Mechanisms of polymerisation of esters and carboxylic acids in a radiofrequency-induced plasma

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Inductively coupled, radiofrequency-induced plasmas of acrylic acid and methyl methacrylate, operated at low electrical power (1–10 W), have been investigated using a combination of mass spectrometry (MS) and deposition rate measurements. Thin films of plasma polymers of both compounds were analysed by X-ray photoelectron spectroscopy (XPS). There is strong evidence that monomeric and oligomeric cations are responsible for the chemical functionalisation of the product. A reaction scheme is proposed which includes the major plasma-phase events.

The plasma polymerisation of volatile organic compounds to yield thin films of controlled chemical composition can be said to represent an emerging technology. Several potential applications of these films have been described in the literature [1–6], ranging from electronic devices to medical implants. The surface-sensitive techniques of X-ray photoelectron spectroscopy (XPS) and secondary-ion mass spectrometry (SIMS) have been most usefully employed in their analysis. These techniques have established the highly functionalised nature of plasma polymers of various methacrylates [7, 8], sulphones [9], and allyl alcohol [10]. The retention of functionality is optimised by a judicious choice of monomer and plasma conditions. A further refinement in the form of cooling of the substrate has been demonstrated in the case of the plasma polymerisation of acrylic acid, propanone, and 2–hydroxyethyl methacrylate [11], by means of SIMS analysis.

Despite the interest generated by the properties of functionalised plasma polymers, our understanding of the relationship between plasma environment and thin-film deposition is still unsatisfactory in many respects [12, 13]. 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. 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 [14] we have shown by mass spectrometry (MS) the presence of cations corresponding to $(2M + H)^+$ in low-power plasmas of methyl and *n*-butyl methacrylate, whereas no neutral species larger than $(M + H)\cdot$ and $(M + 3H)\cdot$ were observed. Similarly, in two accounts [15, 16] of our work on acrylic acid, we described the observation by MS of cations of the form $(2M + H)^+$ and $(3M + H)^+$; again, no neutral oligomeric species were detected. Thus, the MS data from these monomers, at least, challenge the orthodox view of the predominance of free-radical chemistry within polymerising plasmas.

In addition to probing the plasma by MS, we have performed XPS analysis on thin films of various esters and acids. To shed light on the mechanism of plasma polymerisation, both techniques were applied at a variety of settings of the electrical power (P) supplied to the plasma, while keeping the flow rate (ϕ) constant. This enabled a correlation of the plasma-phase and surface properties of the deposition environment. The rate of deposition was monitored using a quartz-crystal mass balance.

Experimental

The apparatus consisted of a plasma-deposition chamber interfaced to a mass spectrometer. These were evacuated using a rotary pump (10^{-3} mbar) and a turbo-molecular pump (10^{-8} mbar), respectively, and species from the plasma were allowed to diffuse into the spectrometer through an aperture of 100-μm diameter. The monomer vapour was pumped through a needle valve to give a the required flow rate, the precise value being adjusted so as to maximise the count rate of the mass spectra. The plasma was sustained by a radio-frequency (13.56 MHz) signal generator and amplifier inductively coupled to the plasma chamber, the electrical power being in the range 0.5–10 W. The spectrometer was fitted with an ionisation chamber so that it could be used to sample both neutral (by electron impact) and charged species emanating from the plasma, as well as for conventional residual-gas analysis in the absence of a plasma.

Results

A typical positive-ion mass spectra is given in Fig. 1, in this case obtained from a plasma of acrylic acid. The base peak occurs at m/z 73, which corresponds to the protonated monomer, $(M + H)^+$, while the most prominent fragments are observed at m/z 39 ($C_3H_3^+$), 55 (CH_2CHCO^+), and 57 ($CH_3CH_2CO^+$). Ions are also detected at m/z 145 and 217, which can be written $(2M + H)^+$ and $(3M + H)^+$, respectively. These clearly represent protonated dimeric and trimeric acrylic acid. Also seen at $\Delta m/z$ 2 to higher mass are weaker signals corresponding to saturation of the alkene and, at $\Delta m/z$ 18 to lower mass, intense signals resulting from the elimination of water. There are other new signals at $m/z > 90$; these appear in clusters corresponding to the sequence $C_nH_m^+$. In the neutral spectrum (obtained by electron impact at 20 eV), the molecular ion is at m/z 72, and predictable fragments are observed at m/z 28 ($CO^{\cdot+}$), 44 ($CO_2^{\cdot+}$), and 55 (CH_2CHCO^+). No signal at $m/z > 72$ is detected.

Similar results were obtained from plasmas of methyl methacrylate. A protonated dimeric cation was detected at m/z 201. Because of the limited mass range of the spectrometer (m/z 0–300), the presence of higher-order oligomers of the ester could not be confirmed.

The C 1s region of the XP spectrum of plasma-polymerised acrylic acid, prepared at $P = 1$ W) is shown in Fig. 2. Curve-fitting of the spectrum shows that five chemical environments can be distinguished, of which four occur at a characteristic chemical shift (ΔE_b) relative to the main (hydrocarbon) component at 290.7 eV. One of these environments is found at $\Delta E_b = 0.7$ eV, and represents the 'β-shift' undergone by carbon atoms directly bonded to a carboxyl group. This introduces the requirement that the components at $\Delta E_b = 0.7$ eV and 4.4 eV be of approximately equal intensity. The numerical results of curve fitting are summarised in the Table. This exercise enables estimation of the degree of retention of carboxylic acid. For the spectrum shown in Fig. 2, this value is 58%. Thin films prepared at higher power showed less retention.

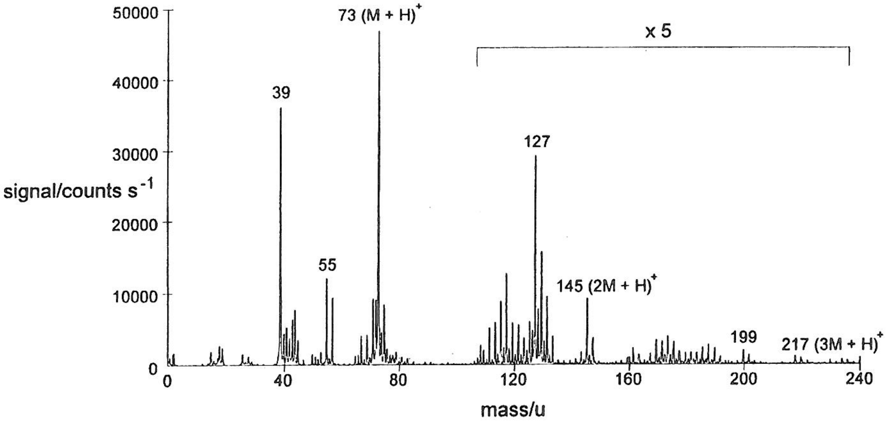

Fig. 1 Positive-ion mass spectrum of a plasma of acrylic acid operated at $P = 3$ W and $\phi = 1.4\ \mathrm{cm}^3_{\mathrm{STP}}$. The area under the horizontal bar has been expanded five-fold

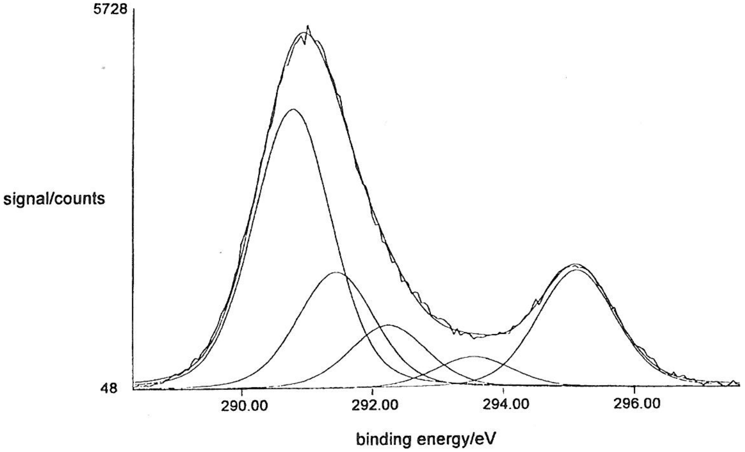

Fig. 2 The C 1s region of the XP spectrum of plasma-polymerised acrylic acid, prepared at $P = 1$ W and $\phi = 1.4\ \mathrm{cm}^3_{\mathrm{STP}}$

Discussion

Intensity measurements from mass spectra such as that shown above, recorded over a range of values of *P*, can be used to shed light on the mechanism of plasma polymerisation. Fig. 3 shows a plot of the ratio of the intensities at *m/z* 217 and 73 versus *P* for acrylic acid, and gives a measure of the degree of gas-phase polymerisation of the starting material at each value of *P*. The same procedure was applied to peaks due to obvious fragments of the monomer, such as *m/z* 55, again normalised to the monomer signal at *m/z* 73. In this case it was found that the normalised intensity is largely insensitive to *P* over the range examined here. Similar conclusions were reached for methyl methacrylate.

Thus one can make a distinction between conditions of low and high *P*. This corresponds to the distinction made by Yasuda [12] between an 'energy-deficient region' at low *P* (or high ϕ) and a 'monomer-deficient region' at high *P* (or low ϕ), and is reinforced by our quantified XPS data, which show that the degree of carboxylic acid retention is also *P*-dependent. Collation of these data allows us to conclude that there is a direct relationship between chemical functionalisation of the product and the relative abundance of the positively-charged oligomeric species identified in the mass spectra. Under conditions of low *P*, there is strong evidence of purely 'molecular' oligomerisation in the plasma phase. Indeed, the neutral spectra show that ample intact starting material is available for reaction with activated species of the form $(M + H)^+$. There is no evidence from the neutral spectra of any significant neutral-neutral reactions: all of the species detected originate from bond cleavage within the monomer, either in the plasma or in the ionisation chamber. In the absence of neutral oligomeric species, we conclude that oligomerisation is most strongly influenced by neutral-positive collisions.

The positive and neutral species detected by mass spectrometry provide the basis for an understanding of the plasma-phase reactions which are likely to lead to plasma polymerisation. Taking again acrylic acid as an example, the mass spectra suggest the processes depicted in the Scheme, which can be easily adapted to describe also the plasma-phase reactions of methyl methacrylate. The processes *A* to *D* constitute a group of reactions beginning with protonation of the monomer, M, and account for most of the species detected in the mass spectra shown in Fig. 1. We speculate that the protonated monomer undergoes intra-molecular transfer of the proton, opening up the carbon-carbon double bond. The carbocation thus formed reacts with a further monomer. The product of that reaction is available for further additions of the monomer repeat unit, as observed in Fig. 1, and it almost certainly makes the greatest contribution towards retention of the carboxylic acid functionality at low *P*. Termination occurs via a further intra-molecular proton transfer. Reactions *C* and *D* yield precursors for the incorporation of other oxygenic functionalities into the plasma polymer, of which alcohols and ketones are unambiguously revealed to be present by XPS analysis, Fig. 2. Reaction *E* is an electron-capture event. Reaction *F* involves fragmentation of the monomer via a six-membered transition state. The latter reactions provide a basis for the rationalisation of all remaining mass spectral signals of any appreciable intensity. The Scheme can be adapted to account for the esters.

In conclusion, these results point to the important rôle played by cations in the formation of functionalised plasma polymers. The correlation of functional group retention with the ratio of ion intensities adds further weight to the supposition that within these plasmas ion chemistry is more important that neutral/free-radical chemistry. Moreover, the availability of detailed reaction schemes such as that presented here represents an important step towards the fine-tuning of the plasma polymerisation process, and the fabrication of highly functionalised 'designer' materials for specialist applications.

References

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	$\underline{\mathrm{C}}$—R^a	$\underline{\mathrm{C}}$—CO$_2$R^a	$\underline{\mathrm{C}}$—O	$\underline{\mathrm{C}}$=O	$\underline{\mathrm{C}}$O$_2$R^a
E_b/eV	290.7	291.4	292.2	293.5	295.1
ΔE_b	—	0.7	1.5	2.8	4.4
% Area	46.01	19.1	10.45	5.2	19.2

^{a} R = C or H

Table Results of curve-fitting of the C 1s region of the XP spectrum of plasma-polymerised acrylic acid, prepared at $P = 1$ W and $\phi = 1{\cdot}4\ \mathrm{cm}^3_{\mathrm{STP}}$

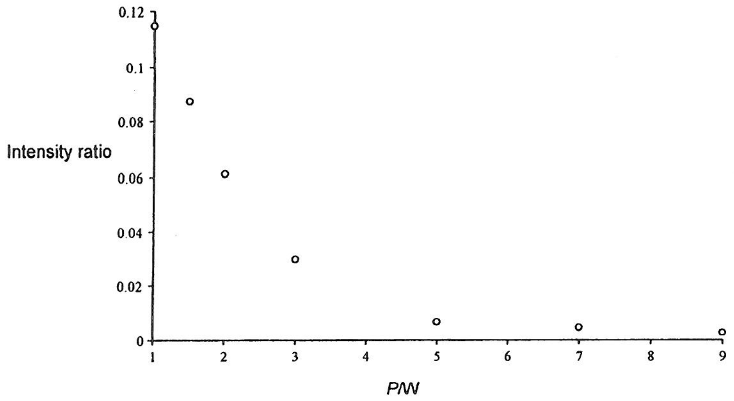
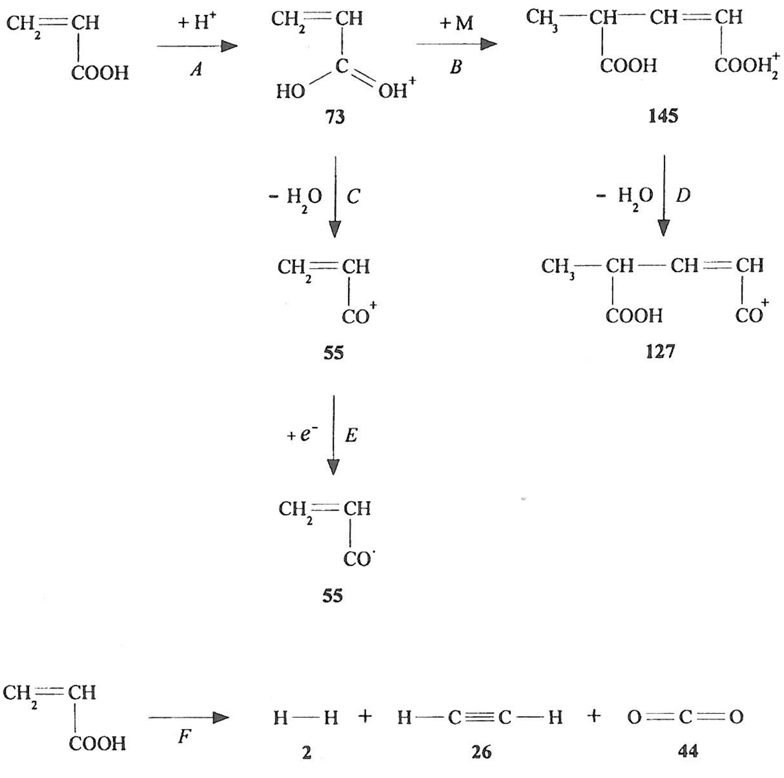


Fig. 3 Plot of ratio of ion intensities measured at *m/z* 217 and 73 in the positive-ion, plasma-mode mass spectra of propenoic acid, versus *P*



Scheme