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A t.o.f.s.i.m.s. and x.p.s. investigation of the structure of plasma polymers prepared from the methacrylate series of monomers: 2. The influence of the *W/F* parameter on structural and functional group retention

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Thin film plasma polymer (PP) coatings from a number of alkyl methacrylate precursors and their unsaturated analogues were deposited onto aluminium supports. Functional group retention and structural retention from the monomers were investigated as a function of the power (W) supplied to the plasma and the monomer flow rate (F) used in the polymerizations. The X-ray photoelectron spectroscopy and secondary ion mass spectrometry data reported herein show very clearly the importance of the W/F parameter in controlling PP chemistry and structure. Comparison of the PPs obtained from unsaturated and saturated monomers has allowed us to speculate on some aspects of the mechanism of polymerization.

(Keywords: thin films; plasma polymers; methacrylates)

INTRODUCTION

The use of radio frequency plasmas for depositing thin polymeric films, termed plasma polymers (PPs), from volatile organic compounds has been extensively investigated, and a number of possible applications have been described in the literature[1–6]. In a recent paper we drew attention to the problems associated with the characterization of these materials[7]. We discussed the development of time of flight secondary ion mass spectrometry (t.o.f.s.i.m.s.) for use in polymer surface studies, and reported on its application to obtain direct structural data from PPs. Work was carried out with PPs prepared from methacrylate monomers; these monomers were chosen because when polymerized under low plasma power (W) to monomer flow rate (F) ratios, i.e. low W/F, monomer functionality is retained in the PP, indicating a low degree of fragmentation in the plasma[6]. PPs were prepared from methyl, ethyl and butyl methacrylate (MMA, EMA and BMA).

In the analyses of the t.o.f.s.i.m. spectra, the methodology we adopted was to compare the PP spectrum with that of its conventional counterpart. The negative t.o.f.s.i.m. spectrum of plasma-polymerized MMA (ppMMA) contained many of the peaks seen for poly(methyl methacrylate) (PMMA)[8], i.e. at $m/z = 31$, 55, 85, 87 and 101. However, there were some notable differences.

1. In the ppMMA spectrum, the peaks at $m/z = 87$ and 101 were much more intense than for the conventional polymer.
2. In the PP spectrum, the peak $m/z = 187$ had replaced the peak at $m/z = 185$ seen for the conventional polymer.
3. The peak at $m/z = 141$ was of lower intensity for the PP than for the conventional polymer.

Our interpretation of these spectral differences was based on arguments developed by Lub and Benninghoven[9], who had studied ion formation in conventional PMMA. These workers have proposed that new end-groups created in PMMA as a result of primary ion beam impacts are chiefly responsible for the well-established negative s.i.m. spectrum of this polymer. These end-groups contain unsaturation and give the peaks seen at $m/z = 85$, 141 and 185. The importance of end-groups was demonstrated in the analysis of a low molecular weight oligomer of PMMA[10]. This was prepared by group transfer polymerization and had fully saturated end-groups, fragments of which dominated the negative s.i.m. spectrum.

In an earlier paper[7], we proposed that the strong signals seen at $m/z = 87$, 101 and 187 reflected a high concentration of fully saturated polymer end-groups within the surface of the PP deposit. Further, we concluded that the weak intensities of the peaks at $m/z = 85$, 141 and 185 indicated a very low chain length in the PP, a result supported by the oily appearance of the PP.

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X-ray photoelectron spectroscopy (x.p.s.) measurements were also made of the ppMMA. Peak fitting of the C1s core level revealed four distinct carbon chemical environments: C–H, C–O, C=O and O–C=O. However, because the analysis was made on a non-monochromated instrument, relatively large full widths at half maximums (FWHMs) of ca. 1.7 were employed in this fit. Quantification revealed that some oxygen was lost from the monomer; of that retained, the majority was in the carboxylate environment. A small excess of C–O and a small amount of C=O were detected.

Drawing the s.i.m.s. and x.p.s. data together, we proposed that the PP consisted of short 'methacrylate-like' chains with no appreciable crosslinking. The issue of whether the initiation of plasma polymerization was monofunctional or multifunctional, and consequently whether the polymer was linear or branched, could not be addressed from the data. This very general description of PP structure is supported by the findings of Ohno *et al.*[11]. Using a rather different plasma polymerization set-up, these workers prepared enough of one ppMMA to enable subsequent analyses by bulk analytical techniques. The ppMMA obtained contained chloroform soluble and insoluble fractions. The soluble fraction was subjected to pyrolysis/gas chromatography (p.g.c.), gel permeation chromatography (g.p.c.), i.r. spectroscopy, ^{1}H n.m.r., ^{13}C n.m.r. and elemental analysis. P.g.c. indicated that the soluble fraction contained appreciable amounts of methyl isobutyrate (MIB), and from the g.p.c. trace the weight average molecular weight was calculated as ca. 7.1×10^3. These results led the authors to conclude that the MIB was not attached at chain-ends (because of the relatively low number of chain-ends in the PP) but as pendant side groups. Because of the good solubility of this fraction in a number of common solvents, it was assumed that there was little or no crosslinking. The authors proposed that the soluble ppMMA consisted, in the main, of a random copolymer of MMA and isobutyric acid methallyl ester. The data from ^{1}H n.m.r. and ^{13}C n.m.r. added further

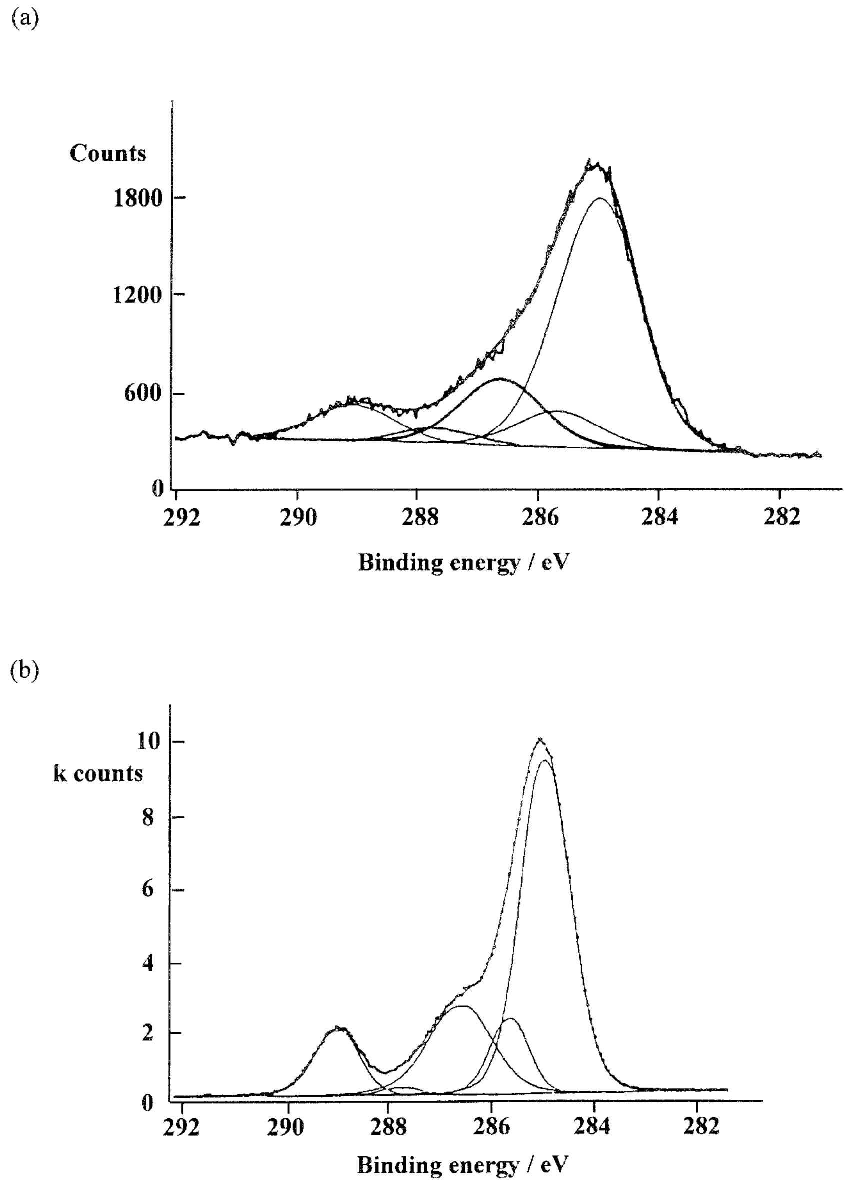


Figure 1 (a) C1s core level spectrum of ppMMA obtained on the CLAM 200. (b) C1s core level spectrum of the same material obtained on the Scienta (high resolution x.p.s.)

Table 1 Results of the C1s core level fitting of ppMMA prepared at $W/F = 1.7^a$

Chemical environment	Conventional PMMA Theoretical area %	Plasma-polymerized MMA x.p.s. area %	 Scienta area %
C–H	40	62	58.7
C–CO_2H/R	20	9	10.2
C–O	20	17	20.3
C=O or O–C–O	0	4	1.1
CO_2H/R	20	9	10.3

[a] The total area % does not necessarily equal 100. The sum of the areas of the peaks fitted is not necessarily equal to the areas under the core lines. Maximum discrepancy <1%

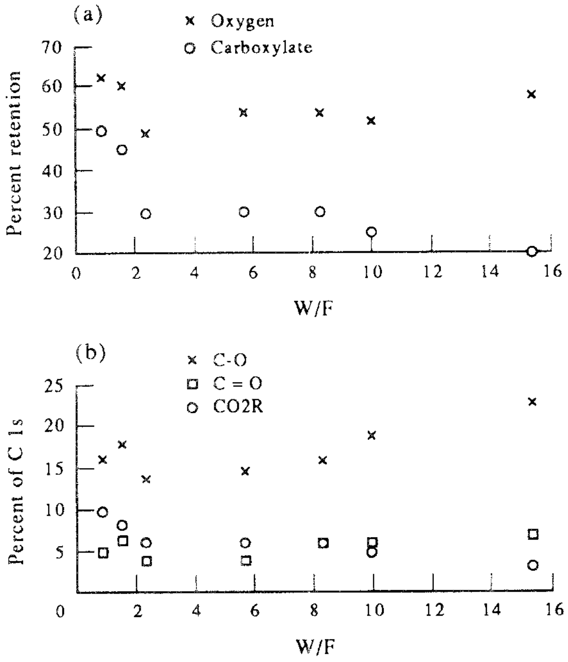


Figure 2 (a) The retention of oxygen and carboxylate (determined by x.p.s.) in ppMMA as a function of *W/F*. (b) Contributions of the component peaks in the C1s core level spectrum for ppMMA as a function of *W/F* (C–H and C–C are not shown)

support to this description. Our ppMMA was of much lower molecular weight, as indicated by its oily appearance, and therefore the concentration of end-groups (located at chain-ends) must be much higher than in the ppMMA of Ohno *et al.* However, we readily acknowledge that some contribution to the end-group signals ($m/z = 87$, 101 and 187) may well have come from side-chain end-groups, as described elsewhere[11]. In this paper, in the light of new data presented, attention is drawn to the very real possibility that MIB pendant groups may contribute appreciably to these peak intensities.

In an earlier paper[7], PPs from EMA and BMA were also prepared and shown to be very similar to the ppMMA, i.e. of low molecular weight and with high concentrations of fully saturated end-groups.

In this paper, we address the influence of the *W/F* parameter on PP structure. PPs from MMA, EMA, BMA and the saturated analogues of MMA and EMA, methyl isobutyrate (MIB) and ethyl isobutyrate (EIB), respectively, were prepared using a number of different *W/F* conditions. The resultant materials were analysed by t.o.f.s.i.m.s. and x.p.s. In an earlier paper[7], no attention was given to the positive ion s.i.m. spectra obtained since these contained little additional information on PP structure; the three PPs analysed were all prepared using low *W/F* conditions. In this work, both negative and positive ions have been considered as we will show that for materials prepared at higher *W/F*, the positive ions do give valuable information.

Our primary interest throughout this study has been the structure of these materials. However, the data reported here also allow us to speculate on the mechanism of polymer formation taking place in the plasma. In particular, comparison of the PPs prepared from unsaturated and saturated monomers provides important information on the processes occurring in the plasma that result in polymer deposition.

EXPERIMENTAL

Plasma polymerization

PPs were prepared in a tubular Pyrex reactor vessel which was kept grease free. A radiofrequency (r.f.) generator was inductively coupled to the reactor through an externally wound copper coil. The set-up is fully described elsewhere[6]. The substrate was placed in the 'in-coil' region and the apparatus was pumped down (ca. 10^{-2} mbar); at this stage the monomer inlet valve was kept closed. The leak rate was measured by closing the cold trap valve and measuring the increase in pressure in the plasma vessel with time. The following equation, derived from the ideal gas equation[12], was used to calculate the leak rate

$$\text{leak rate} = (\mathrm{d}p/\mathrm{d}t)\ 16\,172V/T$$

where p is the pressure (in millibars), t is the time (in seconds), V is the volume of the reactor (in cubic

Table 2 Results of the C1s core level fitting of ppEMA and ppBMA

Chemical environment	Conventional PEMA Theoretical area %	Plasma-polymerized EMA x.p.s. area %	 Scienta area %	Conventional PBMA Theoretical area %	Plasma-polymerized BMA x.p.s. area %	 Scienta area %
C–H	50	61	57.4	62.5	66	65.9
C–CO_2H/R	16.67	12	13.9	12.5	10	10.8
C–O	16.67	14	13.8	12.5	13	10.4
C=O or O–C–O	0	1	1.2	0	1	1.2
CO_2H/R	16.67	12	13.7	12.5	10	10.8

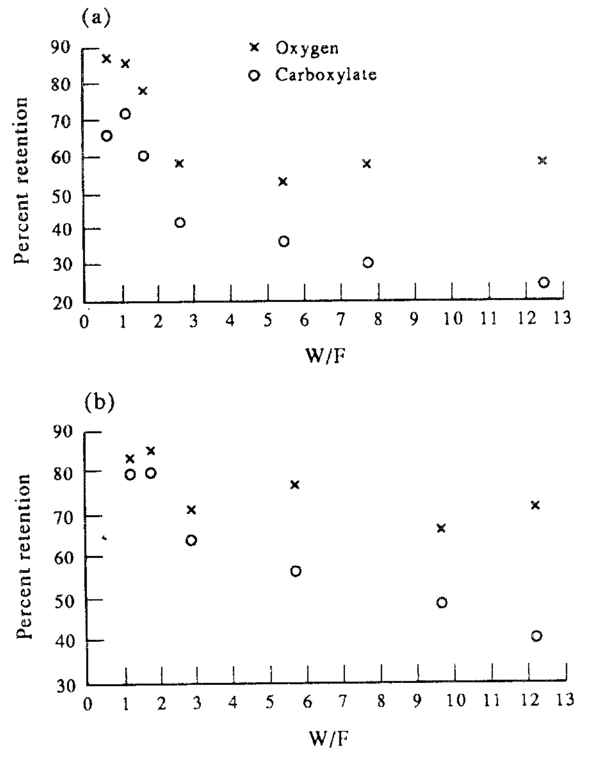


Figure 3 The retention of oxygen and carboxylate in (a) ppEMA and (b) ppBMA as a function of *W/F*

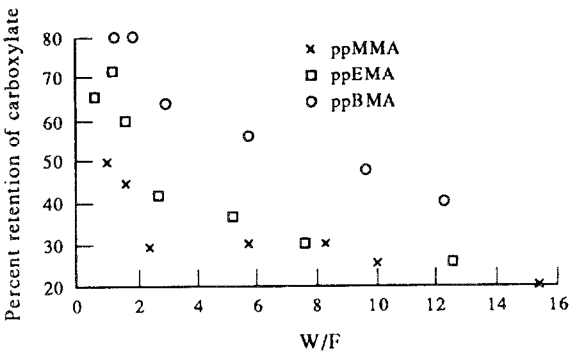


Figure 4 Carboxylate retention in ppMMA, ppEMA and ppBMA as a function of *W/F*

decimetres) and *T* is the temperature (in kelvin). The leak rate has units of cubic centimetres (STP) per minute.

The monomer inlet valve was then opened to allow the vapour of the precursor to flow through the reactor. When the pressure had stabilized, the flow rate was measured using the method described for the leak rate.

All plasma polymerizations were carried out with a dynamic flow of monomer through the apparatus, i.e. the reactor was open to the pumping system during the experiment. The power and matching network controls were adjusted so that the plasma received a power of 10 W. The r.f. generator operated most reliably at a power of 10 W, so all the plasma polymerizations were carried out at this power. Polymerizations were carried out at a number of different *W/F* by varying the monomer flow rate.

A polymerization time of 10 min was generally used. PPs were obtained as thin films on aluminium foil substrates.

Monomers

PPs were prepared from MMA, EMA, BMA, MIB and EIB. All had a purity of 99% and were supplied by Aldrich.

X.p.s.

All PPs were analysed using a VG CLAM 200 photoelectron spectrometer. MgKα X-rays and a take-off angle of 30° with respect to the sample surface were used. A survey spectrum (0–1100 eV) was recorded together with the regions of interest (C1s, O1s, N1s) for each sample. The spectra were obtained as plots of binding energy against counts (binding energy increasing from left to right along the *x* axis). A VGS5250 system was used for data analysis.

Monochromated high resolution x.p.s.

Some selected PPs were analysed on a Scienta ESCA300 spectrometer. This combines a high power (maximum 8 kW) rotating anode and a monochromated X-ray source (AlKα) with high transmission electron optics and a multichannel detector. An electron flood gun was used to effect charge compensation. This system allows the acquisition of high resolution, high intensity spectra with minimal sample damage. The design and performance have been more fully described in the literature.[13,14]

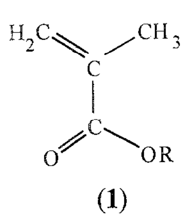
T.o.f.s.i.m.s.

The s.i.m.s. analyses were carried out using a VG Ionex 23LS fitted with a pulsed gallium ion source. This instrument has been described in the literature[15]. The instrument set-up was optimized to obtain the maximum count rate. Charge compensation was used as required. All analyses were carried out in the static regime, i.e. with an ion dose[16] $<10^{13}$ ions cm^{-2}. The spectra were obtained as plots of ion counts against m/z, where m is the mass of the ion and z is the charge of the ion. Both positive and negative ion spectra were recorded.

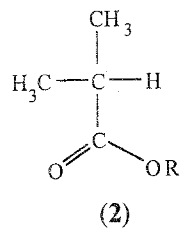
RESULTS AND DISCUSSION

Plasma polymers prepared from MMA, EMA, BMA, MIB and EIB

The general formulae of the monomers used are



(1)



(2)

where (**1**) is the general formula for the alkyl methacrylates and (**2**) is the general formula for the alkyl isobutyrates (i.e. the saturated analogues of the alkyl methacrylates). As in our earlier paper[7], the approach adopted was to characterize extensively the first member of the group (R = CH_3) and then compare the other PPs to this point of reference.

X.p.s.

Figure 1a shows the peak-fitted C1s core level spectrum of a ppMMA which was prepared at low

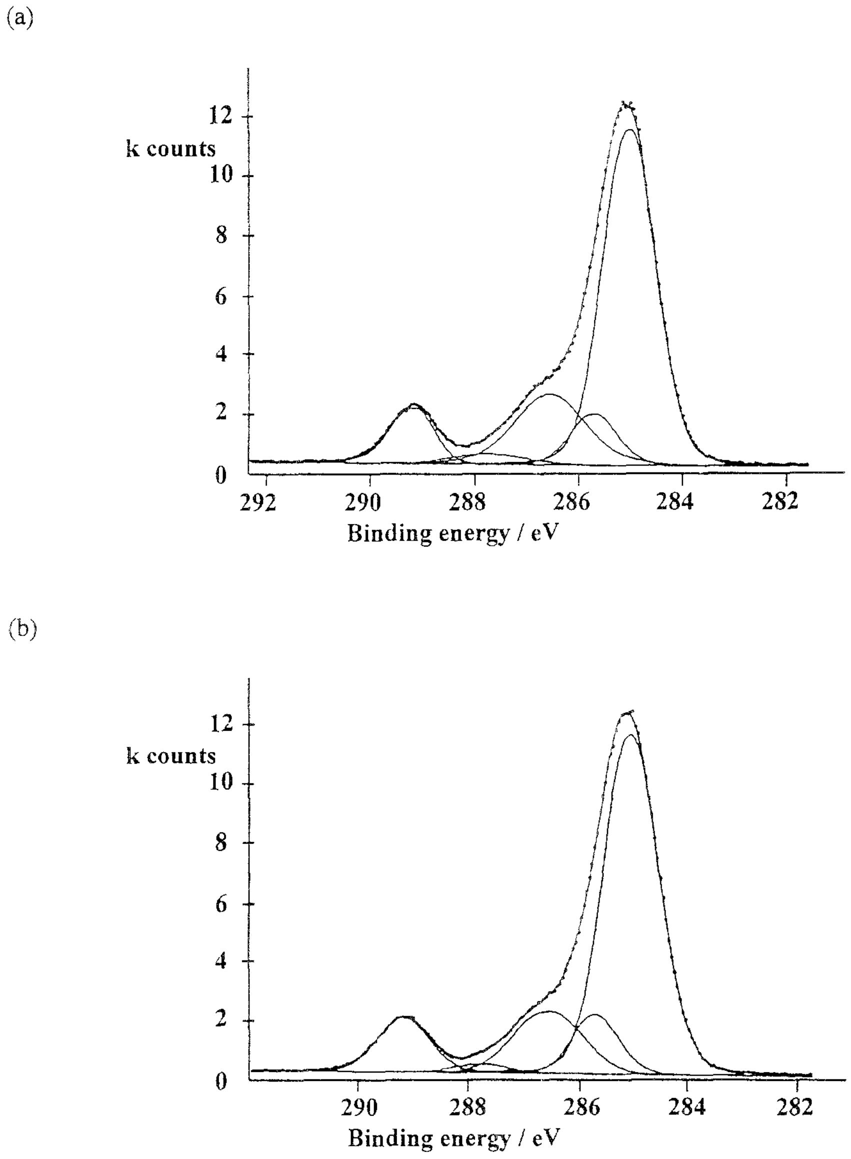


Figure 5 High resolution (Scienta) x.p.s. scans for (a) ppMIB and (b) ppEIB

W/F ($W/F = 1.7$). The component functional groups in this material have been identified and their concentrations quantified; see *Table 1*. The data show that the ppMMA has retained much of the carboxylate functionality from the monomer. However, there was an excess of C–O (when compared to CO_2H/R), and some C=O was also detected. Reported in *Figure 1b* is the high resolution spectrum of this PP, recorded on the Scienta ESCA300. The result obtained on peak fitting of this spectrum is in agreement with that obtained from the peak fit of *Figure 1a*, and adds support to the fitting procedure we routinely employ. (The Scienta data suggest, perhaps, a slight overestimate of the amount of C=O in *Figure 1a*.) The quantification of the high resolution x.p.s. data is also included in *Table 1*.

The ratio of carbon (C) to oxygen (O) in the PP was calculated from the areas of the C1s and O1s core levels. This value was compared to the theoretical value for MMA, and the retention of oxygen calculated. In this case the retention of oxygen was 66%.

A similar method was used to calculate the retention of the carboxylate functionality (presumed to be the ester). The theoretical value for CO_2R in the C1s peak of MMA is 20% of the total area. In this case the CO_2R/H peak accounts for 9% of the area of the C1s peak. The retention of carboxylate was thus 45%.

Retention of both carboxylate and oxygen was measured in a number of PPs prepared at 10 W and at different monomer flow rates. The data obtained are presented graphically in *Figure 2a*. Retention of carboxylate and oxygen was observed to decrease markedly up to a W/F of approximately 2.5, after which retention remained fairly constant, although oxygen retention increased again at $W/F = 15$. The PPs were also found to contain larger amounts of C–O and C=O as the W/F was increased. Changes in component functional groups with W/F are shown in *Figure 2b*.

The same experimental measurements were obtained for PPs of EMA and BMA. The results from peak fitting of the C1s core level spectra of ppEMA and ppBMA (prepared at low W/F), recorded on the CLAM and Scienta, are compared in *Table 2*. Again, a very satisfactory agreement between the results from the two instruments was obtained.

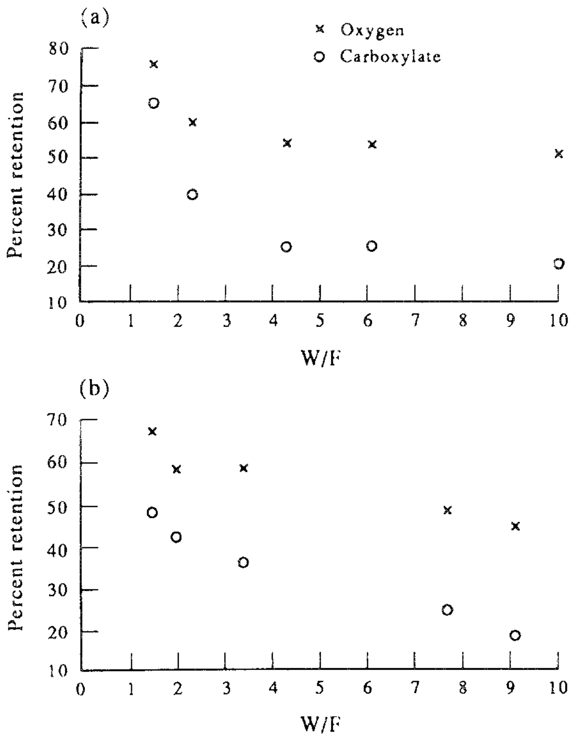


Figure 6 Carboxylate and oxygen retention in (a) ppMIB and (b) ppEIB as a function of W/F

Retention of carboxylate and oxygen in ppEMA also decreased markedly as W/F increased, up to a W/F of about 2.5. Above this value, the amount of carboxylate retention decreased further, but less dramatically with increasing W/F; oxygen retention remained fairly constant above $W/F = 2.5$, again increasing slightly at the highest W/F. These data are illustrated in *Figure 3a*. The same trends were observed for ppBMA: loss of carboxylate with increasing W/F and loss of oxygen with increasing W/F, both up to a W/F of approximately 3. However, there was a more even loss of carboxylate over the entire W/F range investigated, and there was no evidence for increased oxygen retention at the highest W/F. These data are presented in *Figure 3b*.

Whilst the trends revealed for ppEMA and ppBMA were similar to that observed for ppMMA, the actual level of retention at any given W/F varied for the different carboxylate R groups. This may be seen more clearly in *Figure 4* where the retention of carboxylate vs. W/F is compared for the three PPs. The plots show that as the length of the hydrocarbon chain forming the R group was increased, the retention of carboxylate also increased.

The results from the saturated monomers MIB and EIB are particularly interesting. The high resolution Scienta C1s core level spectra for a ppMIB and a ppEIB are displayed in *Figures 5a* and *5b*. The curve fits of these spectra gave very similar results to those obtained from the plasma-polymerized methacrylates (prepared at equivalent W/F). However, we observed that at lower W/F the saturated monomers polymerized much more slowly than their unsaturated counterparts. Graphs of the percentage oxygen and carboxylate retention vs. W/F are presented in *Figures 6a* and *6b* for ppMIB and ppEIB. These graphs show the same trends that were observed for the unsaturated materials. However, these similarities need not imply that the structures of the unsaturated and saturated PPs are the same. The x.p.s. data presented only provide information on the concentrations of the various functional groups in these PPs.

S.i.m.s.

Negative ions. In *Figure 7*, the negative s.i.m. spectra for PPs of MMA and BMA prepared at high and low W/F are shown. These spectra contain all the peaks described earlier[7].

The information contained within these spectra may be semiquantified using a simple numerical procedure termed normalization[17]. The peak signal of interest is normalized to another peak or a region of the same spectrum. For example, the peak at $m/z = 85$ may be normalized to the range $m/z = 50$–110 to give the normalized peak intensity (NPI), Thus, NPI(85) may be obtained by dividing the number of counts obtained for the peak at $m/z = 85$ by the total number of counts for the range $m/z = 50$–110. This may be written $\mathrm{NPI}(85) = I_{85}/I_{50-110}$. This procedure allows trends in the s.i.m.s. data to be observed which may then be related to changes in the structure of the PPs as a function of W/F.

Jackson[18] has shown with conventional PMMA that when normalizing low intensity molecular ion signals, the exclusion from the normalizing range of high intensity elemental ion signals gives very reproducible NPIs. When these elemental ions are included, the high level of reproducibility is lost as the elemental ions are readily affected by contamination. Hence, the normalization ranges employed in this work were chosen to avoid contributions from elemental ions.

In *Figure 8a*, the NPIs determined for the peaks at $m/z = 85$ and 87 for a number of PPs of MMA have been plotted against W/F. The plots show that the intensities of both of these peaks decreased as the W/F increased. This reflects the gradual loss of precursor structure (in the ppMMAs) that took place as the W/F was increased. An increase in the background signal (I_{50-110}) was seen as W/F increased, indicating that the structure of the ppMMAs became more complex (i.e. less regular) at higher W/F.

The data may also be presented as a plot of I_{85}/I_{87} against W/F, as in *Figure 9*. This plot gives an indication of the proportion of ions typical of the PP, either saturated chain-ends or pendant side groups, relative to 'methacrylate-like' polymer chain units. In this respect, it can be seen that the proportion of end-groups/side chains in the PP increased with W/F. The final point ($W/F = 15$) does not follow this trend. At this value of W/F, the peaks at $m/z = 85$ and 87 are merely part of the background, and so large variations in the value of I_{85}/I_{87} might be expected.

For ppBMA, the graph of NPI(85) and NPI(87) is shown in *Figure 8b*. At low W/F, the ppBMA is very like the conventional polymer (PBMA), where $I_{85} > I_{87}$. However, the plot shows that as W/F increased, the NPI(87) increased, whilst the NPI(85) decreased. The trend seen for the NPI(87) indicates that the (overall) concentration of structures giving rise to this peak for the PP increased as the W/F increased, unlike the trend seen for ppMMA. The plot of I_{85}/I_{87} shown in *Figure 9b* is

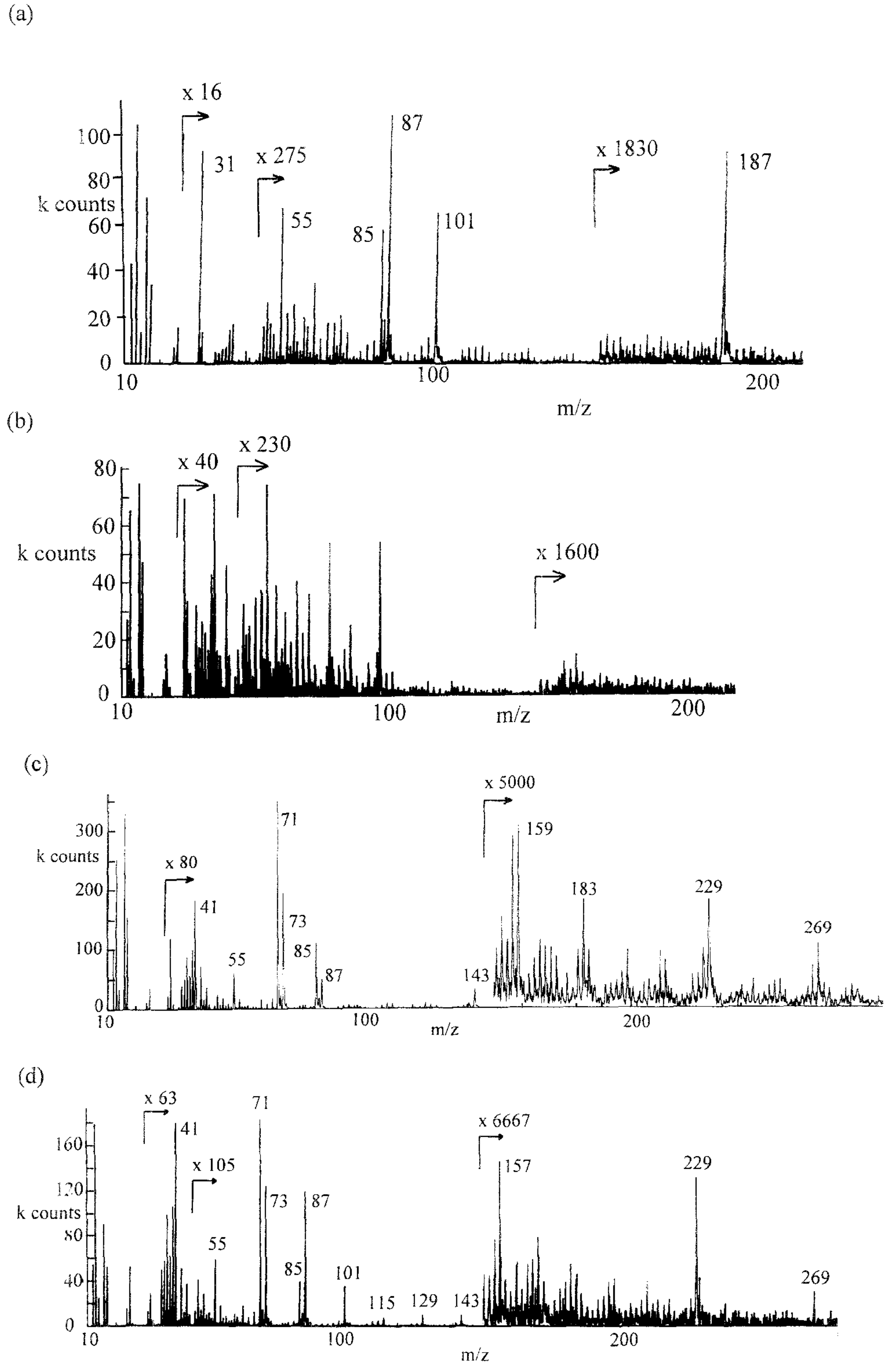


Figure 7 Negative s.i.m. spectra of ppMMA prepared at (a) low and (b) high W/F. Negative s.i.m. spectra of ppBMA prepared at (c) low and (d) high W/F

similar to that for ppMMA, revealing that the proportion of saturated end-groups/side chains relative to the polymer chain units increased with W/F.

The negative s.i.m. spectra of ppEMA were also analysed, and the trends found in the NPIs (85 and 87) resembled closely those seen for ppMMA.

The negative s.i.m. spectrum of a ppMIB prepared at low W/F (1.5) is reproduced in *Figure 10a*. This spectrum contains important peaks at $m/z = 31$, 55, 85, 87, 101 and 187. In this respect, the spectrum is comparable to that obtained from ppMMA. However, this spectrum differs in the relative intensities of particular key peaks. Of note are the very low intensities of the peaks at $m/z = 85$ and 101, and the correspondingly high intensity of the peak at $m/z = 87$. ppMIBs were prepared at a number of different W/F settings and the s.i.m. spectra recorded. In *Figure 8c* the normalized intensities of the peaks having $m/z = 85$ and 87 have been plotted. This graph is in marked contrast to any of those produced for the unsaturated monomers in that the

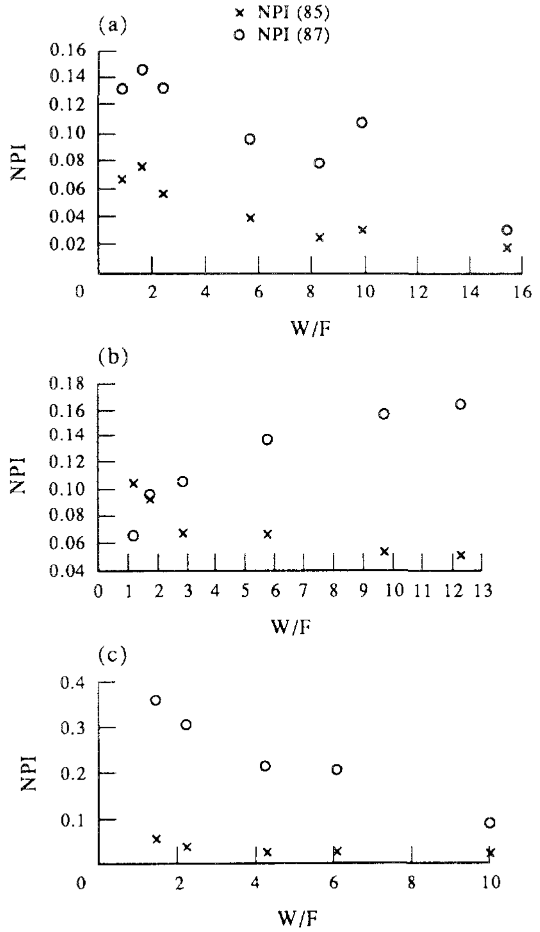


Figure 8 NPIs of the peaks at $m/z = 85$ and 87 for PPs of (a) MMA (b) BMA and (c) MIB as a function of W/F

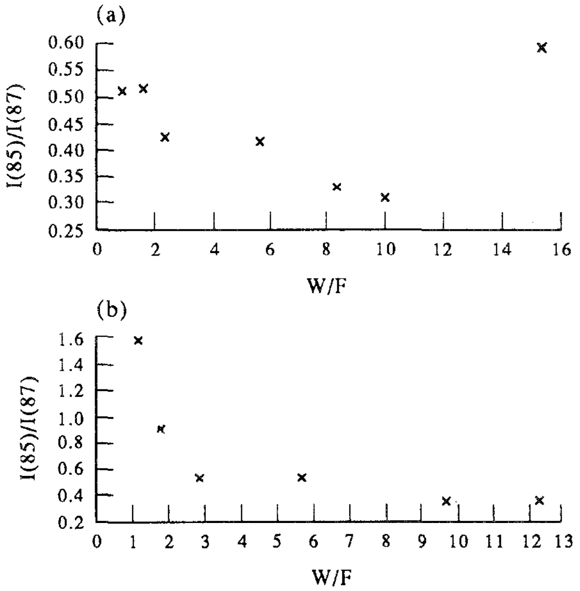


Figure 9 The variation in I_{85}/I_{87} as a function of W/F for PPs of (a) MMA and (b) BMA

normalized peak for $m/z = 85$ is very low across the entire W/F range investigated.

The s.i.m. spectrum of a ppEIB prepared at low W/F (1.5) is shown in *Figure 10b*. This spectrum contains peaks at $m/z = 45$, 55, 85, 87, 101, 115 and 129, and is similar to that of ppEMA[7], except that the peaks at $m/z = 85$ and 101 are of much lower intensity and the $m/z = 87$ peak is considerably stronger. The normalized intensities of the peaks at $m/z = 85$ and 87 were obtained from a number of ppEIBs prepared at different W/F values. These peaks show a similar trend to that seen in *Figure 8c* for ppMIB: the NPI(85) is low across the entire W/F range and the NPI(87) decreases with increasing W/F.

Positive ions. The positive ion spectra of ppMMAs prepared at low and high W/F are shown in *Figure 11*. Attention is focused on the peaks at $m/z = 91$, 105 and 115, which are particularly evident in the s.i.m. spectrum of the high W/F ppMMA. These peaks are seen with considerable intensity for materials that contain aromaticity, e.g. polystyrene[9]. However, Briggs and coworkers[20,21] have considered the formation of these peaks as a result of ion beam damage in polymers. In unsaturated materials, these peaks form well below the prescribed static limit, i.e. 10^{13} ions cm^{-2}, and at this dose these peaks arise also in the s.i.m. spectra of saturated polymers. In *Figure 12* the NPIs for $m/z = 91$, 105 and 115 are plotted for ppMMA, ppBMA and ppMIB as a function of W/F. All three plots show the same trend, i.e. increasing NPI with W/F. This result may indicate the presence of aromaticity in the high W/F PPs, or that these materials are more sensitive to ion beam damage. Grazing angle infra-red spectra of high W/F PPs show weak absorptions at 1602 and 702 cm^{-1}, which indicates small amounts of aromatic material, and these peaks are absent in low W/F materials[6]. However, the s.i.m.s. data are best explained by recognizing that the ion dose employed to obtain these spectra was well in excess of that required to initiate damage in these materials. The increase in NPI with W/F therefore indicates that the high W/F PPs are more susceptible to ion beam damage and most probably contain more unsaturation.

GENERAL DISCUSSION

Time on the Scienta was limited, and therefore only one sample of each PP was analysed. The spectra for three of these PPs are displayed (*Figures 1b*, *5a* and *5b*). Whilst the chemical shifts of most C environments are now well documented[22] when peak fitting the C1s core level of a material that contains a number of different C environments there is inevitably some overlap between peaks. This leads to some uncertainty about the true intensity of a particular signal, and in the case of weak signals as to whether the signal is there at all. Consequently, the higher the energy resolution employed, the less overlap between peaks, and the more confidence one can have in the peak fit. The close agreement between the Scienta fits and those obtained on the lower energy resolution x.p.s. instrument was particularly reassuring, confirming the validity of the fitting procedure employed in the lower resolution spectra.

The x.p.s. results show for all monomers that oxygen retention and functional group retention are, at least crudely, controlled by the W/F. Considering the plot of oxygen and carboxylate retention in ppMMA (*Figure 2*), the data show that with increasing W/F (up to 2.5) there was more fragmentation of the MMA. This is to be expected, since the average amount of energy supplied to each molecule in the plasma was greater at higher W/F.

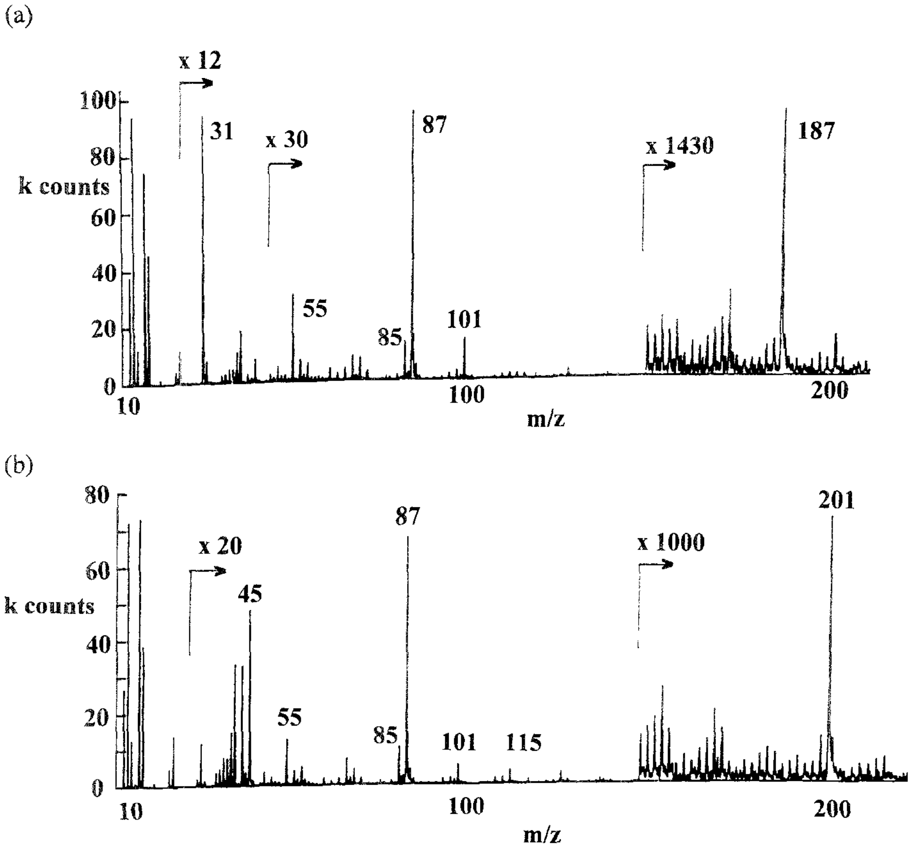


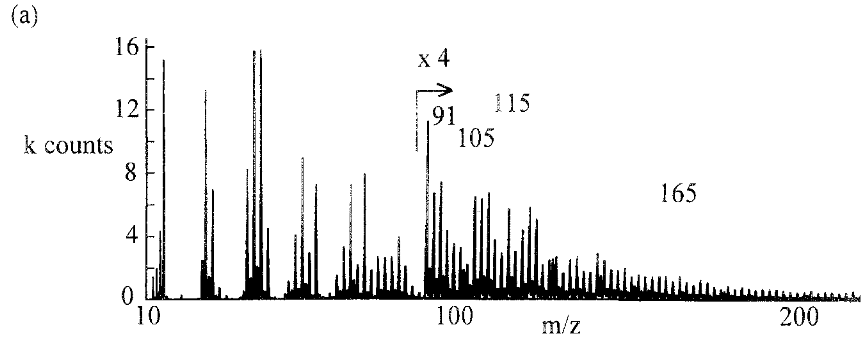
Figure 10 (a) Negative s.i.m. spectrum of ppMIB. (b) Negative s.i.m. spectrum of ppEIB

The rate of change of the slope at about $W/F = 2.5$ is particularly interesting, indicating that at this value a different mechanism (or mechanisms) of polymer formation came into play. However, the available data do not allow one to speculate on what this mechanism might be.

The trends seen in ppEMA and ppBMA were similar, with the greatest retention found in ppBMA at any particular W/F. This could be partially due to statistical effects. For example, MMA has a certain number of sites that may react in the plasma. This may be crudely represented by the number of atoms in the molecule. Thus, EMA has more possible sites for reaction, and BMA has more still. One would therefore expect BMA to show the greatest retention of carboxylate. In reality the situation cannot be as simple as this, as different sites within any molecule will have different propensities to react. The high level of retention seen in all three PPs, particularly at low W/F, clearly indicates that bond breakage in these monomers was not random. The greater retention in ppBMA is much more likely to be related to the stability of this monomer in the plasma. Carboxylate retention of 80% ($W/F = 1$–2) indicates that polymer formation occurred predominantly by a 'non-fragmentary' reaction pathway, possibly through the carbon–carbon double bond.

Although we have chosen to plot oxygen retention as a function of W/F, it is worth noting that oxygen retention is not a measure of the extent of monomer fragmentation in the plasma, nor is it an exact indicator of the extent of functional group retention. Increased fragmentation of the monomer in the plasma will result in the formation of reactive oxygen-containing species, as well as atomic oxygen, and these can in turn react with depositing/deposited polymer, and hence be incorporated into the film. At low W/F, we observed a good correlation between oxygen and carboxylate retention, indicating, perhaps, that monomer fragmentation was taking place in such a manner that carboxylate and, hence, oxygen were lost from the polymer deposit. As the W/F was increased, this process was enhanced. However, at some critical W/F, approximately 2.5 in ppMMA and ppEMA, other modes of fragmentation became important and the reactivity of the oxygen-containing fragments was such that they reacted with the polymer deposit. Strong evidence for this comes from the divergence in oxygen and carboxylate retention at $W/F > 2.5$. Above this value, increased amounts of oxygen were incorporated in the ppMMA with increased W/F, whilst more carboxylate was lost. At $W/F = 15$ the level of oxygen retention was comparable to that seen at the lowest W/F, whereas carboxylate retention was below 20%.

The value of the normalization procedure, first used elsewhere[17], is further demonstrated in the analyses of the s.i.m. spectra of ppMMA, ppEMA and ppBMA. However, whilst the trends seen in the normalized signals from ppMMA and ppEMA are similar, the different behaviour of the normalized negative ion peak at $m/z = 87$ for ppBMA is interesting. We believe that this divergence in behaviour is related to the somewhat greater stability of BMA in the plasma. At $W/F < 2$, the very high level of functional group and structural retention seen in the PP shows that little fragmentation of BMA had taken place in the plasma. As the W/F was increased, and hence the average energy input per monomer unit, more fragmentation occurred. The nature of this fragmentation is unknown, but from the



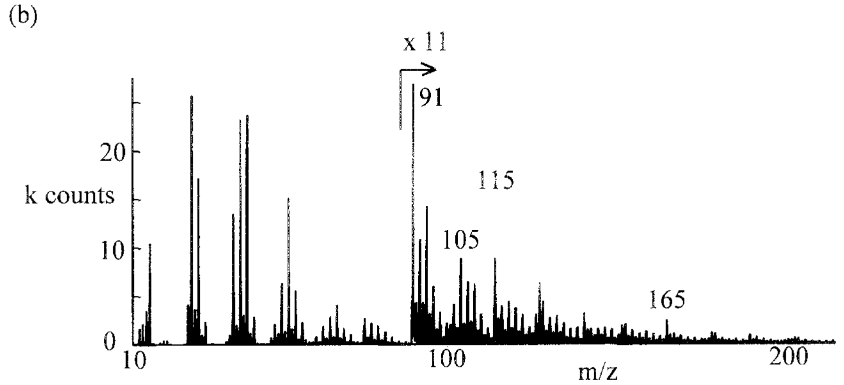


Figure 11 Positive s.i.m. spectra of ppMMA prepared at (a) low and (b) high *W/F*

data we conclude that the first major reaction pathway accessed by the greater energy input led to an increase in the number of end-groups/side chains formed in the polymer, as opposed to random fragmentation of the monomer. In contrast, for MMA and EMA the plots of NPI(87) against *W/F* showed that increased energy input favoured a more random fragmentation.

From the close structural similarities observed between all three PPs (prepared at low (<2.5) *W/F*) and their conventional counterparts, it is worth considering whether at least some polymerization in the plasma has taken place by a chain growth mechanism. Polymer formation via chain growth in plasma polymerization has been discounted by Yasuda[12]. It is worth examining the argument used by Yasuda to discount chain growth mechanisms. He states that chain growth in plasmas is very unlikely because of the pressure dependence of the polymerization ceiling temperature (T_c). In the book by Yasuda[12], a plot of the estimated pressure dependence of T_c is given for MMA, and from this graph it can be seen that within the pressure range normally used in plasma polymerization (50–5000 mtorr), the T_c is between ca. 420 and 350 K. What is not considered is that the various components of the polymerizing gas are at very different temperatures. Whilst the electrons are at high temperature, typically 2 eV or 10^4 K, it is reported that the ions are at only about 500 K and the neutrals at about 300 K[12,23]. Since the average temperature of the neutral species ought to be below the T_c, polymerization by chain growth is a very real possibility. If the above applies to our systems, then it follows that the limitation to chain growth is not the T_c but involves the availability of a suitable unsaturated functionality in the monomer and the stability of the monomer to other reactions, namely fragmentation and/or rearrangement, in the plasma.

The extent of ionization in glow discharge plasmas is low (ca. 1%)[12,23], and it had been thought that ion chemistry was unlikely to play a major role in the formation of a polymer deposit from a plasma[12]. However, only a small fraction of the monomer reacts to form the PP deposit, the remainder being collected in the cold trap as a liquid. So although the concentration of ions in the plasma is relatively low, they may still play some role in the formation of a PP deposit.

The data from the saturated monomers elegantly demonstrate the limitations of x.p.s. for obtaining structural information. The data also add support to the view that some of the intensity of the peak seen at $m/z = 87$ (and perhaps also the peak seen at $m/z = 85$) in the s.i.m. spectra of ppMMA, ppEMA and ppBMA is due to pendant side groups. From the x.p.s. results alone it would be easy to conclude that the saturated monomers were forming deposits that were structurally identical to their unsaturated counterparts. However, the s.i.m.s. data show that this was not the case. The intense peak at $m/z = 87$ seen for both ppMIB and ppEIB confirms the high level of carboxylate retention in these PPs, i.e. their chemical similarity to ppMMA and ppEMA. The weak signal at $m/z = 85$ for both PPs (at all *W/F*) indicates an important structural difference between these PPs and their unsaturated analogues. As discussed in the first paper in this series[7], the $m/z = 85$ and 141 peaks we believe are diagnostic of the main-chain polymer, and the peak at $m/z = 87$ (in particular) we assigned to end-groups. This view has been modified above to include the contribution of pendant side groups to the intensity of the peak at $m/z = 87$. The s.i.m.s. data

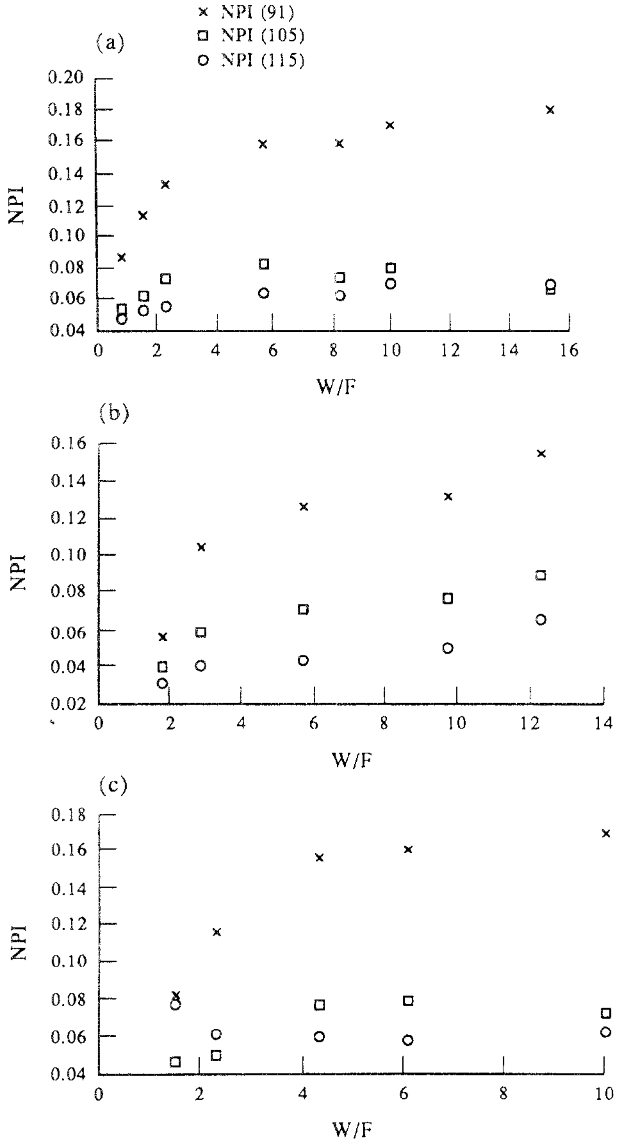
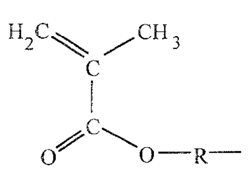
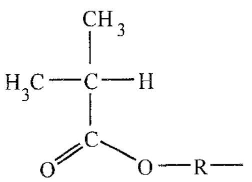


Figure 12 NPIs of the peaks at $m/z = 91$, 105 and 115 for (a) ppMMA, (b) ppBMA and (c) ppMIB

clearly show that in the ppMIB and ppEIB there was little main-chain polymer, but a significant quantity of end-groups/pendant side groups. This result now leads us to reconsider whether for the PPs of the unsaturated monomers some of the intensity of the $m/z = 85$ peak arose from unsaturated pendant side groups. Possible structures for both the saturated and unsaturated side chains are



(3)



(4)

where (**3**) could give rise to a peak at $m/z = 85$ and (**4**) could give rise to a peak at $m/z = 87$. Unfortunately, the importance of pendant side groups in the PPs obtained from unsaturated monomers cannot be assessed from the present data. In keeping with Ohno *et al.*[11], we still maintain that PPs from MMA, EMA and BMA contain portions where reaction has occurred through the carbon–carbon double bond. However, the data reported here suggest that PPs prepared from MIB and EIB do not react through the equivalent bond position. Hence, we conclude that the polymer deposits obtained from the saturated monomers were not formed via a mechanism resembling that found in conventional polymerization. The slow rate of polymer deposition (in comparison with the unsaturated monomers) further supports this view. However, the high retention of carboxylate groups indicates that only limited fragmentation of these saturated monomers took place in the plasma.

CONCLUSIONS

1. High functional group and structural retention can be achieved in the plasma polymerization of unsaturated methacrylate monomers (BMA, EMA, MMA). At any particular *W/F* the amount of retention was greatest for BMA and least for MMA. We point out that some polymer formation may have taken place by a chain growth mechanism. The PPs prepared at high *W/F* contained appreciable amounts of oxygen, but a much lower concentration of carboxylate groups. These polymers also suffered much more from ion beam damage, most likely because they contained higher levels of unsaturation.
2. The alkyl isobutyrates (saturated analogues of MMA and EMA) polymerized to give high functional group retention. However, they are structurally different from the PPs prepared from the unsaturated methacrylates: they contain higher concentrations of fully saturated end-groups/pendant side groups and no (or negligible amounts of) 'methacrylate-like chains'.

As noted earlier, our primary interest has been in the structure and surface chemistry of materials deposited by plasma polymerization and the influence that the *W/F* parameter has on the PP produced. However, the data reported here have also allowed us to comment on the possible reactions taking place in the plasma. To learn more about these processes one must directly probe the plasma itself, a possible method of investigation being plasma mass spectrometry.

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