a redistribution of charge in the sheath.¹⁴ This mode of operation makes the probe insensitive to ion mass. The probes that were used to measure the mass deposition rate and ion flux were separate from the RF system that sustained the plasma and thus did not act as electrodes. They behaved as would any inert material in contact with the plasma, merely providing a loss surface for ions.

Three measurements were made for each of the ion flux and deposition rate data points. The error bars (\pm a standard deviation) were calculated from these values. The error bars (\pm a standard deviation) for the ion energies were calculated using three measurements of the m/z 58 ion energy at 10 W.

The mass spectrometer could be configured to analyze neutral species or positive ions from the plasma. Neutral species from the plasma passed through an ionization chamber and were ionized by electron impact (EI) prior to mass analysis in the spectrometer. The EI mode could also be used for conventional residual gas analysis in the absence of plasma. The electron kinetic energy was 20 eV when EI was employed. Positive ions emanating from the plasma were mass analyzed without further ionization. The spectrometer was tuned using a routine provided

by the manufacturer. In this routine, the signal at the chosen m/z value (in this case 57) was maximized by adjustment of several parameters such as ion energy, spectrometer lens voltages, etc., in an iterative manner. Significant differences in the lens settings (neutrals/positive ions) ensured that no positive ions were detected during acquisition of the neutrals when EI was used.

In both sets of experiments, the flow rate (ϕ) was fixed at ca. 0.8 cm³_{STP} min⁻¹. Allylamine vapor (Aldrich Chemical Co., U.K., 99% purity) was allowed to flow through a needle valve, giving a pressure of ca. 2.5×10^{-2} mbar in the plasma chamber.

Samples for analysis by X-ray photoelectron spectroscopy (XPS) were deposited onto aluminum foil substrates using a flow rate of 2.0 cm³_{STP} min⁻¹ and a power of 2.0 W. The allylamine vapor was allowed to continue flowing through the plasma reactor for ca. 10 min after the RF source had been switched off. XP spectra were acquired on a VG Clam 2 instrument, using Mg K α X-rays to excite a spectrum. The X-ray source was operated at 100 W. The data were analyzed using Scienta software. Curve fitting of the core-level spectra was performed using a least-squares routine, which, in an iterative manner, achieves optimization of each parameter defining the several component peaks contained within the experimental spectral envelope. Experimentally derived sensitivity factors were used to calculate the concentrations of elements.

Results

Figure 1 shows an XP spectrum of pp(allylamine) prepared at low power. Quantification of the data shows that the sample contains carbon (75.4%), nitrogen (20.4%), and oxygen (4.1%). The allylamine precursor contains 66.7% carbon and 33.3% nitrogen. Shown in Figure 2 is the peak-fitted C 1s core line of a pp of allylamine produced from a 2.0-W plasma. The fit contains four component peaks corresponding to the different chemical environments that are present in the sample. The peak at 285 eV was assigned to hydrocarbon (CH_x). The peak at 285.9 eV is due to C–N that might be primary, secondary, or tertiary amine groups. The peak at 286.5 eV has possible contributions from C=N (imine) and C–O (alcohol or ether). Finally, the peak at 288 eV has possible contributions from C=O (carbonyl) and CNO (amide). Acids, esters, and urea functionalities would manifest at higher binding energy, typically 289.3 eV,²⁰ and are not detected. Judging from an earlier study using infrared spectroscopy to analyze pp's of allylamine, we can rule out the possibility of a significant contribution from nitriles.¹⁵

Shown in Figure 3 are the EI mass spectrum of the neutral species and the mass spectrum of the positive ions obtained from a 1-W plasma. Figure 4 displays the corresponding mass spectra from a 15-W plasma. The EI mass spectra (1 and 15 W) are readily interpreted using the principles of conventional EI mass spectrometry. The m/z 57 peak corresponds to the molecular ion of allylamine (M⁺) and the m/z 56 peak to (M–H)⁺. The latter ion is formed by an α -cleavage reaction with loss of a hydrogen radical. The m/z 56 peak is the base at P = 1 W and is still prominent at P = 15 W.

Other prominent fragments correspond to m/z 30, CH₂NH₂⁺; m/z 28, CH=NH⁺, CH₂CH₂⁺ (an odd-electron ion, which is not likely), and a possible contribution from N₂⁺; and m/z 17, NH₃⁺.

The positive-ion mass spectra (Figures 3 and 4) are readily assigned as follows: m/z 17 and 18, NH_x⁺ with a possible contribution from water at m/z 18; m/z 28, CH=NH⁺, CH₂CH₂⁺, and a possible contribution from N₂⁺; m/z 30, CH₂NH₂⁺; and m/z 56, 57, and 58, (M–H)⁺, M⁺, and (M+H)⁺,

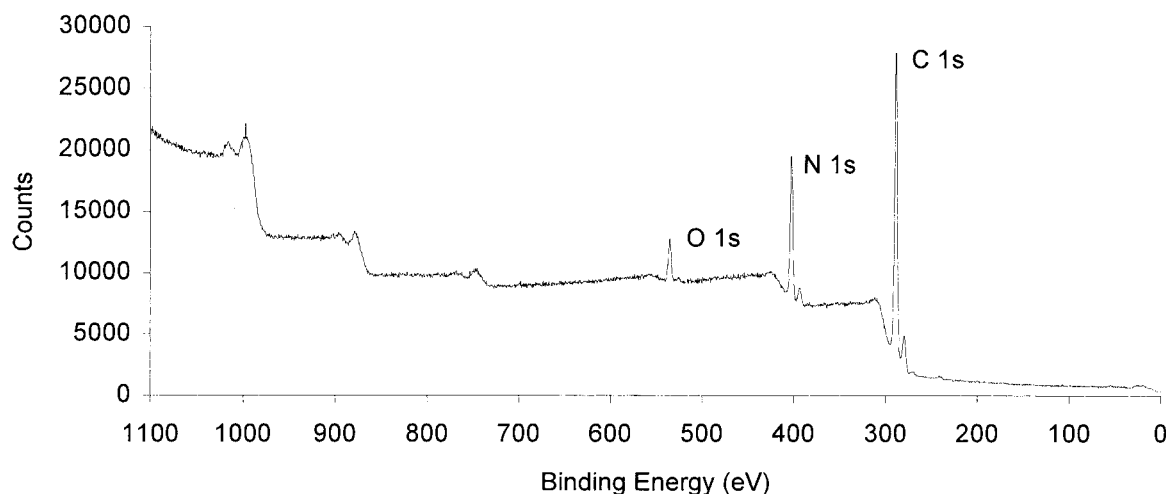


Figure 1. XPS survey scan of pp(allylamine) (prepared at 2 W) showing peaks due to carbon, nitrogen, and oxygen.

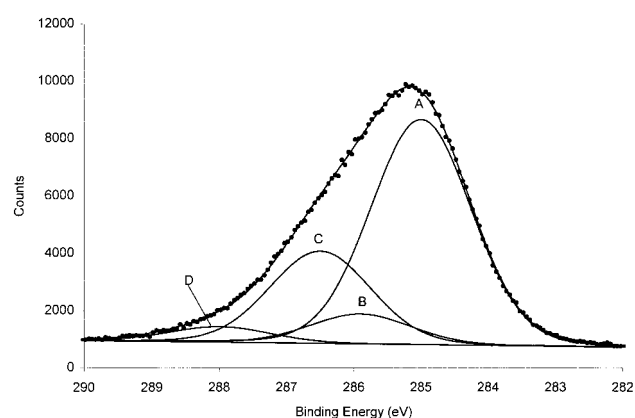


Figure 2. Peak-fitted C 1s core level of pp(allylamine) prepared at 2 W. (A) CH (285.0 eV), (B) C-N (285.9 eV), (C) C=N and C-O (286.5 eV), (D) C=O and CNO (288.0 eV)

respectively. Ions are further assigned to dimeric and trimeric cations with $(2M \pm H)^+$ at m/z 113 and 115 and $(3M \pm H)^+$ at m/z 170 and 172. The dimeric and trimeric species are readily observed up to $P = 15$ W even though the transmission function of the quadrupole causes discrimination against ions of higher mass. The manufacturer of the mass spectrometer has estimated that the dependency of the transmission is somewhere between m^{-1} and m^{-2} . By taking a conservative estimate that transmission is proportional to m^{-1} , it is possible to correct the spectrum for this effect using $I_{\text{real}} = I_{\text{measured}} \times m$. Each intensity data point was multiplied by the mass at which it was recorded, and the base peak was normalized to 1. The relative ion intensities in Figures 3 and 4 were corrected for the mass discrimination of the quadrupole and are redisplayed in Figures 5 and 6. These normalized spectra show that the higher-mass ions are more numerous in the plasma than the raw data would imply. The data in Figures 5 and 6 can be used to calculate the average ion mass as a function of P . For example, in Figure 5, the signal distribution is such that the average ion mass is 107 Da (assuming $z = 1$) or 1.79×10^{-16} μg . The same calculations have been performed across the P range (see Table 1).

Figure 7 shows the P dependence of the ion flux. The ion flux increases steadily up to 3 W; there is then a more rapid increase up to approximately 5 W, followed by a more gradual increase up to the maximum value studied. From Figure 7, it can be seen that the ion flux at $P = 1$ W is 6.58×10^{16} ions $\text{m}^{-2} \text{s}^{-1}$. Multiplying this ion flux by the average ion mass (1.79×10^{-16} μg) yields the mass transported by the ions to the

TABLE 1: Comparison of Total Mass Deposition Rates and Positive-Ion Mass Flux in Allylamine Plasmas

power (W)	average ion mass ^a	total material deposition rate ($\mu\text{g m}^{-2} \text{s}^{-1}$)	positive-ion mass flux ($\mu\text{g m}^{-2} \text{s}^{-1}$)
1	107 (115)	18.7 (45.5)	11.8 (9.6)
3	100	61.7	36.2
5	98 (66)	86 (66)	99.4 (39.6)
15	98 (50)	127.1 (62.2)	226.6 (73.0)

^a Based on the normalized mass spectrometry data (taking intensity $\propto m^{-1}$). The values in parentheses show the comparable measurements made in plasmas of acrylic acid, which were taken from ref 18. The measurements made in plasmas of acrylic acid and allylamine were taken over a period of 2 days.

surface of the deposit (ion mass flux) as $11.8 \mu\text{g m}^{-2} \text{s}^{-1}$ in a 1-W plasma. This is a conservative estimate based on the choice of m^{-1} as the mass transmission of the quadrupole.

Figure 8 shows how the deposition rate of the pp onto the surface of the quartz crystal varies with P . Two regimes are clearly evident. There is a rapid linear increase in deposition rate between 0.2 and 3 W. Between 3 and 15 W, the rate of increase of deposition rate gradually levels off, although the curve still rises slowly at 15 W.

The deposition rate data in Figure 8 can be compared with the calculated ion mass fluxes. At $P = 1$ W, the ion mass flux is estimated to be $11.8 \mu\text{g m}^{-2} \text{s}^{-1}$, and the total measured mass flux is $18.7 \mu\text{g m}^{-2} \text{s}^{-1}$. These values suggest that charged mass could account for at least 63% of the total mass deposited by the plasma ($P = 1$ W). The comparison was repeated for $P = 3, 5$, and 14 W, and the results are summarized in Table 1. At 5 W and above, the positive-ion mass flux exceeds the total material deposition rate.

Figure 9 shows a plot of the ion energy distribution of the m/z 58 signal arriving to a grounded surface in a 5-W plasma. The figure shows that the ion energy distribution is centered at ca. 29 eV, with a spread to lower energy. The energy distribution is of the expected form, where the "peak" ion energy corresponds to ions accelerated across the plasma presheath and sheath without collision (and hence without any loss of energy). The low-energy "hump" arises from ions that have undergone energy losses through collisions. Figure 10 shows how the peak ion energies with respect to a grounded surface of the m/z 58, 115, and 170 ions change as a function of P . Figure 10 shows that these ions (within experimental error) arrive at a grounded surface with the same energy, which we would anticipate, as,

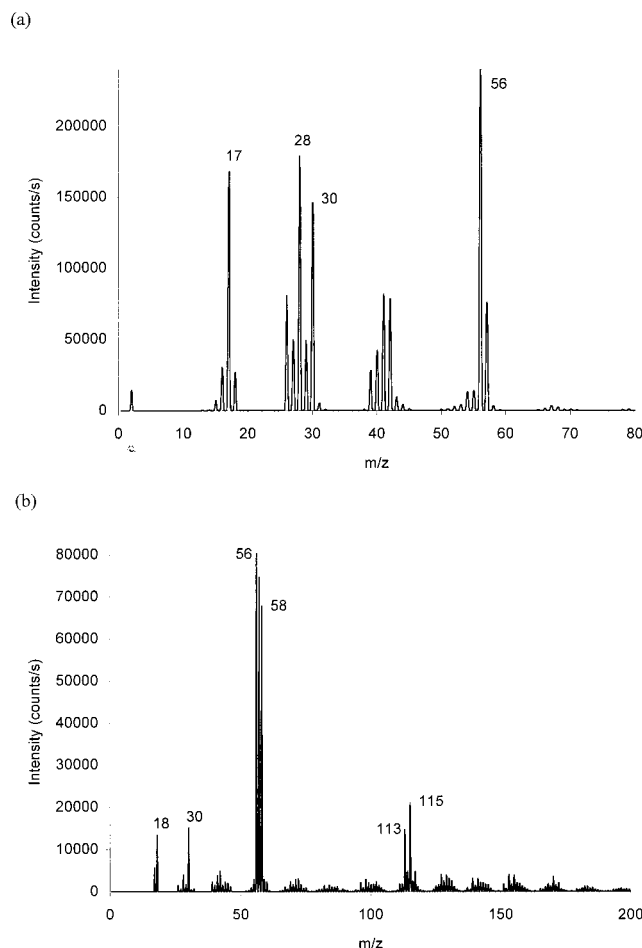


Figure 3. Mass spectra of allylamine plasmas produced at 1 W: (a) electron impact, (b) positive ion.

irrespective of mass, these ions should be subjected to the same difference in potential, V_p , where V_p is the plasma potential. Elsewhere,¹⁹ we have shown that, for ions arriving at a self-biased surface, which is more representative of deposition onto a polymeric surface using an external RF source, a small correction to these energies is necessary. At $P = 3$ W, we would expect a reduction in ion energy of ca. 10 eV, and at $P = 15$ W, we would expect a reduction of about 16 eV.

Discussion

The C 1s core-line fit is broadly in agreement with previously published fits; for example, see refs 15, 16, and 20 (although, in the case of ref 20, a slightly different fitting procedure was employed). The pp's prepared as part of this study did not appear to react significantly on exposure to the atmosphere for 1 day and contained only low concentrations of oxygen (<4%); other workers have prepared similar materials.¹⁶ Some workers,¹⁷ however, have found significant concentrations of oxygen (ca. 18%) in pp's prepared from allylamine, particularly after a few days of storage in the atmosphere. On storage for 41 days, a modest increase in oxygen was observed (7%). The subsequent aging of pps of allylamine over 300 days is detailed elsewhere.²¹

The low oxygen content of our pps might be due to certain features of the plasma polymerization procedure that we followed. In an attempt to minimize post-plasma reactions with the atmosphere, the allylamine vapor was allowed to continue flowing through the plasma reactor for some time after the plasma had been extinguished. The rationale behind this procedure was that it would allow many of the active sites in

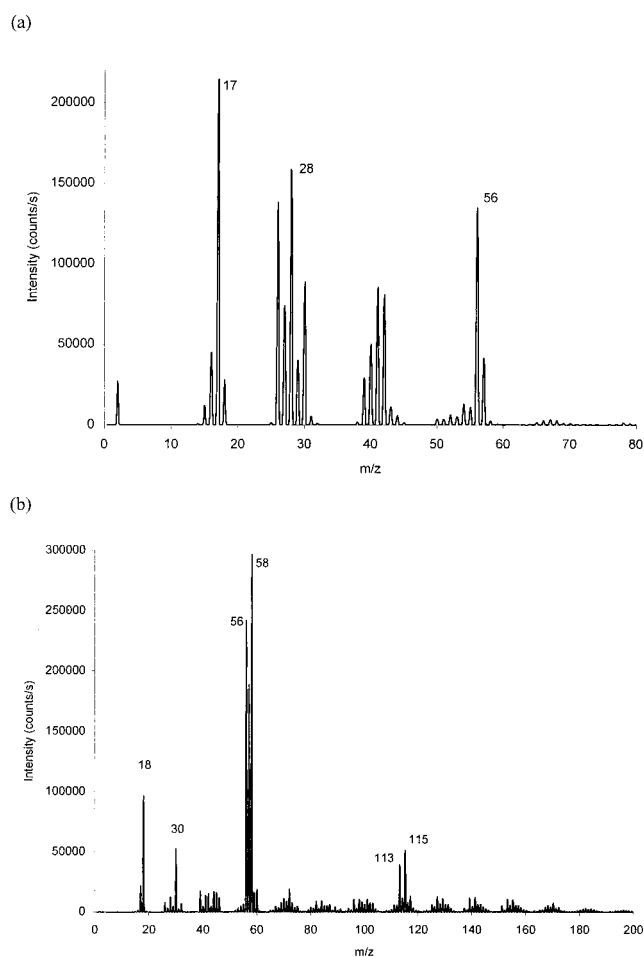


Figure 4. Mass spectra of allylamine plasmas produced at 15 W: (a) electron impact, (b) positive ion.

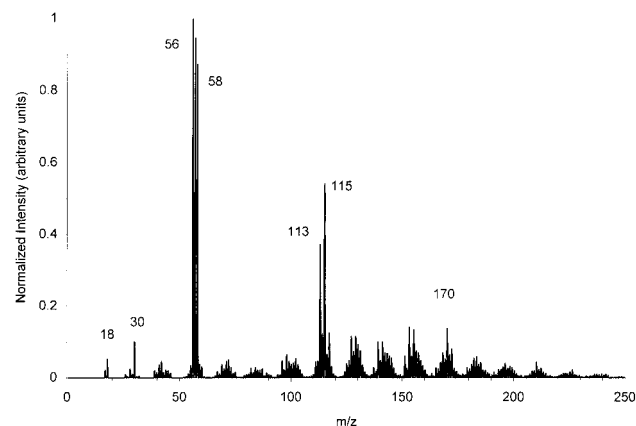


Figure 5. Normalized ($\propto m^{-1}$) positive-ion mass spectrum of allylamine plasma produced at 1 W.

the pp to decay or to react with the allylamine before the pp was exposed to the atmosphere. Allylic compounds do not typically polymerize by radical mechanisms, as termination by hydrogen-atom abstraction by the growing radical chain end is very effective. Passing allylamine over the surface of the plasma polymer after extinction of the plasma might have resulted in the quenching of some radical sites. Alternatively, the low acceleration of the ions (see Figure 9), particularly at low P , might account for the low level of oxygen uptake observed. In a plasma at a power of, say, 3 W, polyatomic ions arriving at an organic surface would typically have energies of ca. 10 eV. On average, these polyatomic ions contain >10 bonds (e.g.,

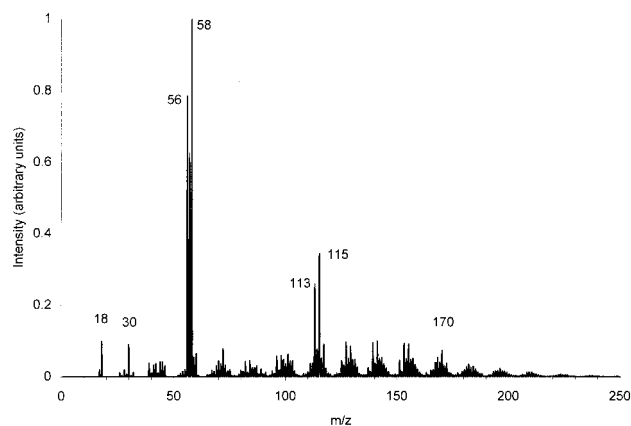


Figure 6. Normalized ($\propto m^{-1}$) positive-ion mass spectrum of allylamine plasma produced at 15 W.

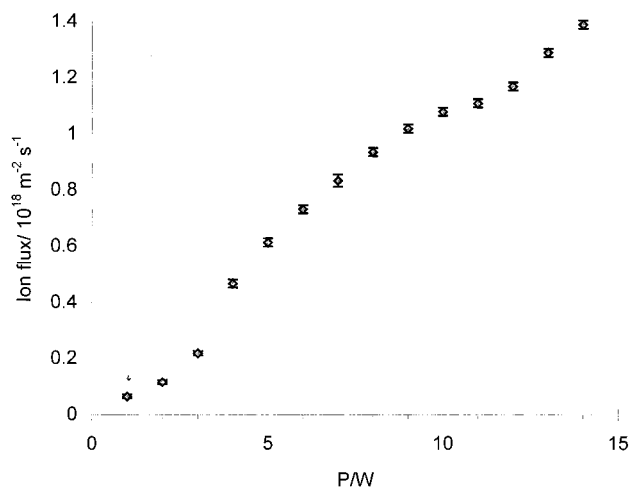


Figure 7. Variation in ion flux with P .

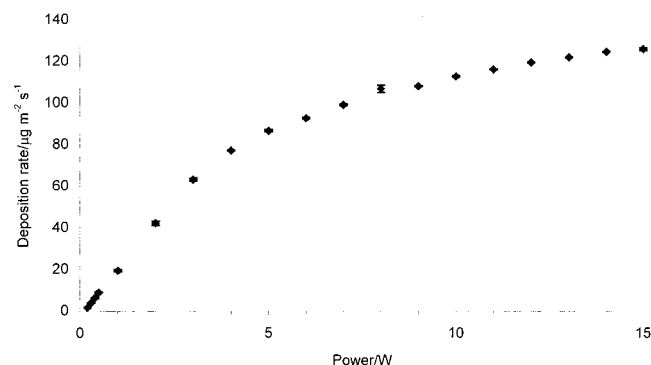


Figure 8. Relationship between deposition rate and power.

m/z 57 contains 11 bonds), and this equates to approximately 1 eV per bond. This value is well below the typical 3–5 eV threshold required to break bonds. Such ions would produce limited fragmentation in the ion and at the surface and, hence, little or no radical production.

The mass transported by the ions was calculated at $P = 1, 3, 5$, and 14 W. At the lowest power, $P = 1$ W, plasma mass spectrometry shows the greatest level of oligomerization in the gas phase. At similar low powers, a high retention of nitrogen from the allylamine was found in the plasma polymer deposit.¹⁵ XPS also shows that, whereas ca. 60% of the amine functionality is incorporated into the film, other functional groups such as imines (C=N) are also observed.¹⁵

The EI mass spectra in Figures 3 and 4 reveal that there is increased fragmentation of the allylamine with P but, that in

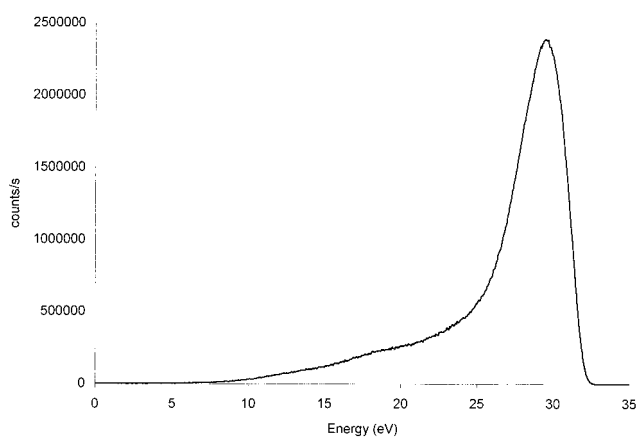


Figure 9. Ion energy distribution of the ion at m/z 58 arriving at a grounded surface in a 5-W plasma.

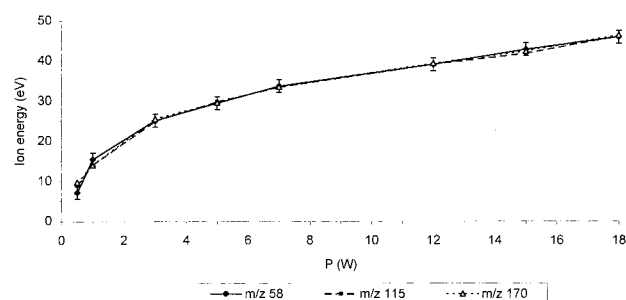


Figure 10. Trend in ion energy (relative to V_g) with power. The ion energy that gave the maximum count rate for each ion is shown in the graph. The error bars (\pm a standard deviation) for the ion energies are shown on the m/z 58 curve only, for clarity.

both the 1- and 15-W plasmas, there is still an abundance of intact monomer (allylamine). This finding contrasts markedly with what has previously been reported in plasmas of acrylic acid.²⁰ For plasmas of this monomer, in a 1-W plasma, approximately 80% of the acrylic acid molecules have fragmented, and at $P > 6$ W, there is virtually no signal from the “intact” monomer (m/z 72) in the EI mass spectra of the neutrals.

From Figures 3 and 4, it can be seen that oligomerization is also relatively P -insensitive. This can also be seen from Table 1, where the average ion mass remains constant at ca. 100 Da across the P range under investigation. Again, this result contrasts starkly with what has previously been reported in plasmas of acrylic acid,^{18,19} where oligomerization is found to be very P -sensitive. The average ion mass at $P = 1$ W was 115 Da, whereas by $P = 5$ W, it had fallen to 66 Da, well below the value for the intact monomer (73 Da). The relative insensitivity to P of the plasma-gas-phase species in allylamine is reflected in the chemistry of the deposit. Here, the distribution of functional groups in the pp also changes only slightly as the power is increased. This dependency is described more fully in ref 15.

A comparison of the calculated charged mass flux at $P = 1$ W and the measured total mass deposition suggests that the former could account for ca. 63% of the deposit. This amount is much higher than a similar estimate made for acrylic acid (ca. 22%) and serves to underline the possible importance of ions in the plasma and their influence on the chemical properties of the pp. The remaining ca. 40% of the deposit could be accounted for by neutral monomer or fragments arriving at and reacting with the surface. Using the ion flux measurement at $P = 1$ W, it can be calculated that, at a pressure of 10^{-2} mbar, there are ca. 300 000 neutrals arriving per unit area for every

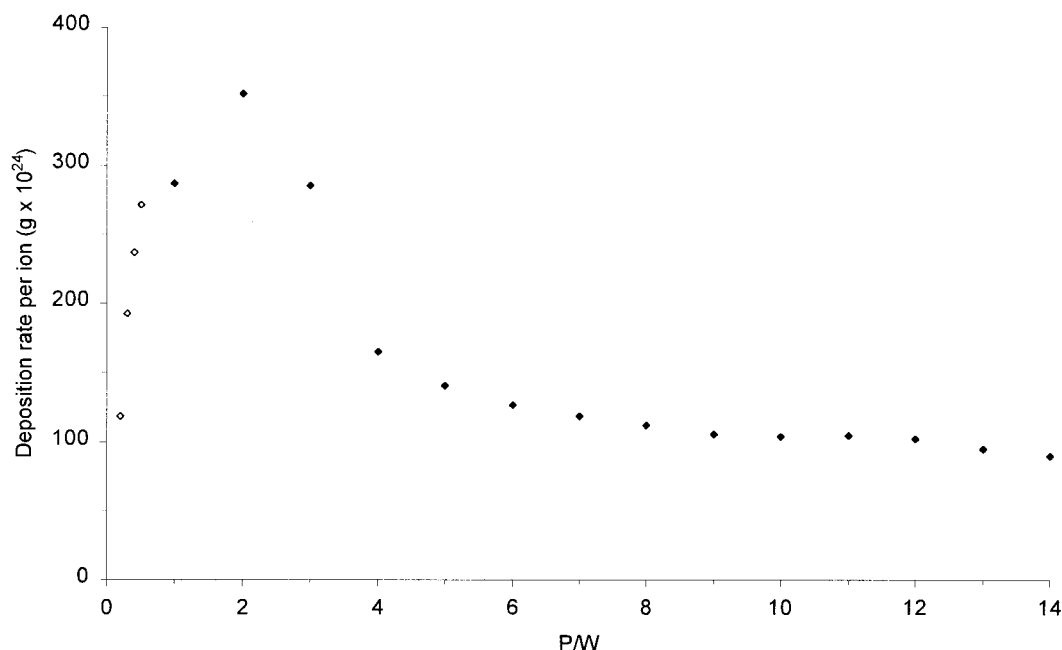


Figure 11. Deposition rate per ion vs power. (The unfilled diamonds represent the calculated data points.)

one ion. Some neutral species with masses greater than M were detected by mass spectrometry of the plasma-phase neutrals. However, the signals were of very low intensity and did not correspond to oligomers. The highest-mass peak (not shown), observed at 104 Da, can be assigned to cyanopyridine ($C_6N_2H_4$). This possibly forms as a result of extensive loss of H from the dimer $(2M - H)^+$ at m/z 113. This indicates that radical–radical or radical–neutral combinations do not contribute significantly to the growth of larger compounds ($>M$) in the plasma phase. It does not, however, rule out such reactions taking place at the surface. Radical sites could be created by ion or photon bombardment, and then neutral species could be grafted at these sites. However, the radical addition of allylamine through its carbon carbon double bond by a process akin to radical polymerization is thought to be unlikely. First, termination of a growing chain by H abstraction would be very effective. Second, the allylic radical itself, because of its stability, would not propagate polymerization effectively.

The deposition rate per ion was obtained by division of the deposition rate (Figure 8) by the ion flux (Figure 7) and is plotted as a function of P in Figure 11. The deposition rates were measured for all of the values shown. However, the experimental configuration employed to record the ion flux did not allow for measurements to be recorded below 1 W. A crude linear extrapolation, assuming zero ion flux at $P = 0$ W, was employed to obtain ion flux values for $P < 1$ W. These values were used to calculate the additional data points for $P < 1$ W as shown in Figure 11. The general form of the curve is remarkably similar to that produced for acrylic acid over a very similar power range. The curve shows that, as P increases, there is a rapid increase in the deposition rate per ion, reaching a maximum at ca. 3 W. The deposition rate per ion then falls off rapidly at first, followed by a more gradual decrease as P is increased further.

Figure 11 suggests a complex relationship between the ion contribution to the total deposit mass and P . This graph is best understood through a worked example. If it were assumed that the deposit was being grown from a beam of monomeric ions $(M + H)^+$, with no fragmentation or sputtering in ion or surface, respectively, then the deposition rate per ion would be 94.6×10^{-24} g. At this point, the ion sticking probability does not

require consideration as ions that do not stick would not be counted. A deposition rate below this value could, in principle, be accounted for by a flux of pure monomeric ions. A deposition rate above this value could be accounted for by flux that contained heavier ions, but judging from the results in Table 1, it would not be reasonable to postulate, for example, a flux comprising pure dimer $(2M + H)^+$ (115 Da). Of course, in plasma polymerization the ion flux comprises not a single species but rather a mixture of charged trimers, dimers, and monomers and fragments thereof. Judging from the mass spectral data, the “largest” average ion mass was calculated to be 107 Da at $P = 1$ W. An ion flux comprising ions of this mass (only) would give a deposition rate of 177×10^{-24} g. This flux alone could not account for the deposition rate per ion estimated between $P = 0.5$ –4 W, assuming the limiting-case scenario of no fragmentation in the arriving ion and no sputtering of surface material. Therefore, it is clear that the deposit must be growing by more than a single mechanism (and probably several). Above $P = 4$ W, the ion flux could potentially account for all deposit mass. Most interestingly, at very low P , judging from the deposition rate per ion, it is possible that the ion flux could account for all of the deposit.

Our interpretation of Figure 11 suggests that, at very low P , ions could contribute up to 100% of the deposit’s mass. In a 1-W plasma of allylamine, the peak ion energy measured using the ion energy facility on the Hiden mass spectrometer was 10 eV, but this measurement was relative to a grounded surface. Judging from the data in ref 19, we postulate that, relative to a self-biased surface, the ion energy would be lower, perhaps <5 eV. Elsewhere,¹⁹ we have discussed the idea that low ion energies are consistent with substantial conservation of ion molecular structure in the deposit, whereas high ion energies are not. This hypothesis is supported by secondary ion mass spectrometry of low- P plasma polymers²² and by studies using low-energy ion beams.²³ Elsewhere, we show a striking similarity in surface chemistry (XPS) and molecular structure (SIMS) between polymer deposits grown from a plasma of HMDSO (low P) and a low-energy ion beam (15 eV) created from HMDSO using the m/z 147 ion ($HMDSO-CH_3$)²⁴.

In the interpretation of Figure 11, it is assumed that the sticking probability is unity, or at least remains a constant with

ion energy. The authors are unaware of any study on the sticking probabilities of atomic or polyatomic ions on organic surfaces. The sticking probability is likely to depend enormously on the specific ion, surface, and effect that the ion has on the surface.

On the basis of this study and earlier work,¹⁵ a more comprehensive picture of the plasma polymerization of allylamine is emerging. The ion contribution to the deposit growth appears to be very important over the entire *P* range. Allylamine does not appear to fragment to the same extent as acrylic acid across the *P* range studied, and the availability of intact monomer across the *P* range supports extensive oligomerization (which is relatively *P*-insensitive, cf. what has previously been reported for acrylic acid¹⁹). The surface chemistry of pps of allylamine do not show any significant variation over the *P* range studied. This finding fits well with the observed gas-phase chemistry, but not with the ion energy data. This result could indicate that the increase in ion energies seen over the *P* range (Figure 10) does not have a significant bearing on surface chemistry, which, in turn, would suggest that polyatomic ions with energies below 25–30 eV do not significantly fragment or cause sputtering of surface material.

That ions play such a significant role in the plasma deposition of an allylic compound should, perhaps, not be surprising. In conventional polymerization, these compounds generally polymerize not by radical processes but rather by ionic routes.²⁵

Conclusion

Measurements of the ion flux and mass deposition rates at the surface of a newly forming pp have been combined with mass spectrometry of the plasma-gas phase and analysis of the pp surface by XPS. Mass spectrometry has shown that reactions between ions and molecules are important in the gas phase. The ionic mass transported to the surface is significant (even at low powers), so it is likely that similar reactions are taking place at the surface of the pp. Active sites in the pp surface, formed as a result of ion impact followed by grafting of neutral species (including intact monomer), would account for some of the mass deposited.

Mass spectrometry has shown that the degree of cationic oligomerization in the gas phase does not change markedly across the *P* range studied. The XPS data showed that the retention of nitrogen also changes little. This is in contrast to the behavior of acrylic acid plasmas and illustrates that the chemical nature of the precursor has a great influence on the plasma chemistry at low *P*.

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