

## The Rôle of Cations in Low Power Radio Frequency Plasmas of Propenoic Acid

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In radio frequency (RF) sustained plasmas of propenoic ('acrylic') acid, trimeric cations are detected by MS, and their concentration correlates with retention of acid functionality in the polymer product.

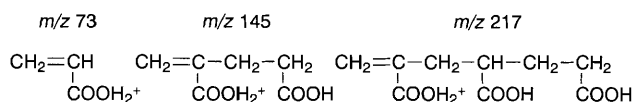
The synthesis of thin polymeric films, known as plasma polymers (PPs), from RF glow-discharge sustained plasmas of small organic molecules is well documented.<sup>1</sup> Traditionally, PPs have been thought of as materials ideally suited for use as inert, protective coatings. However, careful control of the plasma parameters power ( $P$ ) and flow rate ( $\phi$ ), enables the fabrication of films that feature a high degree of retention of the chemical functionality of the monomeric precursor. The influence of these parameters on film chemistry has been studied in the plasma polymerisation of sulfones,<sup>2</sup> alcohols,<sup>3</sup> and methacrylates;<sup>4</sup> a clear correlation is observed between the composite parameter  $P/\phi$  and functional group retention.

However, our understanding of the relationship between plasma environment and thin-film deposition is still unsatisfactory in many respects.<sup>1,5</sup> It is known that there is fragmentation and recombination of the monomeric starting material within the plasma, but the importance of each of the various processes taking place, and the identity of those that lead to polymer formation, remain uncertain. While there are a number of reports concerned with the study of the plasma environment in the polymerisation of fluorocarbon<sup>6</sup> and organosilicon<sup>7</sup> compounds, the coverage of  $\alpha,\beta$ -unsaturated acids and esters is sparse. Apart from our studies, only one example is known to us in which the plasma gas is directly probed by means of MS: this reports the products of fragmentation of methyl methacrylate, but does not provide any evidence of plasma polymerisation.<sup>8</sup> In general, attention has focused on the rôle that free radicals/neutrals play in polymer formation, with the rôle of ionic species considered secondary. However, in a recent paper,<sup>9</sup> we have shown the presence of cations corresponding to  $(2M + H)^+$  in plasmas of methyl and *n*-butyl methacrylate (MMA and *n*-BMA), whereas no neutral species larger than  $M + H$  and  $M + 3H$  were detected. (In plasmas of methyl isobutyrate, the saturated analogue of MMA, dimerisation was seen in both the neutral and positively charged states.) Thus, the MS data from the unsaturated monomers, at least, challenge the orthodox view of the predominance of free-radical chemistry within polymerising plasmas.

Observation of larger species within the plasmas of MMA and *n*-BMA was not possible because of the limited mass range of the spectrometer, namely  $m/z$  0–300. For that reason we have undertaken a mass spectrometric investigation of plasmas of propenoic acid, of which the molecular ion corresponds to  $m/z$  72. A mass spectrometer (Hiden Analytical HAL EQP 300) was interfaced to the plasma deposition chamber. These were evacuated using a turbomolecular pump and a rotary pump, respectively, and species from the plasma were allowed to diffuse into the spectrometer through an aperture of 100  $\mu\text{m}$ . The spectrometer was fitted with an ionisation chamber to facilitate the investigation of neutral species. The plasma was sustained by an RF generator (13.56 MHz) and amplifier inductively coupled to the plasma chamber. The electrical power was in the range 1–7 W. Propenoic acid (Aldrich, >99% purity) was pumped through a needle valve to give a fixed flow rate,  $\phi$ , of 1.4  $\text{cm}^3_{\text{STP}} \text{min}^{-1}$ , at a pressure of  $5 \times 10^{-2}$  mbar. Surface analysis of PP films was carried out by ESCA, on a VG CLAM 200 spectrometer.

Fig. 1 shows the positive-ion mass spectrum of a propenoic acid plasma. It clearly shows ions at  $m/z$  73, 145 and 217, corresponding to  $(M + H)^+$ ,  $(2M + H)^+$  and  $(3M + H)^+$ ,

respectively. For these cations the following structures may be drawn:



Equally likely structures can be drawn which contain carboxonium ions.

Also seen at  $m/z$  2 to higher mass are weaker signals corresponding to saturation of the alkene. At  $m/z$  18 to lower mass, intense signals resulting from the elimination of water are seen. Other species detected correspond to the fragmentation products of these ions.

In the neutral spectrum, ions at  $m/z$  72 (M), 44 ( $\text{CO}_2$ ), 28 (CO), 26 ( $\text{C}_2\text{H}_2$ ) and 18 ( $\text{H}_2\text{O}$ ) were detected. No species at  $m/z$  >72 were observed. A negative-ion spectrum could not be obtained.

Although intensity measurements gathered from different spectra cannot be directly compared, one can make use of the ratios of peak intensities provided that the same tuning procedure is used in all spectral acquisitions. The ratio of peak intensities at  $m/z$  217 and 73 is used as a measure of the extent of trimer formation in the plasma at various power settings. In Fig. 2, this ratio is plotted and the resultant curve is seen to decay smoothly with increasing power. (N.B., the numbers on the vertical axis should not be interpreted as molar ratios.) Fig. 2 shows that with increasing  $P/\phi$  there is less trimer formation. Similar data for those ions due to obvious fragments of the monomer, such as  $m/z$  55, show that the concentration of those fragments is largely insensitive to the power setting over the range used here.

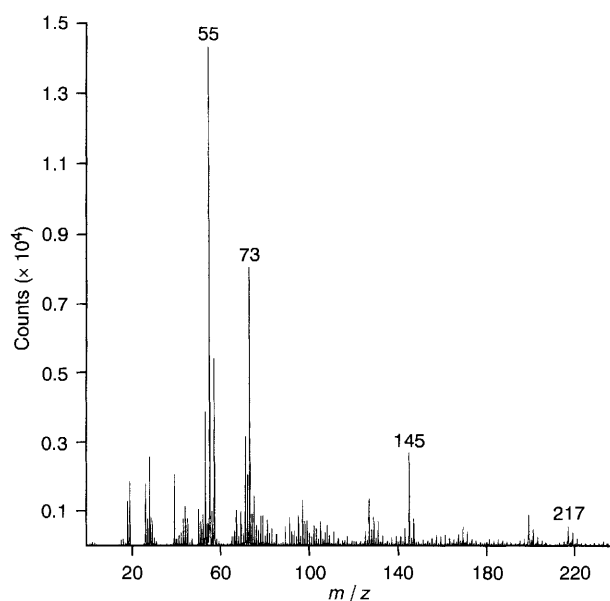


Fig. 1 Positive-ion mass spectrum of a propenoic acid plasma, in which  $P = 1$  W and  $\phi = 1.4 \text{ cm}^3_{\text{STP}} \text{min}^{-1}$

The effect of  $P/\phi$  on carboxylic acid retention in the PP was determined by ESCA. Curve-fitting of the C 1s envelope revealed that acid retention decreases with increasing  $P/\phi$ . For example, retention of carboxylic acid decreases from 80.5% at  $P/\phi = 0.5 \text{ W cm}^{-3}_{\text{STP}} \text{ min}$ , to 19.5% at  $P/\phi = 13 \text{ W cm}^{-3}_{\text{STP}} \text{ min}$ . Thus, there appears to be a direct correlation between trimer formation and retention of functionality.

These results point to the important rôle played by cations in the formation of functionalised plasma polymers. The observation of cations in the plasma corresponding to  $(2M + H)^+$  and  $(3M + H)^+$  offers evidence of positive-neutral reactions taking place within the plasma environment. There is no similar evidence from the neutral spectra of any significant neutral-neutral reactions; the species detected all originate from homolytic bond cleavage within the monomer, either in the plasma or in the ionisation chamber. The correlation of functional group retention with the ratio of ion intensities, Fig. 2, adds further weight to the supposition that within these

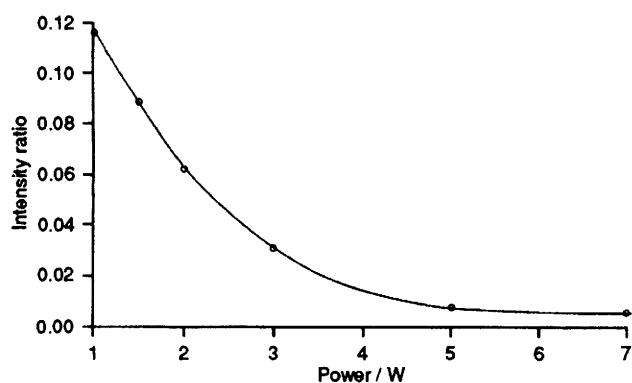


Fig. 2 Intensity ratios of the signals at  $m/z$  217 and 73 in the positive-ion mass spectra of propenoic acid plasmas, in which  $P = 1-7 \text{ W}$  and  $\phi = 1.4 \text{ cm}^3_{\text{STP}} \text{ min}^{-1}$

plasmas ion chemistry is more important than neutral/free radical chemistry.

Yasuda<sup>1</sup> argues against such a rôle for ions within polymerising plasma on the basis of an analogy with radiation polymerisation, where even trace amounts of water inhibit polymerisation by a cationic mechanism. However, this comparison may well be unjustified: in radiation polymerisation cations are formed by ionizing radiation such as  $\gamma$  rays or high-energy electron beams, whereas in plasmas of propenoic acid, cations are formed by proton attachment and rearrangement. Moreover, the plasma environment, being subject to an oscillating electric field, is very different to that of radiation polymerisation. Because plasmas are electron-deficient (electrons are more mobile than ions, and hence diffuse to any surfaces in contact with the plasma), and are only sustained by the constant supply of energy to them, we feel that the importance that we attach to cationic species in our experiments is reasonable.

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