

# The Effect of Positive Ion Energy on Plasma Polymerization: A Comparison between Acrylic and Propionic Acids

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Using a novel RF biasing technique, the energy of positive ions at a depositing substrate is controlled, independently of other parameters. Under bias conditions which gave the maximum and minimum ion energies, plasmas of propionic and acrylic acid were investigated using mass spectrometry, an ion flux probe, quartz crystal microbalance, and X-ray photoelectron spectroscopy (XPS). For both compounds investigated, the ion energy affects the deposition rate but leaves the neutral gas-phase chemistry and positive ion fluxes unchanged. The chemistry of the polymer deposit for acrylic acid is unaffected by the change in ion energy, but the chemistry of the propionic acid plasma polymer changes markedly. We argue that the results presented are consistent with the hypothesis that, under the plasma conditions explored, the carbon–carbon double bond present in acrylic acid plays a significant role in the formation of the polymer. Conversely, the absence of this bond in propionic acid leads us to conclude that positive ions contribute significantly to film formation for this compound.

## Introduction

The production of thin film polymeric materials using low-pressure radio frequency (RF) plasmas is well established.<sup>1,2</sup> Materials produced using these techniques have found many uses, such as corrosion or gas diffusion barriers. More recently, the use of these materials in the life sciences has been the subject of much research.<sup>3–6</sup> While much work has been focused upon biological response and surface chemistry or topography of the derived films, relatively little attention has been paid to the intrinsic properties of the plasma. For example, global parameters such as monomer pressure and generator power output are commonly used to define the process, yet little is known about how these parameters relate to intrinsic plasma properties of plasma potentials (both DC and RF), plasma densities, or electron temperature.

This knowledge gap can inhibit the production of similar films in different reactors and can hinder the design of new reactors intended for production scale-up from laboratory to factory. More fundamentally, the lack of knowledge about the intrinsic plasma properties can hinder the understanding of the mechanistic processes which create these films. Given the rich variety of energetic species in the plasma—electrons, ions (positive and negative), metastables, and photons—it is unlikely that all monomers deposit by the same pathways. This view is supported by the wide range of global parameters used to produce these films. Parameters such as generator power, monomer pressure, and pulse conditions (generator on and off times) are all adjusted to optimize film characteristics in terms of a chosen output

parameter. Altering these global parameters will affect some or all of the intrinsic plasma properties, and so it is difficult to disentangle the effects of individual plasma parameters on derived film properties.

In this study, we use a specially developed method that allows us to control the energy of positive ions arriving at the substrate surface, independently of other plasma parameters. Furthermore, while doing so, we are able to simultaneously monitor several key properties of the plasma, namely, ion energy, ion flux, neutral and positive ion mass spectra, film deposition rate, and through postproduction analysis, film chemistry through XPS.

This novel methodology is applied to the study of the plasma polymerization of two compounds: acrylic acid (C<sub>3</sub>H<sub>4</sub>O<sub>2</sub>) and its saturated analogue, propionic acid. Acrylic acid is an important monomer compound, finding application as a coating in, for example, a novel cell-delivery vehicle.<sup>6</sup> The extension of this study to the saturated analogue of acrylic acid, propionic acid, allows us to clearly demonstrate the importance of the carbon–carbon double bond in the deposition of acrylic acid.

## Experimental Section

The basis of the technique has been described in detail in earlier publications,<sup>7,8</sup> and so only a brief description is given here. Normally, in an RF plasma, there is an RF potential difference between the bulk plasma and the substrate, across the sheath region.<sup>9</sup> This RF potential controls the ion energy distribution at the substrate,<sup>9,10</sup> broadening the energy distribution into a characteristic, twin-peaked profile.<sup>8,10</sup>

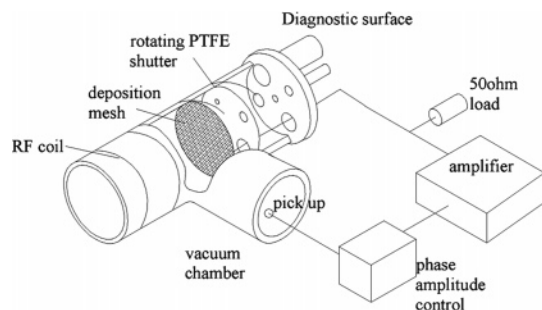
We control the ion energy at the substrate by applying an RF potential to the substrate which nulls the RF sheath potential. To reach the minimum ion energy (floating potential), the RF voltage applied must be matched in both phase and amplitude to the RF potentials already present in the sheath<sup>11</sup> to ensure

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**Figure 1.** Schematic of the deposition chamber, showing the diagnostics built into a common surface. The RF power which generates the plasma is supplied from a separate source through a coil (not shown) which is wrapped around the outside of the glass chamber major axis. The signal from the pickup is adjusted in phase  $F$ , and amplitude,  $V$ , for the 13.56 MHz and the first two harmonics, amplified, and applied to the mesh. No RF current flows through this circuit, and hence no power is deposited into the plasma.

that no current, and hence no power, flows into the plasma. Once this condition is satisfied, the bulk plasma is unperturbed and independent control of the ion energy is achieved.

The presence of the RF sheath potentials causes a DC potential shift between the plasma and the substrate. This is defined as the self-bias potential  $V_{sb}$ , which is more negative than the DC floating potential,  $V_f$ .<sup>9</sup> Hence, by nulling the RF sheath potentials, we manipulate the time average potential difference between the limits  $V_p - V_{sb}$  (upper energy limit, no bias potential applied) and  $V_p - V_f$  (lower energy limit, with the nulling RF potentials applied).<sup>7</sup>  $V_p$  is the time average plasma potential. The self-bias and floating potentials were monitored through a high-impedance RF filter. This measurement was used as a guide to setting up the substrate bias potentials, prior to data being taken. However, once the substrate has been coated with a thin polymer film, the measured DC voltage no longer represents the potential at the film surface. As a check procedure, the ion energy distribution function was measured directly using the mass spectrometer, to ensure that the ion energy was indeed minimized.

In our current system<sup>8</sup> shown in Figure 1, the use of a large planar substrate allows the incorporation of several diagnostics: an energy resolving mass spectrometer, a quartz crystal microbalance, an ion flux probe, and an XPS sample stub. In this way, we are able to make in-situ measurements as the ion energy is varied.

The reactor is a glass T-piece, with RF power introduced into the vessel through a four-turn coil, which is wrapped around the major axis. The earth return path is provided by the stainless steel flanges which close the cylindrical sections. The RF bias potential is provided by a separate power supply, which amplifies a signal taken from an electronic module. The module uses a phase reference signal, taken from a pickup electrode, to provide an input into the amplifier which can be varied in both phase and amplitude with respect to the pickup.<sup>11</sup> In this way, it is possible to provide a voltage to the substrate which is matched to the RF potential in the plasma, for the 13.56 MHz fundamental and the first two harmonics at 27.1 and 40.7 MHz.

## Results

Either acrylic or propionic acid compounds were introduced into the chamber through a needle valve, and a pressure of  $3 \times 10^{-2}$  mbar was maintained for each monomer. A discharge was struck at 5 W generator power, and data were taken. Without applying any bias potential to the substrate, the time average self-bias potentials were  $-3.0$  V and  $-1.4$  V for acrylic

and propionic acid, respectively. Applying the RF bias potential increased the time average voltage to the DC floating potentials of 54.4 V and 54.0 V. The difference in the self-bias potentials could arise from either differences in electron temperatures or RF amplitudes within the plasmas of the respective compounds.<sup>9</sup>

The plasma potential was estimated, using the Hidden EQP, for both monomers by examination of the maximum energy of the ion energy distribution spectrum. This gave plasma potentials of 75.0 V and 71.2 V for acrylic and propionic acid, respectively. These potential values were unaffected by the application of the bias potential, confirming that the technique did not significantly perturb the plasma.

The maximum energy gained by ions as they travel through the sheath to the substrate is given by the potential difference  $V_p - V_{sb}$  (maximum energy, without applied bias) and  $V_p - V_f$  (minimum energy, with applied bias). These energies are calculated as being, for acrylic acid, 78.0 and 20.6 eV. For propionic acid, these potential differences are 72.6 and 16.8 eV.

In a pure, noble gas DC plasma, the potential difference  $V_p - V_f$  may be used to estimate the electron temperature through the expression<sup>9</sup>

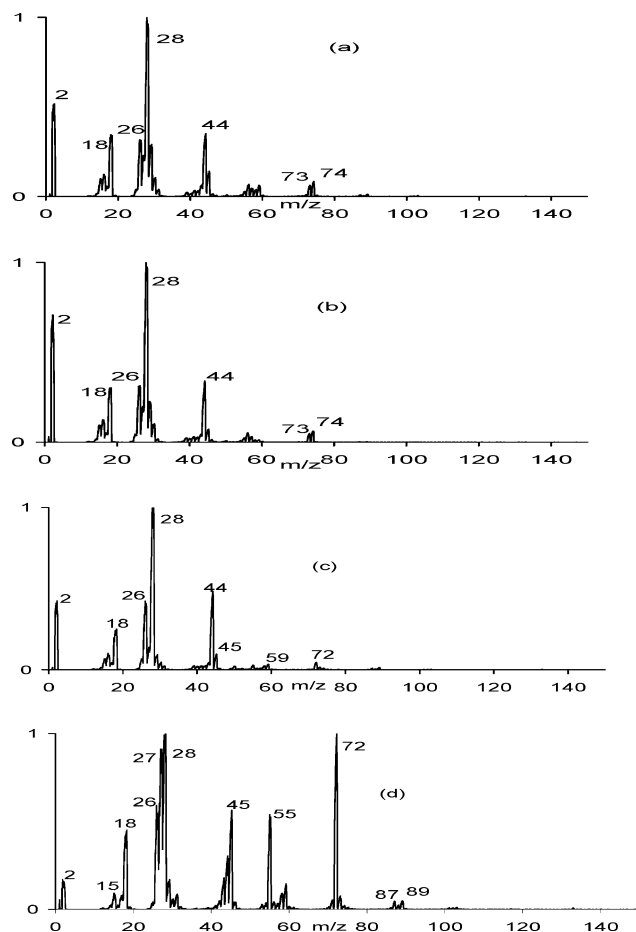
$$V_p - V_f = -T_e \ln \left( \exp \left( -\frac{1}{2} \right) \sqrt{\frac{M_i}{2\pi m_e}} \right) \quad (1)$$

where  $T_e$  is the electron temperature (in volts),  $M_i$  is the ion mass, and  $m_e$  is the electron mass. When the bias potential is applied to the substrate, and the RF sheath potentials are nulled, we create a DC sheath condition, which makes this equation applicable. Hence, assuming that the plasmas produced here are not significantly electronegative, and using the most common ionic species for the ion mass, we can estimate the electron temperature in these plasmas from the measured potentials  $V_p$  and  $V_f$ . Once the substrate is biased, the average ion mass values, calculated from the positive ion mass spectrum (discussed later), are  $m/z = 55$  and  $m/z = 59$  for acrylic and propionic acid, respectively. The measured DC sheath potential differences of 20.6 and 16.8 V give electron temperatures of about 4.8 ( $\pm 0.1$ ) eV and 3.8 ( $\pm 0.1$ ) eV for acrylic and propionic acid, respectively.

In principle, the application of the RF bias potential affects only the ion energy and not the ion flux. That is, there is no increase in plasma density. To test this, the ion fluxes were directly measured using an ion flux probe, supplied by Scientific Systems Ltd. The design and operating principle of this probe makes the device insensitive to the buildup of the polymer film.<sup>12</sup> For acrylic acid, the ion flux was measured as  $3.5 (\pm 0.1) \times 10^{17}$  ions  $m^{-2} s^{-1}$  and  $3.7 (\pm 0.1) \times 10^{17}$  ions  $m^{-2} s^{-1}$  for the maximum and minimum ion energy conditions, respectively. These values are in good agreement with those previously measured in a similar reactor, under these conditions.<sup>13</sup> For propionic acid, the measured fluxes were  $3.4 (\pm 0.1) \times 10^{17}$  ions  $m^{-2} s^{-1}$  and  $3.4 (\pm 0.1) \times 10^{17}$  ions  $m^{-2} s^{-1}$ . The similarity of these figures when the ion energy is changed is encouraging, because it demonstrates that the RF biasing does not deposit a significant amount of power into the plasma, which would be detected as an increase in ion flux.<sup>13</sup>

Because the flux of ions is constant across the sheath,<sup>9</sup> we can use the Bohm criterion<sup>9</sup> to estimate the bulk plasma density of the acrylic and propionic acid plasmas through the relationship

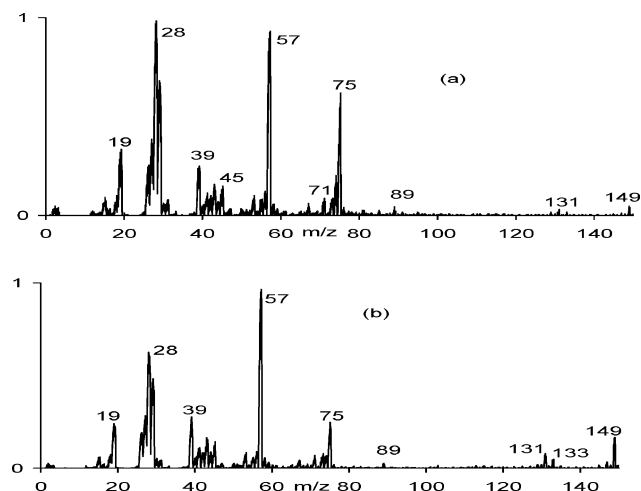
$$\Gamma_i = n_i \exp \left( -\frac{1}{2} \right) \sqrt{\frac{kT_e}{M_i}} \quad (2)$$



**Figure 2.** Normalized neutral (electron impact) spectrum of propionic acid at  $3 \times 10^{-2}$  mbar, 5 W generator power, with (a) and without (b) the applied substrate bias. The similarity of the spectra indicates that the application of the bias does not significantly perturb the bulk plasma. We assign the following compounds to the  $m/z$  values: 26 =  $C_2H_2^+$ , 28 =  $C_2H_4^+$ ,  $OC^+$ ,  $N_2^+$ , 44 =  $C_2OH_4^+$ ,  $CO_2^+$ , 73 =  $C_3H_5O_2^+$ . Spectrum c shows the neutral spectrum of acrylic acid under similar discharge conditions, which is virtually indistinguishable from those of propionic acid. Again, for acrylic acid, the spectrum is unaffected by the application of the bias potential. Spectrum d shows the acrylic acid spectrum without the plasma. Note the predominance of the intact monomer signal ( $m/z = 72$ ), indicating that the plasma fragments the majority of the monomer.

where  $\Gamma_i$  is the ion flux to the substrate,  $n_i$  is the bulk plasma density,  $M_i$  is the mean ion mass, and  $k$  is Boltzmann's constant. Performing the calculation gives plasma densities of about  $2.1 (\pm 0.4) \times 10^{14} \text{ m}^{-3}$  for acrylic acid and about  $2.3 (\pm 0.4) \times 10^{14} \text{ m}^{-3}$  for propionic acid.

For acrylic and propionic acids, mass spectra were obtained for both neutral species (residual gas analysis, RGA) and positive ions. These measurements were repeated with and without the substrate bias potentials applied, that is, for maximum and minimum ion energy conditions. Several general features were observed. First, applying the substrate bias (reducing the ion energy) had no observable effect upon the neutral species spectra of either acrylic or propionic acid. This result also suggests that no significant power is deposited into the plasma by applying the bias voltage, as increasing the power level increases fragmentation of these monomers.<sup>13,14</sup> Neutral spectra for propionic acid with and without applied bias are shown in Figure 2. Also shown in Figure 2 for comparison is a neutral spectrum of acrylic acid. This spectrum differs from the spectrum obtained for propionic acid in that the signal from the cation  $C_2H_5^+$  ( $m/z = 29$ ) and the protonated monomer signal



**Figure 3.** Positive ion spectra of propionic acid, at  $3 \times 10^{-2}$  mbar and 5 W, without (a) and with applied bias (b). Adding the bias potential decreases the peaks around  $m/z = 28$  and causes the emergence of peaks above  $m/z = 100$ . We assign the following structures to the peaks:  $m/z$  19 =  $OH_3^+$ ; 28 =  $C_2H_4^+$ ,  $N_2^+$ ,  $OC^+$ ; 39 =  $C_3H_3^+$ ; 57 =  $C_3OH_3^+$ ; 75 =  $C_3O_2H_7^+$ ; 149 =  $C_6O_4H_{13}^+$ .

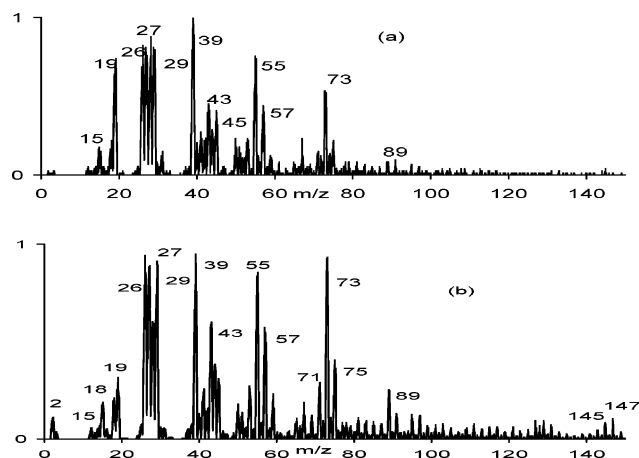
( $m/z = 73$ ) are both suppressed with acrylic acid. However, considering that the presence of the carbon–carbon double bond in acrylic acid could create reaction pathways which would be unavailable to propionic acid molecules, the spectra are remarkably similar.

This apparent similarity of spectra may be to some extent spurious because a certain level of fragmentation is due to the electron impact source of the instrument, which could mask any differences in the spectra brought about by the substrate biasing. To reduce this effect, the energy of the ionizing electrons within the instrument was reduced to 30 eV. Reducing the energy below this value greatly reduced the count rate yet made no detectable difference to the observed spectra. Spectra taken for both compounds without the plasma showed that in both cases, the plasma caused significant fragmentation of the compounds, which is shown for acrylic acid in Figure 2d. This is consistent with earlier studies<sup>14</sup> from which it can be concluded that the majority of the monomer (>75%) is fragmented under these plasma conditions.

Positive ion spectra were obtained for both monomers and under both bias conditions. Unlike the neutral species, the positive ion spectra were greatly affected by the application of the bias potential, with reduced fragmentation being observed when the bias was applied. Spectra for propionic acid with and without the bias are shown in Figure 3. This result is interesting as, in principle, our biasing technique only affects the sheath region immediately adjacent to the substrate. Hence, the change in spectra suggests a change in either the number of collisions in the sheath or the type of collisions. The number of sheath collisions could be affected by a change in the sheath thickness or the ion–neutral collision cross section. Simple analysis of the sheath thickness using the Child Langmuir law shows that RF sheaths are only slightly thicker than their DC counterparts by a factor of about 1.36.<sup>9</sup> Hence, we estimate that the observed spectral change is primarily due to a change in the ion–neutral collision cross section as the ion energy is reduced.

The positive ion spectra for acrylic acid, again with and without the bias potential, are shown in Figure 4. Again, reducing the ion energy has the effect of introducing higher mass fragments and decreases the level of fragmentation compared with the spectra obtained without the bias potential.





**Figure 4.** Positive ion mass scan of acrylic acid at 5 W (a) without and (b) with applied RF bias. Applying the RF bias causes the emergence of higher mass fragments. We assign  $m/z$  values to 15 =  $\text{CH}_3^+$ , 19 =  $\text{OH}_3^+$ , 26 =  $\text{C}_2\text{H}_2^+$ , 27 =  $\text{C}_2\text{H}_3^+$ , 29 =  $\text{C}_2\text{H}_5^+$ ,  $\text{COH}^+$ , 43 =  $\text{C}_2\text{OH}_3^+$ , 45 =  $\text{C}_2\text{OH}_5^+$ , 59 =  $\text{C}_3\text{OH}_7^+$ , 73 =  $\text{C}_3\text{O}_2\text{H}_5^+$ .

This is despite the ion fluxes being very similar between the two conditions.

Although both monomers exhibited reduced fragmentation when the bias was applied, the spectra taken for acrylic acid showed a rich structure compared with that seen for propionic acid. This rich structure indicates that the carbon–carbon double bond is the source of significant amounts of ion chemistry in the gas phase.

From the estimated plasma density, the ionization fraction,  $n_e/n_g$ , where  $n_g$  is the gas density, is about  $10^{-5}$ . Because of this low ionization fraction, the number of ion–neutral collisions will be very much greater than the ion–ion collision frequency.

In the bulk plasma, a positive ion would have a thermal energy ( $\sim 0.026$  eV). As the ion is transported to the wall, though the sheath, the energy is increased up to about 20 or 70 eV, with and without the applied bias potential. Because the cross sections for the various types of ion–neutral collisions are energy dependent,<sup>9</sup> changing the ion energy within the sheath would favor particular reaction pathways. This is highlighted in Figure 4b, where reducing the ion energy increases the proportion of positive ions with masses greater than the monomer unit (73 Da). This is particularly noticeable for acrylic acid, where opening of the carbon–carbon bond can lead to the formation of an oligomeric ion.

The change in ion spectra, without a corresponding alteration in the neutral spectra, provides an opportunity to investigate the comparative roles of ions and neutrals in forming the derived film. If the film chemistry changes when the bias potential is applied, the implication is that ions play a significant role in film production, that is, they deposit mass at the substrate surface as well as energy. Conversely, if no change in film chemistry is observed, neutral species would be assumed to be more important in film growth.

Film chemistries for both propionic and acrylic acid films were obtained using XPS. Data were taken with and without applied bias and are shown in Table 1 for both monomers. Analysis of the surface chemistry shows that films produced in acrylic acid are virtually unaffected by the change in ion energy. Conversely, the films obtained using propionic acid as a monomer exhibited reduced oxygen incorporation when the ion energy was reduced. This was confirmed by curve fitting to the C 1s region of the XPS spectrum, which revealed a marked reduction in the level of carboxyl group retention when the ion energy was reduced.

**TABLE 1: Surface Oxygen to Carbon Ratio, Expressed as a Percentage, and Area Percentage of the C1s Line for Different Chemical Groups**

	ion energy	O/C	C–C	C–O	C=O	COOR/H
acrylic acid	high	39.2	59.3	9.8	4.3	13.2
	low	39.5	62.2	8.0	4.1	12.8
propionic acid	high	29.5	66.8	12.5	2.6	9.1
	low	19.0	81.3	8.9	1.7	4.0

**TABLE 2: Measured Deposition Rates for Each Monomer in  $\mu\text{g m}^{-2} \text{s}^{-1}$ . Note That the Deposition Rate for Propionic Acid is Substantially Lower Than That for Acrylic Acid**

	high energy	low energy
acrylic acid	54	33
propionic acid	8	4

The derived film chemistries suggest that the presence of the carbon–carbon double bond in the acrylic acid monomer leads to a significant amount of neutral grafting onto the substrate. The absence of this bond in propionic acid reduces, or removes altogether, the amount of neutral grafting and increases the proportion of the film produced by positive ions.

This view is supported by examination of the deposition rates obtained, which are given in Table 2. For both monomers, the deposition rate was reduced as the ion energy was lowered. This demonstrates that the energy transported to the substrate by the ions is an important parameter for film growth, irrespective of the dominant growth mechanism. Furthermore, increasing the ion energy up to the maximum value used, about 70 eV, actually increased the deposition rate. This is despite an increase in energy being associated with higher sputtering and etching rates.<sup>9</sup> However, the measured deposition rate for propionic acid was substantially lower than that seen for acrylic acid, with and without the applied bias. Recalling that the ion fluxes are near equivalent for both acrylic and propionic acid, this result suggests that the carbon–carbon double bond could be responsible for ca. 80% of the mass deposit for acrylic acid.

## Discussion

The ability to independently control the ion energy allows us to make some assessments as to the role of the positive ions and the carbon–carbon double bond in forming the polymer film.

While the plasma is maintained, the substrate is continually bombarded with energetic particles: photons, neutrals, and positive ions. For a particle to contribute to the film material, we can define a sticking probability, which will be a function of particle energy. The sticking probability will also include, on average, the possibility that a particle will strike the surface and create a free-radical site, onto which a further particle may attach. Summing over all masses, for each particle (ion and neutral) gives the total deposition rate

$$d = \sum p_j M_j \Gamma_j \quad (3)$$

where  $M_j$  is the particle mass,  $\Gamma_j$  is the flux of particle  $j$ , and  $p_j$  is the effective sticking coefficient for species  $j$ . Any removal of material through etching and sputtering while the plasma is maintained is seen as a reduction in the effective sticking probability. As we have measured the total ion flux to be about  $3.4 \times 10^{17} \text{ m}^{-2} \text{s}^{-1}$  for both monomers, and we can estimate the total neutral particle flux to be about  $2.4 \times 10^{23} \text{ m}^{-2} \text{s}^{-1}$ , we

can recast eq 3 to give the approximate solution for ions and neutrals

$$d \approx \bar{p}_i \bar{M}_i \Gamma_i + \bar{p}_n \bar{M}_n \Gamma_n \quad (4)$$

where the bars indicate mean values, and the subscripts i and n refer to positive ions and neutral species, respectively. By calculating a mean mass,<sup>13</sup> taken from the positive ion mass spectra, and neglecting the contribution to film growth from neutral particles in propionic acid, we can obtain some limiting values to the overall sticking probabilities.

For propionic acid, the mean ion mass was calculated as being 46 and 55 Da without and with the applied bias, respectively. These values give ion mass flow rates of 25.9 and 31.5  $\mu\text{g m}^{-2} \text{s}^{-1}$ , which compare with the measured deposition rates of 8 and 4  $\mu\text{g m}^{-2} \text{s}^{-1}$ , respectively. This means that a film could, in principle, be assembled entirely from positive ions. As the ion energy is reduced, the measured deposition rate falls, while the mass flow rate to the substrate is increased. The reduction in measured deposition rate suggests a change in the surface processes, which is expressed as a reduction in the overall ionic sticking probability at the surface.

Performing a similar calculation for acrylic acid (mean masses of 46 and 59 Da) gives an ionic mass flow rate to the surface of 27 and 36  $\mu\text{g m}^{-2} \text{s}^{-1}$  for the high- and low-energy conditions, respectively. These values are very close to those obtained with propionic acid, because the ion fluxes between the two monomers are equal, yet the measured deposition rates differ by a factor of between 6.75 and 8.25 as the ion energies are reduced. This is a very clear indication of the importance of the carbon–carbon bond in film formation through neutral grafting.

This picture is supported by the fact that the film chemistry of acrylic acid films is unaffected by altering the positive ion energy, while the films produced from propionic acid show marked changes in chemistry as the ion energy is varied.

## Conclusions

We have applied a technique of RF substrate biasing to investigate the role of plasma ion energy upon the deposition rates and film chemistries of acrylic and propionic acid plasma polymers. We have found that in all cases, the application of the RF bias does not significantly perturb the bulk plasma, as the ion flux and neutral particle mass spectra are unaffected by the technique. Direct measurement of the ion energy spectra shows that the technique does control the ion energy at the substrate.

We find that for both acrylic and propionic acid, the positive ion spectra at the substrate is changed, with higher mass fragments being seen for both compounds with biasing applied. The ion spectra for acrylic acid shows a rich structure, which is not seen with propionic acid. This suggests that, for acrylic acid, a large amount of ion–neutral chemistry is taking place within the bulk plasma. Despite this, it appears that the more significant pathway in film growth for acrylic acid is neutral grafting onto free radical sites, which is interesting because on the basis of the neutral spectrum (Figure 2c), only a small proportion of intact monomer remains in the system. The significance of grafting as a polymerization mechanism is highlighted by the observation that the overall deposition rate for acrylic acid is much greater than that seen for propionic acid and that changing the ion energy, and therefore species, has no discernible effect upon the derived film chemistry. Conversely, the film chemistry for propionic acid is affected by changing the ion energy, and we conclude that the absence of the carbon–carbon double bond inhibits grafting at the film surface and hence that ion attachment is a more significant parameter in film growth.

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