Characterization of Plasma Polymers of Acrylic Acid and Propanoic Acid

Liam O'Toole,* Alison J. Beck, and Robert D. Short

University of Sheffield, Department of Engineering Materials, Laboratory for Surface and Interface Analysis, Sir Robert Hadfield Building, Mappin Street, Sheffield, U.K. S1 3JD

Received December 13, 1995; Revised Manuscript Received April 23, 1996⊗

ABSTRACT: Plasma polymers of acrylic (propenoic) acid and propanoic acid were prepared from inductively coupled, radio-frequency-induced plasmas excited in vapors of the starting materials. The plasma polymers were characterized by X-ray photoelectron spectroscopy (XPS), infrared reflection absorption spectroscopy (IRAS), and static secondary-ion mass spectrometry (SIMS). Detailed interpretation of the spectra allows determination of the distribution of chemical functionalites at the surface of the product and of the influence of unsaturation and plasma power on this distribution. The results are discussed in the context of previously proposed mechanisms of plasma polymerization of the compounds under investigation.

Introduction

The use of radio-frequency-induced plasmas for the deposition of thin polymeric films from simple organic starting materials has been abundantly described.[1−6] Because these films, termed plasma polymers, are difficult to prepare in thicknesses of more than 1 μm,[1] the surface-sensitive technique of X-ray photoelectron spectroscopy (XPS) has been a popular choice for the purpose of their characterization. This is demonstrated by the large number of reports which have appeared in recent years, in which XPS has been applied to the analysis of methacrylates,[7−9] sulfones,[10] allyl alcohol,[11] and carboxylic acids.[12−15] The emphasis has usually been placed on those plasma conditions which lead to a high degree of retention of the chemical functionality of the starting material in the product. In some cases,[9,12,13] XPS analysis has been supplemented by mass spectrometry of the polymerizing gas, thus providing useful mechanistic information. Applied to carboxylic acids, even low-resolution XPS can enable determination of the degree of retention of functionality, by virtue of the large chemical shift undergone by carbon atoms in a carboxylic acid environment.

To delineate the effects of side reactions within the plasma, which lead to the introduction of new functional groups in the product, is less straightforward. Complete characterization of plasma polymers of acrylic acid and propanoic acid by unmonochromated, *i.e.*, low-resolution, XPS alone[13] is hindered by the close proximity on the binding-energy (E_b) scale of alcohols/ethers and aldehydes/ketones, some or all of which may be present in the product. In an effort to remove this uncertainty, we have analyzed plasma polymers of acrylic acid and propanoic acid using a high-resolution XPS instrument, which allows subtle changes in the shape of the C 1s core level with choice of plasma power (P) and starting material to be monitored. We have also recorded the valence-band region of the spectrum ($E_b = 0-40$ eV) under conditions of low resolution but high sensitivity. This compromise is made necessary by the low cross-section to photoionization of valence levels compared to core levels, when the ionizing radiation is in the X-ray region. Because of the similar chemical shift undergone by the C 1s orbital of acids and esters, the relative abundance of these groups was cross-checked using infrared reflection absorption spectroscopy (IRAS) of films deposited onto gold-covered substrates. Films were also analyzed using static secondary-ion mass spectrometry (SIMS), and the spectra were compared to those obtained previously under similar conditions.[16] By these means we aim to achieve a more thorough characterization of the thin-film products than has been possible heretofore. A further objective is to use the results of surface analysis as a test of previously proposed mechanisms of plasma polymerization of acrylic acid and propanoic acid.[13]

Experimental Section

Plasma Reactor. The apparatus used for plasma polymerization has been described in detail elsewhere.[11] The reactor was evacuated to a base pressure of better than 10^{-3} mbar, and the sample vapor was pumped through a needle valve to give an operating pressure of 1.7×10^{-2} mbar and a flow rate of 1.0 $\mathrm{cm^3_{STP}\ min^{-1}}$. The plasma was sustained by a radio-frequency (13.56 MHz) signal generator and power amplifier inductively coupled to the reactor, the electrical power being in the range 1−10 W. To prepare samples for XPS analysis, a piece of aluminum foil was wrapped around a microscope cover slip and placed in the reactor. It was found that a deposition time of 15 min was sufficient to yield films of thickness greater than the XPS sampling depth.

Measurements. XPS spectra were acquired on two instruments. Survey and core-level spectra were recorded using the Scienta ESCA300 spectrometer housed at the Research Unit for Surfaces, Transforms and Interfaces at Daresbury, U.K. Excitation was provided by monochromated Al Kα X-rays. The source was operated at 300 W. The pass energy was set to 150 eV. During the acquisition of survey spectra the slit width was 1.9 mm; for core-level spectra this was reduced to 0.5 mm. Under the latter conditions, the absolute resolution of the spectrometer is taken to be 0.29 eV.[17] Curve fitting of the core-level spectra was performed using software supplied by the manufacturer. This employs 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. The electron takeoff angle subtended at the sample surface was 45°, which gives an estimated sampling depth of 5 nm.[18] Electrical charging of the sample was controlled using a low-energy electron flux, the precise energy being adjusted to obtain the best peak shape. Unless otherwise stated, curve-fitted XPS spectra were corrected for sample charging by applying a binding-energy shift such that the hydrocarbon component of each C 1s region was centered on 285.00 eV.

---

* To whom correspondence should be addressed at University of Birmingham, School of Physics and Space Research, Edgbaston, Birmingham B15 2TZ, U.K.

⊗ Abstract published in *Advance ACS Abstracts,* June 1, 1996.

S0024-9297(95)01841-9 CCC: $12.00

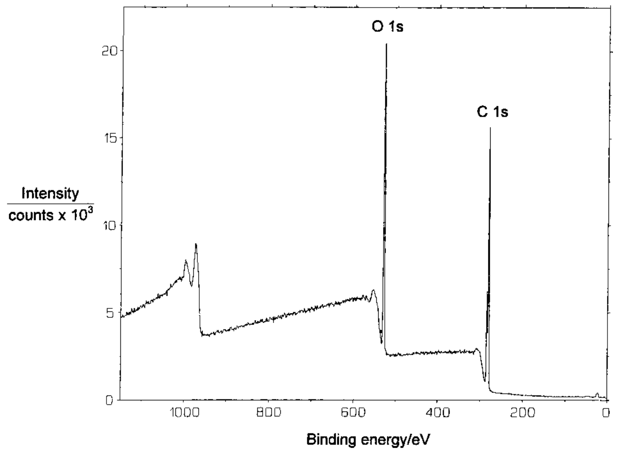

Figure 1. Survey XPS spectrum of plasma-polymerized acrylic acid, prepared at $P = 1$ W.

Table 1. Results of Quantification of the Survey XP Spectra of Plasma-Polymerized Acrylic Acid and Propanoic Acid, Prepared at $P = 1$ W and 10 W

	acrylic acid			propanoic acid	
	1 W	10 W		1 W	10 W
$A_{\mathrm{C\ 1s}}$/(counts × 10^4)	2.41	2.56		2.17	2.44
$A_{\mathrm{O\ 1s}}$/(counts × 10^4)	2.80	2.57		2.46	1.94
$F_{\mathrm{C\ 1s}}$			1.00		
$F_{\mathrm{O\ 1s}}$			2.80		
O:C ratio	0.414	0.355		0.404	0.284

Valence-band spectra were recorded on a VG Clam 2 spectrometer at the University of Sheffield, using Mg Kα X-rays to excite a spectrum. The source was operated at 100 W, and the pass energy was set to 50 eV. In this manner a valence-band spectrum of acceptable resolution and signal: noise ratio could be obtained in less than 45 min, in which time sample deterioration is negligible. The electron takeoff angle was 30°, giving a sampling depth of *ca.* 3 nm. No variation of gross spectral features was observed with change of takeoff angle.

IRAS spectra were obtained using a Perkin-Elmer spectrometer fitted with a liquid nitrogen-cooled MCT detector. For these measurements the samples were prepared on gold-coated glass slides, gold offering high reflectivity in the IR region. The angle of incidence was 10° relative to the sample surface.

Static SIMS spectra were acquired on a VG Ionex IX23LS fitted with a pulsed liquid gallium ion source. The primary ion dose was restricted to *ca.* 10^{11} ions cm^{-2}, which is well within the range of the "static regime".[19] Because of the greater sensitivity of the SIMS technique to impurities, in this case samples were prepared on 10% nitric acid-etched and distilled water- and methanol-rinsed silver foil.

Materials. Acrylic acid and propanoic acid were obtained from Aldrich at >99% purity and, apart from several freeze−pump−thaw cycles, were used as received.

Results

XPS Spectra. A typical survey spectrum is shown in Figure 1, in this case obtained from a plasma polymer of acrylic acid prepared at $P = 1$ W. The binding-energy scale has not been corrected for electrical charging of the sample during analysis. Only carbon and oxygen are detected, of which the 1s levels occur at 280 and 528 eV, respectively. The ratio of the areas, *A*, under these peaks, adjusted by empirically derived sensitivity factors, *F*, to take account of differences in cross-section to photoionization, gives an estimate of the atom number ratio of carbon and oxygen at the sample surface. The values obtained from all four samples are collected in Table 1.

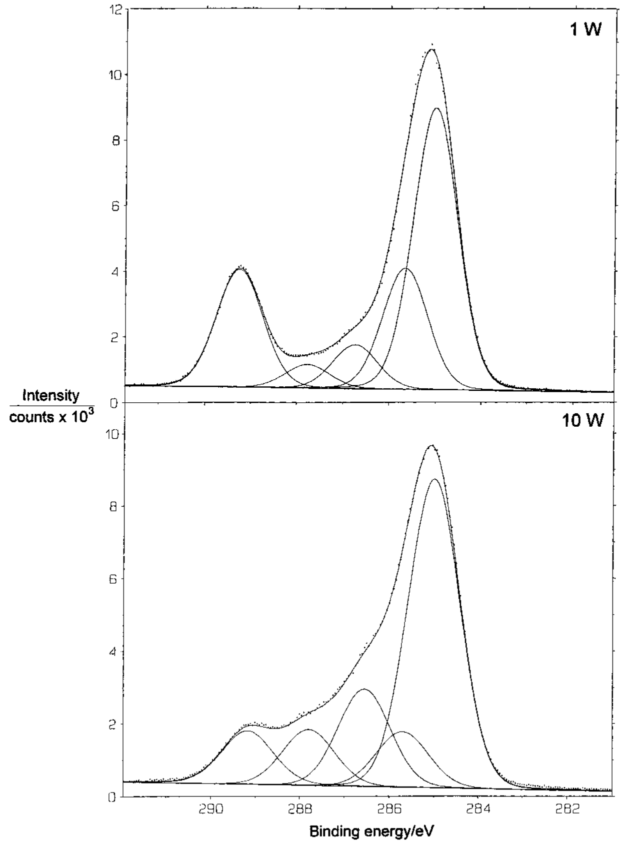

Figure 2. C 1s core-level spectra of 1-W and 10-W plasma-polymerized acrylic acid.

Figure 2 shows the C 1s core-level spectra of 1-W and 10-W plasma-polymerized acrylic acid. Peak shape is strongly influenced by plasma power, and changes in peak shape were quantified by curve-fitting. The number of components required to obtain a good fit was determined from chemical rather than mathematical considerations. In the C 1s region for example, carbon environments of the form *C*—R, *C*—O, *C*=O, and CO$_2$R (R = C or H) are expected to be present, each exhibiting a characteristic chemical shift (ΔE_{b}). Because of the high electronegativity of the carboxyl group, one can also expect an environment of the type *C*—CO$_2$R to be distinguishable from a purely hydrocarbon one. Furthermore, the *C*O$_2$R and *C*—CO$_2$R components will necessarily have approximately equal intensity. (Any deviation from equality will be due to extensive fragmentation of the starting material, leading to the incorporation of irregular structures into the plasma polymer. At the low values of *P* used in this experiment, this effect is highly unlikely.) At high *P*, to simplify the fit, and to obtain a result which is acceptable on chemical grounds, the full widths at half-maximum (FWHM) of all components in a given region were forced to adopt the same value. This value was then allowed to vary freely during the optimization process. The Voigt ratios (the ratios of Gaussian:Lorentzian character) were treated in the same manner.

The above approach enabled a unique "best fit" of each spectrum to be obtained, as drawn in Figure 2. In accordance with convention, the centroid of the hydrocarbon component was placed at 285.00 eV, and the positions of the other centroids adjusted accordingly. The parameters which characterize the fits are summarized in Table 2. There is a near coincidence in the values of ΔE_{b} obtained at low and high *P*, which increases confidence in the fitting methodology. Ex-

Table 2. Results of Curve-Fitting of the C 1s Core Level XP Spectra of Plasma-Polymerized Acrylic Acid, Prepared at P = 1 W and 10 W[a]

	E_b/eV		ΔE_b/eV		% area	
	1 W	10 W	1 W	10 W	1 W	10 W
C—R[b]	285.00 (1.18)	285.00[c]			47.0	53.7
C—CO$_2$R[b]	285.56 (1.17)	285.70[c]	0.56	0.70	20.5	9.7
C—O	286.69 (1.12)	286.55[c]	1.69	1.55	8.2	17.0
C=O	287.79 (1.04)	287.79[c]	2.79	2.79	3.8	9.8
*C*O$_2$R[b]	289.23 (1.18)	289.17[c]	4.23	4.17	20.5	9.7

[a] In the second column, the figures in parentheses are the values of FWHM, in eV. [b] R = C or H. [c] FWHM = 1.37 eV.

Table 3. Results of Curve-Fitting of the C 1s Core Level XP Spectra of Plasma-Polymerized Propanoic Acid, Prepared at P = 1 W and 10 W[a]

	E_b/eV		ΔE_b/eV		% area	
	1 W	10 W	1 W	10 W	1 W	10 W
C—R[b]	285.00 (1.20)	285.00[c]			49.2	64.3
C—CO$_2$R[b]	285.60 (1.20)	285.78[c]	0.60	0.78	17.7	5.6
C—O	286.65 (1.19)	286.47[c]	1.65	1.47	10.2	15.8
C=O	287.78 (1.07)	287.78[c]	2.78	2.78	5.2	8.7
*C*O$_2$R[b]	289.25 (1.20)	289.14[c]	4.25	4.14	17.7	5.6

[a] In the second column, the figures in parentheses are the values of FWHM, in eV. [b] R = C or H. [c] FWHM = 1.45 eV.

amination of the percentage areas of the *C*O$_2$R components confirms the P dependence of carboxylic acid retention, as determined using unmonochromated XPS.[13] The fit also reveals that the full width at half-maximum is a function of P: the increase from an average value of 1.14 eV—comparable with conventional poly(acrylic acid)[17]—to 1.37 eV reflects the greater chemical complexity of the sample prepared at higher P.

High-resolution XPS spectra were recorded of plasma polymers of propanoic acid, prepared under conditions identical to those reported above for acrylic acid. Curve-fitting of the C 1s core-level spectra yields the parameters collected in Table 3. The trends in carboxylic acid retention and in FWHM noted above are duplicated here, but in more extreme form. Furthermore, in all cases the absolute FWHM is greater than for a comparable sample obtained from acrylic acid. This indicates that the surface chemistry of plasma-polymerized propanoic acid is of greater complexity, which in turn suggests that there is a greater number of reaction pathways which result in film deposition from the plasma.

Discussions of carboxylic acid retention have assumed, explicitly or implicitly, that the ester contribution to the *C*O$_2$R and *C*—CO$_2$R components is absent or negligible. In the case of plasma-polymerized acrylic acid prepared at low P, this assumption is supported by comparison of the signal intensity of the *C*O$_2$R environment (20.5%) to that of the *C*—O (8.2%) in Table 2. In a pure ester, these environments would be expected to have an equal intensity. In the saturated analogue, Table 3, the distinction is not so marked. In the plasma polymers prepared at high P, the relative intensities of these two types of chemical environments are inverted. The values of FWHM for the C 1s region obtained here also support the assumption that the carboxyl group is present as carboxylic acid as opposed to ester, again at least when applied to those plasma polymers prepared at low P.

To aid in the clarification of this issue, valence-band XPS spectra of all four samples were recorded under conditions of low resolution and high sensitivity, using the VG spectrometer. These spectra are reproduced in Figures 3 and 4 for acrylic acid and propanoic acid, respectively. A sample of plasma-polymerized acrylic acid, prepared at 1 W, was also analyzed on the Scienta instrument, but no improvement in resolution was achieved. This demonstrates that the quality of the spectra in Figures 3 and 4 is determined by the chemical properties of the samples rather than by the performance of the spectrometer. Allowing for broadening of spectral features due to the chemically heterogeneous nature of the sample, the 1-W spectrum of acrylic acid, Figure 3, closely resembles that of conventional poly(acrylic acid).[17] There is further loss of structure when P is increased to 10 W, but a redistribution of intensity can be discerned from the peak at 11 eV to the broad peak at 18 eV. This effect is even more pronounced in the case of propanoic acid, Figure 4. An exhaustive interpretation of these effects is not available at this stage, but some information can be obtained by reference to a previous experimental and theoretical study of the valence energy levels of conventional poly(acrylic acid), poly(methyl methacrylate), and poly(vinyl acetate).[20] Examination of the valence-band spectra of the esters reveals that an intense feature at 18 eV is present; with the aid of *ab initio* molecular orbital calculations this is determined to represent an orbital of predominantly sσ (C 2s—C 2s) bonding character. In the acid, by contrast, this feature is much attenuated. Thus our XPS spectra provide some circumstantial evidence, at least, for ester formation at high P. This is especially true of the saturated monomer.

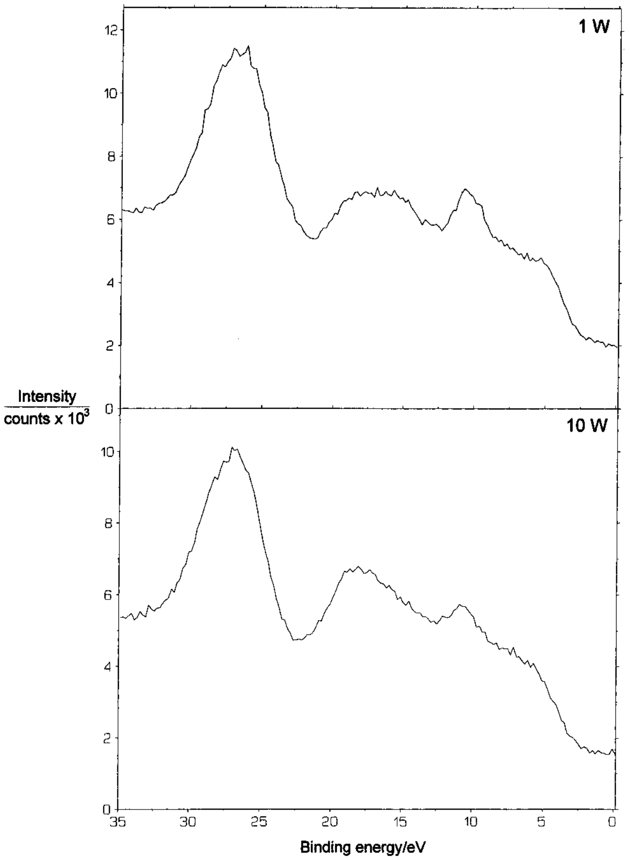

Figure 3. Valence-band XPS spectra of 1-W and 10-W plasma-polymerized acrylic acid.

IRAS Spectra. The problem of acid/ester ambiguity can also be approached by reference to the IRAS spectra of these compounds. The IRAS technique differs from XPS in the important respect that the entire polymer film is sampled, by virtue of reflection of the incident

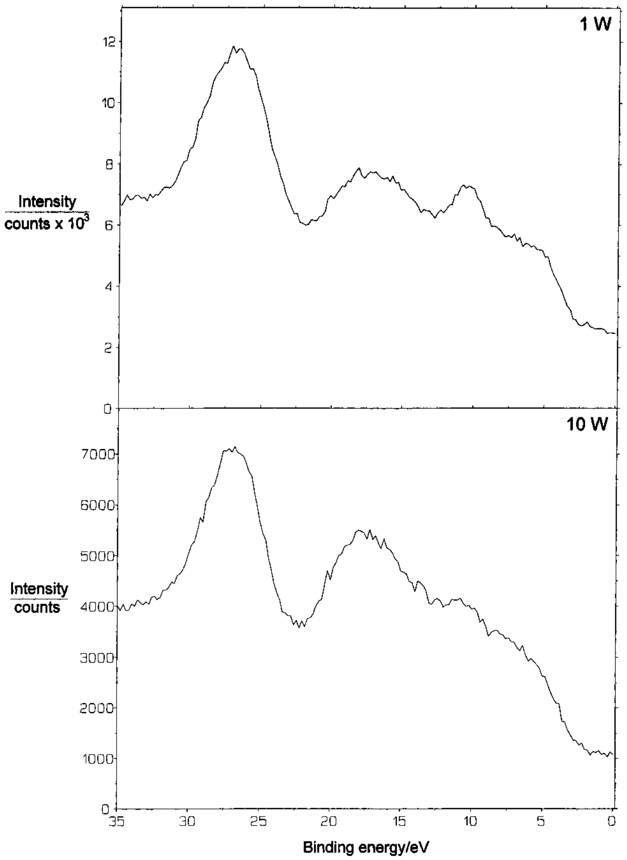

Figure 4. Valence-band XPS spectra of 1-W and 10-W plasma-polymerized propanoic acid.

IR beam on the gold substrate, whereas in the XPS experiment the effective sampling depth is limited to a few nanometers. Nevertheless, because we find that the XPS spectra of our samples do not vary with takeoff angle, demonstrating that the films are vertically homogeneous, it is valid to compare directly the results of the two spectroscopies.

The spectra of 1-W and 10-W plasma-polymerized acrylic acid in the range 3800–1300 cm^{-1} are given in Figure 5. Both spectra show a high water content, which is to be expected in a hygroscopic sample. The most prominent feature in both spectra is the carbonyl stretch, occurring at 1735 and 1729 cm^{-1} at low and high P, respectively. The spectra differ most obviously in the greater hydrocarbon activity at *ca.* 2950 cm^{-1} in the spectrum of the 10-W sample, which is consistent with the core-level XPS results reported above. In the same spectrum we observe a shoulder (to the carbonyl signal) at 1650 cm^{-1}, which suggests that unsaturation is present at high P. In the spectrum of the 1-W sample, a weak, broad absorbance occurs which is centered at *ca.* 2600 cm^{-1} and which is much weaker at high P. This is possibly due to the hydrogen-bonded hydroxyl stretch of the carboxylic acid group.

The values of the carbonyl stretching frequency quoted above are too similar to shed any light on the question of the relative contributions of acid and ester to the total carbonyl signal. We have performed a simple experiment, however, in which plasma polymer-treated, gold-covered glass slides were allowed to stand in a saturated solution of $NaHCO_3$ for 10 min. The samples were then washed thoroughly in distilled water. Any acid groups present can be expected to react to give salts of the form $RCOO^-Na^+$, immobilized in the polymer network, whereas esters should undergo no reaction. Figure 6 shows the carbonyl region of the spectra of 1-W and 10-W plasma-polymerized acrylic acid, before and after exposure to $NaHCO_3$. Extensive reaction has occurred in the sample prepared at low P, as evidenced by the emergence of two new, strong peaks at 1590 and 1410 cm^{-1}, which may be assigned to the salt. The spectrum of the sample prepared at high P, by contrast, shows that only minor quantities of acid were available for reaction. We therefore conclude that the 10-W sample contains a greater proportion of ester rather than acid groups, which serves as confirmation of our interpretation of the valence-band XPS spectra.

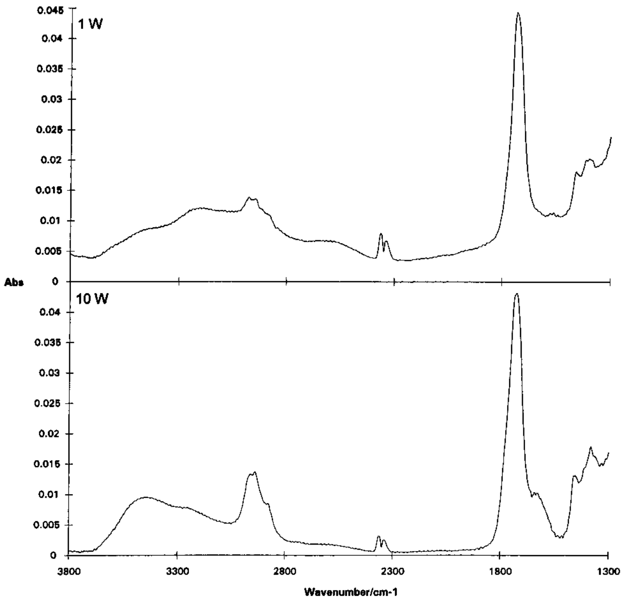

Figure 5. IRAS spectra of 1-W and 10-W plasma-polymerized acrylic acid in the region 3800–1300 cm^{-1}.

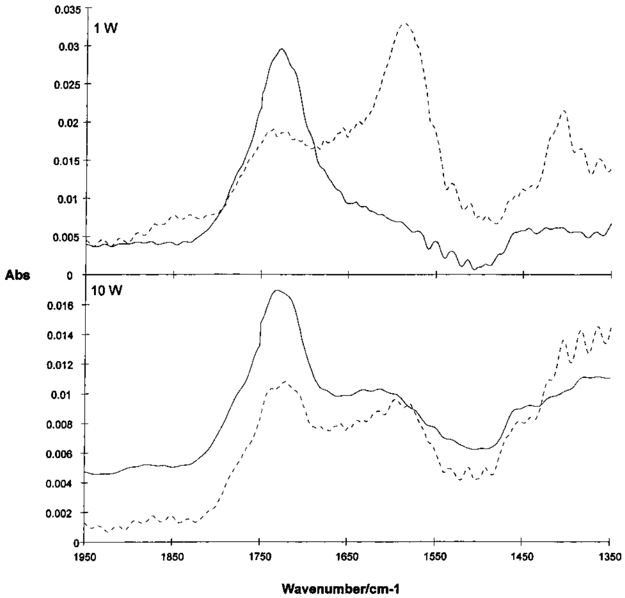

Figure 6. Carbonyl region of the IRAS spectra of 1-W and 10-W plasma-polymerized acrylic acid, before (solid line) and after (dashed line) exposure to a saturated solution of $NaHCO_3$.

The spectra we obtained from plasma polymers of propanoic acid are virtually indistinguishable from the spectra in Figures 5 and 6 and are not reproduced here.

SIMS Spectra. The positive- and negative-ion SIMS spectra of acrylic acid, plasma-polymerized at 1 W, are given in Figure 7. Spectra obtained from the other samples are not shown. Instead, important spectral

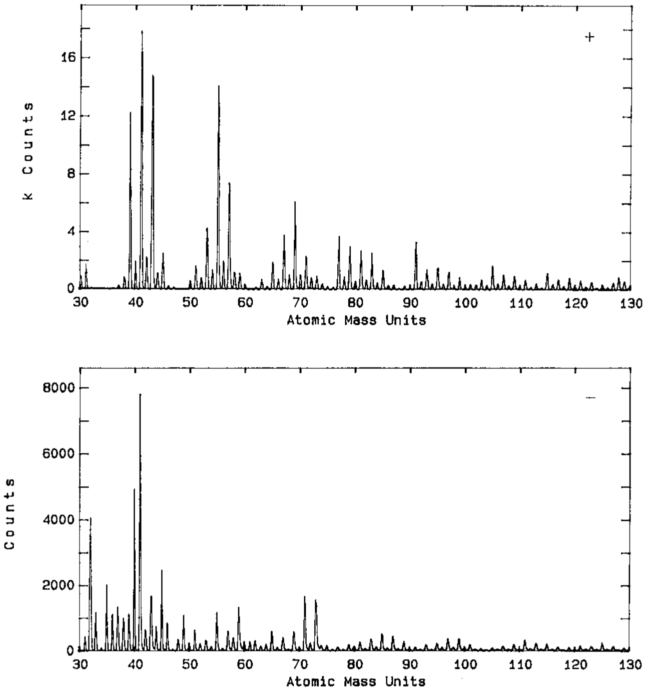

Figure 7. Positive- and negative-ion SIMS spectra of 1-W plasma-polymerized acrylic acid.

Table 4. Quantified Peak Intensities from the SIMS Spectra of Plasma-Polymerized Acrylic Acid and Propanoic Acid

		acrylic acid		propanoic acid	
		1 W	10 W	1 W	10 W
positive ions	39	5.52	5.55	5.14	4.96
	41	9.29	9.73	8.41	8.73
	69	3.30	3.66	2.98	2.42
negative ions	41	1.12	0.987	1.37	0.666
	59	0.296	0.205	0.540	0.125
	71	0.316	0.144	0.385	0.0771
	73	0.384	0.241	0.771	0.247
	73/71	1.22	1.67	2.00	3.21

differences are illustrated by means of a comparison of the normalized intensities of key peaks, as in Table 4. (Intensities were normalized by dividing the peak intensity by the total intensity over the range *m/z* 0–100. The result was multiplied by 100 to give a figure of convenient magnitude.) Spectral interpretation is facilitated by reference to the previously published spectra of plasma polymers of acrylic acid and of the conventional analogue, poly(acrylic acid).[16] Moreover, the thoroughness of that report renders an exhaustive description of our spectra unnecessary. Instead, subtle differences among the spectra of our samples will be highlighted.

In positive-ion mode, peaks characteristic of poly(acrylic acid) are observed at *m/z* 39 ($CH_2{=}C{=}CH^+$) and 41 ($CH_2{=}C^+{-}CH_3$). These peaks are less intense for propanoic acid at a given *P*, indicating that the samples bear less resemblance to conventional poly(acrylic acid). These are also peaks which are absent or are of negligible intensity in the conventional analogue but which are promoted in our samples. One of these occurs at *m/z* 69 ($C_5H_9^+$), a value associated with polymers based upon the propylene repeat unit.[21] At higher mass, signals at *m/z* 77 and 91 are detected, values which are normally associated with aromatic samples. However, Briggs and co-workers[2,22] have considered the formation of ions of these masses as a result of ion beam damage in polymers. In the spectra of unsaturated, aliphatic polymers, these peaks are seen well below the prescribed static limit of 10^{13} ions cm^{-2}. At the static limit, these ions are also seen in the SIMS of fully saturated polymers. Elsewhere,[8] we have shown that the abundance of these ions is greater in plasma polymers prepared at high *P*, and we have attributed this result to higher levels of unsaturation, leading to greater susceptibility to ion beam damage.

The negative-ion spectra feature prominent signals at *m/z* 41 ($CHCO^-$), 59 (CH_3COO^-), 71 ($CH_2{=}CHCOO^-$), and 73 ($CH_3CH_2COO^-$). The peaks at *m/z* 71 and 73 are of course due to ions which differ only by the extent of unsaturation. In the conventional polymer, the peak at *m/z* 73 has negligible intensity, whereas in our samples it assumes much greater importance. In the spectrum of 1-W acrylic acid in Figure 7, the peaks at *m/z* 71 and 73 are of approximately equal intensity, and Table 4 shows that the relative intensity of the *m/z* 73 peak increases in the order 1-W acrylic acid < 10-W acrylic acid < 1-W propanoic acid < 10-W propanoic acid. Thus this intensity ratio serves as a measure of how closely the plasma polymer resembles the conventional material. Elsewhere, we have used the ion ratio *m/z* 87/85 to investigate molecular structure in a series of plasma-polymerized alkyl methacrylates.[7,8] The SIMS spectra of these plasma polymers were compared to those of their conventional counterparts. On the basis of previously established fragmentation schemes, the *m/z* 85 ion was taken as representative of precursor monomer units that had bonded in a linear fashion, as in the conventional polymer. (Note that the intact monomer unit is not observed, due to facile loss of the ester R-group.) The *m/z* 87 ion was attributed to fully saturated chain ends or pendant side groups. At low *P*, plasma-polymerized materials which closely resembled their conventional counterparts were prepared from unsaturated alkyl methacrylates. However, at high *P*, from the *m/z* 87/85 ratio, it was evident that a more highly branched product was being produced, in which the proportion of saturated end groups and/or side chains had substantially increased. The plasma polymerization of fully saturated alkyl methacrylates produced more highly branched polymers, irrespective of *P*. In this study, examination of the ratio *m/z* 73/71 reveals a similar effect with regard to saturation.

At higher mass, conventional poly(acrylic acid) gives a signal of moderate intensity at *m/z* 143, which may be reasonably assigned to a molecular ion of the form $(2M - H)^-$. Such a signal cannot be unambiguously detected in our spectra above a background which it typical of the SIMS of plasma polymers and which arises from what has been described as the "atomic" nature of plasma polymerization.[23]

Discussion

Based on a mass spectrometric study[13] of the plasma polymerization of acrylic acid at low *P*, we have proposed that polymerization takes place predominantly through the carbon–carbon double bond and that this gives rise to the high levels of functionalization as measured by XPS. We were less clear on how polymerization occurs in the case of propanoic acid, although in plasmas of both monomers cations corresponding to $(M + H)^+$, $(2M + H)^+$, and $(3M + H)^+$ were detected by mass spectrometry. An important distinction was made between the two monomers at low *P*: the deposition rate of acrylic acid was 5 times that of propanoic acid. From our data we concluded that at low *P*, in plasmas of acrylic acid, the mechanism of polymerization resembles that of cationic chain growth. At higher *P*, free-radical reactions are likely to assume greater importance.

To substantiate our hypothesis, it is necessary to demonstrate that in low-*P* plasma-polymerized acrylic acid the monomer units have combined through the carbon−carbon double bond and that the carboxylic acid functionality remains essentially unreacted. The spectroscopic evidence presented in this paper clearly supports this supposition. The FWHM employed in the C 1s peak fit of this plasma polymer correspond very closely to those determined in the conventional polymer, demonstrating the uniqueness of each chemical environment. The valence band spectrum confirms the presence of acid (as opposed to ester) in the plasma polymer. This conclusion is reinforced by the formation of a salt on exposure to $NaHCO_3$ solution, indicating that the carboxylic acid has not reacted during polymerization. The positive- and negative-ion SIMS spectra bear a close resemblance to those of the conventional polymer. Taken together, the evidence that polymerization has proceeded through the carbon−carbon double bond is very strong indeed.

At high *P*, the selectivity in the reaction site has been lost. The spectroscopic data reveal some loss of carboxyl from the monomer, presumably as CO_2, which is then pumped away. The carboxyl retained in the product is present as both acid and ester. This implies direct incorporation of oxygen within the polymer network. The increase in the ion ratio *m/z* 73/71 can be taken to indicate a greater degree of branching, giving a higher concentration of end groups.

The reaction(s) leading to polymer formation in plasmas of propanoic acid are much less clear. The spectroscopic data reported here reveal that there is no unique mechanism of plasma polymerization. The larger FWHM (*cf.* plasma-polymerized acrylic acid) used to fit the C 1s core line indicates a greater multitude of chemical environments. The ion ratio *m/z* 73/71 suggests a still greater degree of branching. The effect of increased *P* is to promote this deviation from the structure of conventional poly(acrylic acid).

Conclusions

In ref 13 we anticipated differences in the molecular structure of plasma polymers prepared from acrylic acid and propanoic acid. The former were expected to contain molecular units which are bonded in a linear manner, as in the conventional analogue. The spectroscopic data obtained from low-*P* plasma-polymerized acrylic acid confirm this. Plasma polymers of propanoic acid, on the other hand, were not expected to contain these linear sequences of repeat units; instead, we anticipated a higher concentration of end groups. From our data we can conclude that, even at low *P*, there is greater randomization in molecular structure.

In plasma polymers prepared at high *P*, we see greater involvement of oxygen in the molecular network, which points to the greater importance of free-radical chemistry in polymer formation.

References and Notes

(1) Morita, S.; Hattori, S. In *Plasma Deposition, Treatment, and Etching of Polymers*; d'Agostino, R., Ed.; Academic Press: London, 1990; Chapter 6.
(2) Chilkoti, A.; Ratner, B. D.; Briggs, D. *Anal. Chem.* **1991**, *63*, 1612.
(3) Gombotz, W.; Hoffman, A. *J. Appl. Polym. Sci.* **1989**, *37*, 91.
(4) Inagaki, N.; Matsunga, M. *Polym. Bull.* **1986**, *13*, 349.
(5) Sanchez Urrutia, M.; Schreiber, H. P.; Wertheimer, M. R. *J. Appl. Polym. Sci., Polym. Symp.* **1988**, *42*, 305.
(6) Munro, H. S.; Ward, R. J.; Davies, M. C.; Short, R. D. *Polymer* **1993**, *34*, 2250.
(7) Ward, A. J.; Short, R. D. *Polymer* **1993**, *34*, 4179.
(8) Ward, A. J.; Short, R. D. *Polymer* **1995**, *36*, 3439.
(9) O'Toole, L.; Beck, A. J.; Short, R. D.; Ameen, A. P.; Jones, F. R. *J. Chem. Soc., Faraday Trans.* **1995**, *9*, 1363.
(10) Ward, A. J.; Short, R. D. *Surf. Interface Anal.* **1994**, *22*, 477.
(11) Ameen, A. P.; Short, R. D.; Ward, R. J. *Polymer* **1994**, *35*, 4382.
(12) Beck, A. L.; O'Toole, L.; Ameen, A. P.; Short, R. D.; Jones, F. R. *J. Chem. Soc., Chem. Commun.* **1995**, *10*, 1053.
(13) O'Toole, L.; Beck, A. J.; Short, R. D.; Ameen, A. P.; Jones, F. R. *J. Chem. Soc.*, Faraday *Trans.* **1995**, *91*, 3907.
(14) Cho, D. L.; Claesson, P. M.; Gölander, C. G.; Johansson, K. *J. Appl. Polym. Sci.* **1990**, *41*, 1373.
(15) Ko, T. M.; Cooper, S. L. *J. Appl. Polym. Sci.* **1993**, *47*, 1601.
(16) López, G. P.; Chilkoti, A.; Briggs, D.; Ratner, B. D. *J. Polym. Sci., Polym. Chem.* **1992**, *30*, 2427.
(17) Beamson, G.; Briggs, D. *High Resolution XPS of Organic Polymers*; John Wiley and Sons: Chichester, U.K., 1992.
(18) Clark, D. T.; Thomas, H. R. *J. Polym. Sci., Polym. Chem. Ed.* **1977**, *15*, 283.
(19) Briggs, D.; Hearn, M. J. *Vacuum* **1986**, *A3*, 1322.
(20) Endo, K.; Inoue, C.; Kobayashi, N.; Aida, M. *J. Phys. Chem. Solids* **1994**, *55*, 471.
(21) Briggs, D.; Brown, A.; Vickerman, J. C. *Handbook of Static Secondary Ion Mass Spectrometry*; John Wiley and Sons: Chichester, U.K., 1989.
(22) Briggs, D. *Surf. Interface Anal.* **1990**, *15*, 734.
(23) Yasuda, H. K. *Plasma Polymerisation*; Academic Press: London, 1985.

MA9518417