polymer papers

A time-of-flight secondary ion mass spectrometry and X-ray photoelectron spectroscopy investigation of the structure of plasma polymers prepared from the methacrylate series of monomers

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Plasma polymers (PPs) have been prepared from methacrylate precursors and analysed by time-of-flight secondary ion mass spectrometry (ToF-SIMS) and X-ray photoelectron spectroscopy (X.p.s.). The negative SIMS data for plasma polymerized methyl methacrylate (ppMMA) were compared with that of a low molecular weight oligomer and a high molecular weight conventional poly(methyl methacrylate). This facilitated the interpretation of the SIMS data and has enabled a qualitative structure for ppMMA to be proposed. The secondary ion mass spectra from PPs of ethyl methacrylate and butyl methacrylate are shown to be very similar to ppMMA, where the methyl group is replaced by an ethyl and a butyl group, respectively. The X.p.s. data for ppMMA showed that the PP had retained ~80% of the oxygen from the monomer. Much of this was present as the ester group which indicates that extensive fragmentation of the monomer had not occurred during plasma polymerization. Evidence that the monomer structure had been retained in the PP was also provided by the SIMS data; a number of negative ions (e.g. at $m/z = 85$, 87, 101 and 187) have structures which contain a complete monomer unit.

(Keywords: ToF-SIMS; X.p.s.; plasma polymers)

INTRODUCTION

The use of radio-frequency (r.f.) plasmas for depositing thin polymeric films from volatile organic precursors has been extensively investigated[1-5]. The characterization of these polymers, termed plasma polymers (PPs), is not straightforward. PPs are normally insoluble in common solvents and difficult to prepare as films that are >2000 nm thick[1]. These restrictions limit the use of n.m.r. and i.r. spectroscopy in the analysis of PPs[2]. To date, X-ray photoelectron spectroscopy (X.p.s.) has been the most widely used technique in the analysis of these materials. X.p.s. is routinely employed in the analysis of polymeric materials, providing both elemental and functional group information. From this data, some information on polymer structure can be inferred. In general, however, X.p.s. analysis does not provide direct structural data. In this report it is shown how this information can be obtained for alkyl methacrylate PPs by the use of time-of-flight secondary ion mass spectrometry (ToF-SIMS).

Much has been made of the molecular specificity of the SIMS technique to detect molecular ions representative of moieties present in polymer surfaces[6]. Of particular relevance to this study are the secondary ion mass (SIM) spectra for a conventional poly(methyl methacrylate) (PMMA) and a low molecular weight oligomer reported by Hearn and Briggs[7] and Lub and Benninghoven[8], respectively. These workers have assigned structures to secondary ions from these polymers which are diagnostic of the polymer backbone, side chains and end groups.

The PPs analysed in this study were prepared at low plasma power (W) to monomer flow rate (F) ratios i.e. low W/F, in an attempt to reduce monomer fragmentation in the plasma and to retain monomer functionality. The data obtained suggested that the PPs had relatively low molecular weights and that there was little crosslinking. This is in contrast to the highly crosslinked PPs that may be prepared at high W/F.

The approach adopted here has been to compare the SIM spectra obtained from the PPs, with their conventional poly(alkyl methacrylate) counterparts. This approach is justified, as the SIM spectra of the PPs are similar in many ways to those of their conventional counterparts. However, the structure of the PPs is not identical to that of their conventional counterparts. This was highlighted by the spectral differences between the conventional polymers, and PPs.

EXPERIMENTAL

PPs were prepared from methyl methacrylate (MMA), ethyl methacrylate (EMA) and butyl methacrylate (BMA).

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They all had a purity of 99% and were supplied by Aldrich Chemical Co. Ltd (Gillingham, UK). The plasma apparatus used in this work was similar to a reactor described in the literature[9]. Polymerizations were carried out at a pressure of ~27 Pa, a flow rate of monomer (*F*) between 0.5 $cm^3_{STP}\ min^{-1}$ and 2 $cm^3_{STP}\ min^{-1}$, a r.f. power (*W*) of 10 W, and a polymerization time of 10 min. The ppMMA, ppEMA, and ppBMA were prepared at power to flow rate ratios (*W/F*) of 4.8, 11.9 and 9.7, respectively. The PPs were obtained as thin films on aluminium foil substrates.

SIM spectra from conventional polymers were obtained from neat films cast from redistilled solvents. The polymers used were BDH secondary standards (BDH Chemicals Ltd, Poole, UK).

The X.p.s. analysis was carried out using a VG CLAM 200 photoelectron spectrometer. Mg Kα X-rays and a take-off angle of 30° with respect to the sample surface were used. A VGS5250 system was used for data analysis.

The SIMS analyses were carried out using a VG Ionex 23LS ToF-SIMS fitted with a pulsed gallium ion source. The analyses were carried out within the static regime (i.e. ion dose $<10^{13}$ ions cm^{-2}). Charge compensation was not required for the PP films, but was required to obtain negative SIM spectra from the neat conventional polymer films.

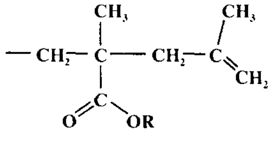
RESULTS AND DISCUSSION

ppMMA: spectral assignments

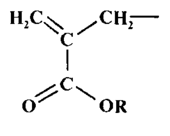
ToF-SIMS. The negative SIM spectra of ppMMA and of the conventional PMMA are shown in *Figure 1*. Similar spectra for conventional PMMA have been reported and structures for ions assigned[7]. It has been established that the negative ion spectrum offers several peaks that are unambiguously diagnostic of PMMA and appear with considerable intensity. Ions at lower mass ($m/z<30$) arise from the elemental ions H^-, C^- and O^-, and small molecular fragments, $C_nH_m^-$ and OH^-. These ions do not provide information about the polymer structure and are not considered further. The principle ions of interest in this study occur at $m/z=31$, 55, 85, 87, 101, 141 and 185, and these have been assigned to structures based on the polymer repeat unit as shown in *Table 1*.

In the negative SIM spectrum of ppMMA, many of these peaks are also present, i.e. $m/z=31$, 55, 85, 87 and 101. There are however, some notable differences between the two SIM spectra in *Figure 1*. In the PP, the peaks at $m/z=87$ and 101 are much more intense, and the peak at $m/z=185$ in the conventional polymer is replaced by a peak at $m/z=187$ in the PP.

The formation of ions detected in the SIMS analysis of conventional PMMA has been considered by Lub and Benninghoven[8]. Using the fragmentation scheme of Hearn and Briggs[7], Lub and Benninghoven proposed that the detected ions arise from new polymer end groups created in the polymer as a result of primary ion beam impacts. Following an impact, side chain elimination occurs, followed by main chain scission and radical rearrangements resulting in the formation of two new polymer end groups (A and B, see below). These new end groups then give rise to the characteristic negative SIM spectrum of PMMA.

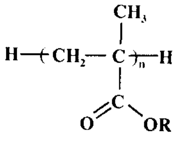


R = Me A



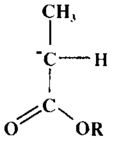
B

The probable origins of the high intensity peaks seen at $m/z=87$, 101 and 187 in the negative SIM spectrum of ppMMA can be identified from the study of Lub and Benninghoven of a low molecular weight MMA oligomer ($M_w=1890$)[8]. This oligomer was prepared by group transfer polymerization[10] and has the structure:

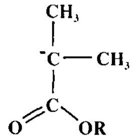


R = Me

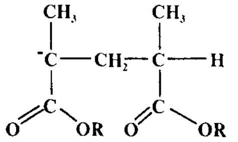
Particular attention is drawn to the end groups of this material. These end groups correspond closely with the new end groups proposed in the fragmentation model of Hearn and Briggs[7], except that they do not contain any unsaturation. The end group on the right-hand side corresponds to the new end group B with two additional hydrogens (2H). The end group on the left-hand side corresponds to the end group A with the $C(CH_3)=CH_2$ group replaced by H. SIMS analysis of this oligomer yielded the typical PMMA spectrum, but with much more intense signals at $m/z=87$, 101 and 187. These peaks were assigned by Lub and Benninghoven[8] to the following structures derived from the original polymer end groups:



i



ii



iii

R = Me

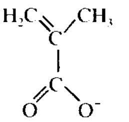
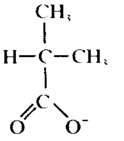
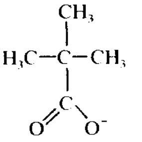
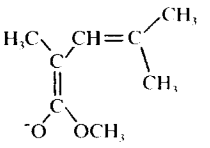
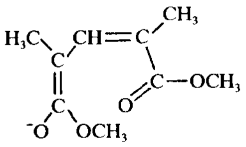
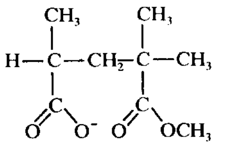
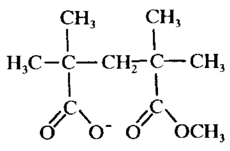
It is therefore proposed that in the SIM spectrum of ppMMA, the strong signals at $m/z=87$, 101 and 187 reflect a high concentration of polymer end groups.

The presence of a high concentration of end groups in the conventional PMMA is not likely. The initiator used in the preparation of this polymer was azobisisobutyronitrile and the residue of this initiator will be present at one end of the polymer chain. No spectral evidence for the initiator was obtained. The chemical structure of the other end group will depend on whether the predominant mechanism of termination in the polymerization is combination or disproportionation. However, in either case, the concentration of this end group will be very low as the PMMA has a molecular weight of 100 000.

X.p.s. The survey scan of the range 0–1100 eV detected only carbon and oxygen; no aluminium was detected. This implies that the PP film was thick enough to prevent the substrate from affecting the results of the X.p.s. and SIMS. The oxygen–carbon atom number ratio calculated from the corresponding core levels showed that 80% of the oxygen from the monomer was retained in the PP.

Figure 2 shows the peak fitted C 1s core level spectrum of the ppMMA. The peak fitting procedure described in

Table 1 Prominent peaks in the negative SIMS of ppMMA, high molecular weight PMMA and low molecular weight PMMA

Secondary ion structure	m/z	Possible origin	ppMMA	High molecular weight PMMA	Low molecular weight PMMA
CH_3O^-	31	Ester group[7]	+	+	+
$H_2C{=}C{=}CHO^-$	55	Monomer unit[7]	+	+	+
	85	Main chain[7]	+	+	+
	87	End group[8]	+	ND	+
	101	End group[8]	+	ND	+
	141	Main chain[7]	ND	+	+
	185	Main chain[7]	ND	+	+
	187	End group[8]	+	ND	+
	201	End group[8]	ND	ND	+

+, Peak present; ND, not detected

reference 11 was employed. The chemical shifts with respect to the C–H peak (which was set to 285.0 eV) were as follows: C–CO_2H/R, +0.7 eV; C–O, +1.6 eV; C═O or O–C–O, +2.8 eV; CO_2R/H, +4.0 eV. These chemical shifts are in agreement with commonly accepted values[11].

This analysis reveals that the majority of oxygen detected is in carboxylate environments (i.e. CO_2R/H) and that the CO_2R/H peak in *Figure 2* has ~60% the intensity of that observed for the conventional PMMA. However, a small excess of C–O and a small amount (3%) of C═O were detected (*Table 2*). This implies that there has been little rearrangement of the monomer in the plasma. This is consistent with the SIMS data where a number of ions (e.g. $m/z = 85$, 87, 101 and 187) containing a complete monomer unit were detected.

ppEMA and ppBMA: spectral assignments

The SIM spectra for ppEMA and ppBMA, shown in *Figures 3a* and *b*, respectively, correspond closely with the SIM spectra acquired for their conventional counterparts*. However, there are a number of spectral differences and the more important of these are considered below.

A strong signal appears at $m/z = 87$ in both the negative SIM spectra of ppEMA and ppBMA. The structure assigned by Lub and Benninghoven[8] for this ion (structure i) retains the ester R group and cannot, therefore, account for the $m/z = 87$ in ppEMA and

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*The SIM spectra for PEMA and PBMA are not shown as they have been reported in other publications[7]

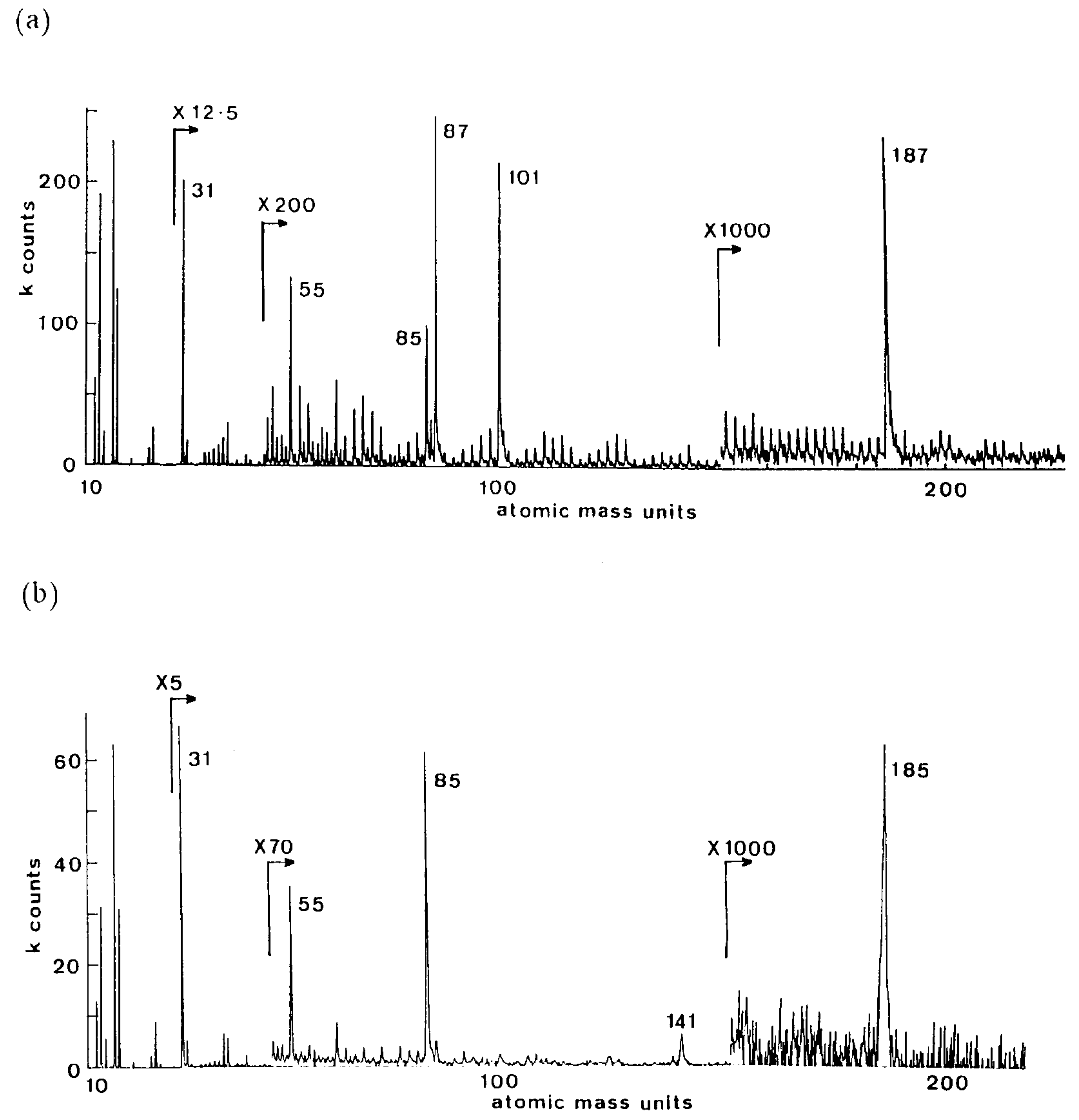
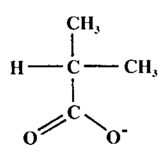


Figure 1 Negative SIM spectra for (a) ppMMA and (b) conventional PMMA

ppBMA. In keeping with the assignment of Hearn and Briggs[7], structure iv is assigned to the ion at $m/z = 87$ for ppMMA, ppEMA and ppBMA, where loss of the ester R group has occurred. The $m/z = 87$ ion is still thought to be diagnostic of original polymer chain ends.



$$\mathrm{H-\overset{CH_3}{\underset{CO_2^-}{C}}-CH_3}$$

iv

In the SIM spectra of the PPs, the peak at $m/z = 101$ is considerably more intense than in the SIM spectra of the conventional polymers. In ppMMA, the intensity of this peak is similar to that of the peak at $m/z = 87$, whereas in ppEMA and ppBMA the signals at $m/z = 101$ are not as strong. According to Lub and Benninghoven[8], the peak at $m/z = 101$ can be assigned to an ion that originates exclusively from polymer end groups retaining the ester R group (structure ii). If the methyl substituent (R) in structure ii was replaced by either an ethyl or a butyl group, the resultant ions would have m/z values of 115 and 143, respectively. A peak at $m/z = 115$ is readily seen in the SIM spectrum of ppEMA, and likewise an ion at $m/z = 143$ in the SIM spectrum of ppBMA. The absence of these ions in the negative SIM spectra of the conventional methacrylate polymers adds support to the above assignment. However, structure ii does not explain

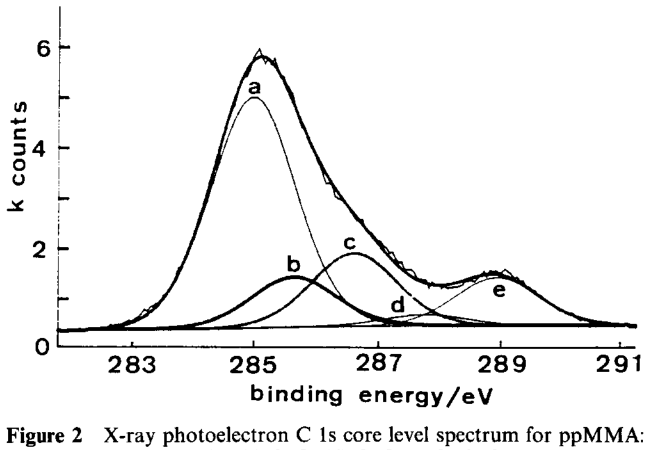
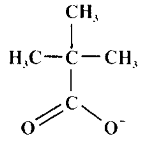


Figure 2 X-ray photoelectron C 1s core level spectrum for ppMMA: (a) $\underline{\mathrm{C}}$–H; (b) $\underline{\mathrm{C}}$–$\mathrm{CO_2R/H}$; (c) $\underline{\mathrm{C}}$–O; (d) $\underline{\mathrm{C}}$–O or O–$\underline{\mathrm{C}}$–O; (e) $\underline{\mathrm{C}}\mathrm{O_2R/H}$

the $m/z=101$ peaks seen in the SIM spectra of ppEMA and ppBMA. Therefore, we propose that these signals are best represented by an ion that has lost the ester R group. This is in accordance with Hearn and Briggs[7].

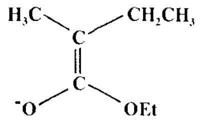


v

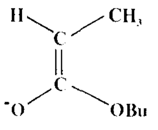
This ion originates from polymer end groups, as witnessed by the negligible signal at $m/z=101$ in the SIM spectra of conventional PEMA and PBMA. In ppMMA, the high intensity of the $m/z=101$ peak probably arises from the mass coincidence of structures ii and v.

The peak at $m/z=187$ in ppMMA is thought to correspond to the ion at $m/z=87$ (structure iv) with an extra monomer unit attached. Analogous peaks appear in the negative SIM spectra of ppEMA ($m/z=201$) and ppBMA ($m/z=229$).

The following structures are postulated for the ions observed at $m/z=129$ in the SIM spectra of ppEMA and ppBMA:



m/z=129, ppEMA



m/z=129, ppBMA

A peak at $m/z=129$ was also observed in the SIM spectrum of PBMA and the above structure was assigned[7]. It is unclear at present whether these peaks

Table 2 Results of the C 1s core level fitting

Chemical environment	Area[a] (%)
C-H	56
C-CO_2R/H	12
C-O	18
C=O or O-*C*-O	3
CO_2R/H	12

[a] The computer output is only given to two significant figures. This has resulted in an error of 1% in the overall area of the C 1s peak, i.e. the total area is given as 101%

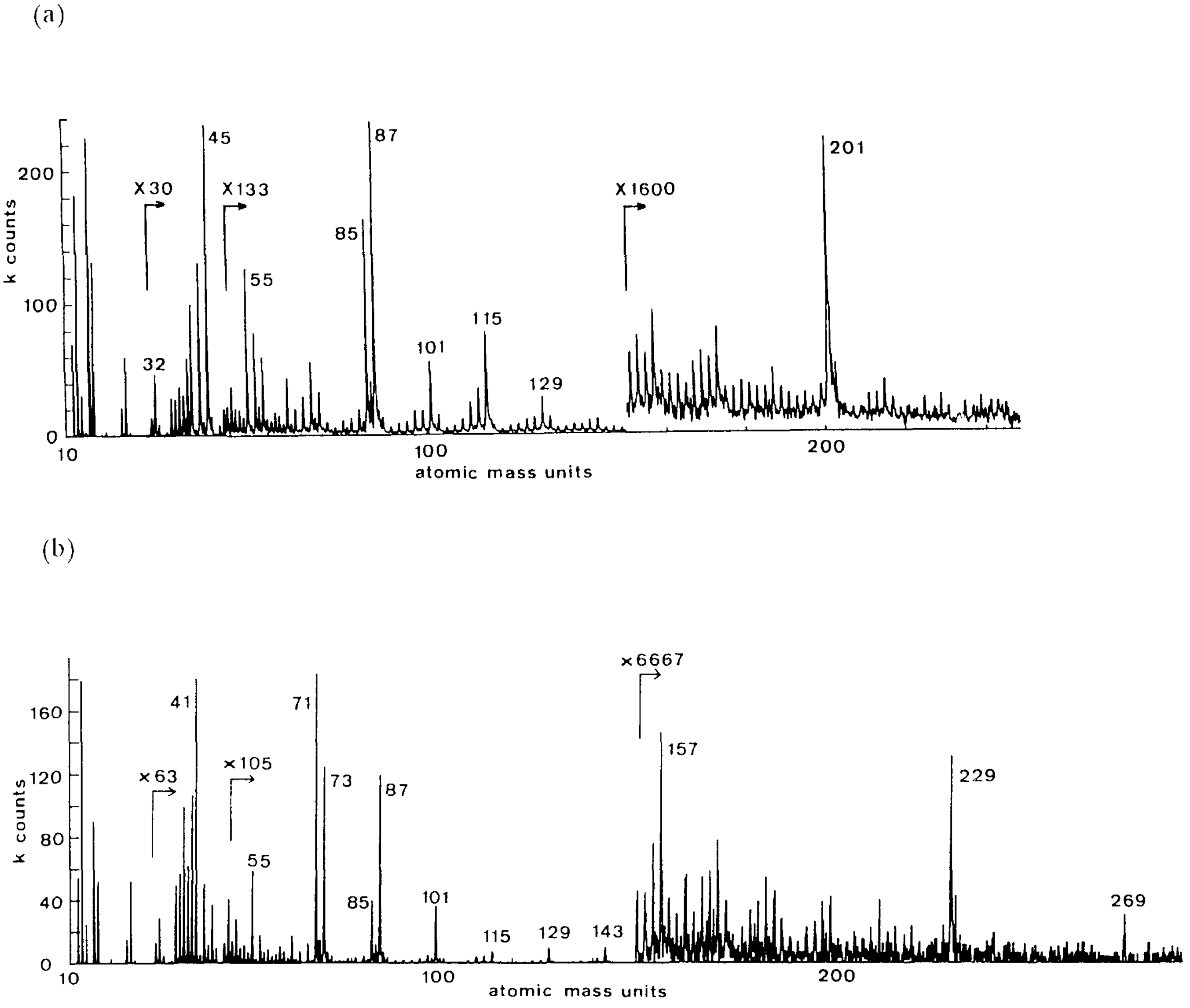
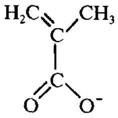
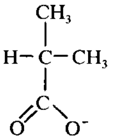
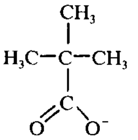
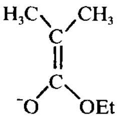
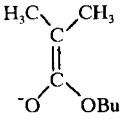
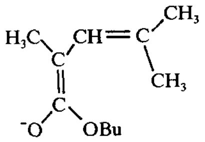
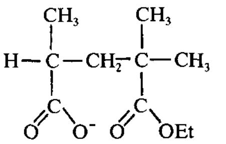
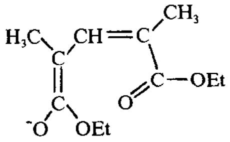
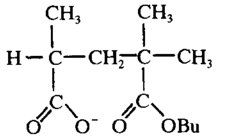
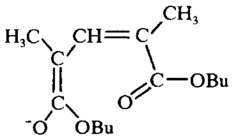


Figure 3 Negative SIM spectra for (a) ppEMA and (b) ppBMA

Table 3 Prominent peaks in the negative SIM spectra of ppEMA, PEMA, ppBMA and PBMA

Secondary ion structure	*m/z*	Possible origin	ppEMA	PEMA	ppBMA	PBMA
C_2HO^-	41	Monomer unit[7]	D	D	+	+
$CH_3CH_2O^-$	45	Ester[7]	+	+	○	○
$CH_2=C=CHO^-$	55	Monomer unit[7]	+	+	+	+
$CH_3CH=CHCH_2O^-$	71	Ester[7]	○	○	+	+
$CH_3CH_2CH_2CH_2O^-$	73	Ester[7]	○	○	+	+
	85	Main chain[7]	+	+	+	+
	87	End group[8]	+	D	+	ND
	101	End group[8]	+	D	+	ND
	115	End group	+	D	×	○
	143	End group	○	○	+	D
	183	Main chain[7]	○	○	ND	+
	201	End group	+	ND	○	○
	213	Main chain[7]	ND	+	○	○
	229	End group	○	○	+	ND
	269	Main chain[7]	○	○	D	+

+, Peak present; ND, not detected; D, detected, but low intensity; ○, this ion retains the ester R group. As expected this ion was not detected for this polymer; ×, an ion of this *m/z* was detected. However, its structure has not been assigned originate from the main polymer chain or the polymer chain ends.

A more complete comparison of the SIMS data from these PPs with their respective conventional counterparts is made in *Table 3*.

Curve fitting of the corresponding X.p.s. spectra for the ppEMA and ppBMA reveals that both of these PPs have retained considerable carboxylate functionality. The calculated oxygen–carbon number ratios from the O 1s and C 1s core levels show that a similar high retention of oxygen from the monomer has occurred.

DISCUSSION

PPs are commonly prepared under high W/F conditions. In the case of hydrocarbon precursors (e.g. acetylene) this results in a PP which is branched, crosslinked and contains a high concentration of free radicals[13]. PPs prepared from oxygen-containing monomers are similar but contain a much lower concentration of free radicals[12]. As the W/F ratio is decreased the concentration of free radicals in the PP decreases even further. The PPs studied here were prepared under low W/F conditions and are therefore unlikely to contain a high concentration of free radicals. Further, the PPs studied here show significant retention of the functional group from the methacrylate precursor. In contrast, Yasuda[12] noted that PPs prepared from oxygen-containing monomers, at high W/F, do not retain appreciable amounts of the original functional groups from the monomer. The use of low W/F conditions in this work, has therefore resulted in plasma polymerized alkyl methacrylates that are notably different from PPs prepared at high W/F.

From the X.p.s. data alone, it is evident that retention of monomer functional group has occurred in the PPs. Further, the presence of small amounts of C=O indicates that some rearrangement of the monomer has taken place in the plasma. SIMS analysis provides additional and complementary information to the X.p.s. data. From the detection of fragments diagnostic of the conventional poly(alkyl methacrylate)s in the SIM spectra of the PPs, it can be deduced that structurally these polymers are similar. This implies that in the plasma at least some monomer units are polymerizing head-to-tail through the C=C bond. In the SIMS data reported there is evidence of fragments containing two repeat units. Spectral differences in the SIMS, between the PP and its conventional poly(alkyl methacrylate) counterpart, may be attributed to end groups in the PPs. From the considerable intensities of end-group peaks, it is clear that their concentration in the PPs must be comparatively high. This result, coupled with the oily appearance of the PPs, points to these materials consisting of very short 'methacrylate like chains', which may be branched or linear but with very little crosslinking. The issue of whether the initiation of plasma polymerization is mono- or multifunctional, and consequently whether the polymers are linear or branched, cannot be addressed from the present data. The low intensity of the $m/z = 141$ ion in ppMMA, when compared with the conventional PMMA, may be explained by the very short chain length of the PP. From the fragmentaton model of Hearn and Briggs[7], a minimum of three repeat units (per chain) are required for formation of the new end groups that give rise to this ion. For the formation of this new end group to occur in any significant concentration, a much greater chain length is required.

The SIMS results reported here clearly demonstrate the close structural relationship between PPs of alkyl methacrylate monomers, prepared at low W/F, and their conventional counterparts; such a relationship has not been revealed in previous SIMS studies of PPs[2,13]. This relationship is currently being further investigated.

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REFERENCES

1 Millard, M. 'Techniques and Applications of Plasma Chemistry' (Eds J. R. Hollahan and A. T. Bell), Wiley, New York, 1974, Ch. 5

2 Chilkoti, A., Ratner, B. D. and Briggs, D. *Anal. Chem.* 1991, **63**, 1612

3 Gombotz, W. and Hoffman, A. *J. Appl. Polym. Sci.* 1989, **37**, 91

4 Inagaki, N. and Matsunga, M. *Polym. Bull.* 1986, **13**, 349

5 Sanchez Urrutia, M., Schreiber, H. P. and Wertheimer, M. R. *J. Appl. Polym. Sci., Appl. Polym. Symp.* 1988, **42**, 305

6 Briggs, D. *Br. Polym. J.* 1989, **21**, 3

7 Hearn, M. J. and Briggs, D. *Surface Interface Anal.* 1988, **11**, 198

8 Lub, J. and Benninghoven, A. *Org. Mass. Spectrosc.* 1988, **24**, 164

9 Munro, H. S. and Till, C. *J. Polym. Sci., Polym. Chem. Edn* 1986, **24**, 279

10 Webster, O. W., Hertler, W. R., Sogah, D. Y., Farnham, W. B. and Rajanbabu, T. V. *J. Macromol. Sci. Chem.* 1984, **A21**, 943

11 Briggs, D. and Seah, M. (Eds) 'Practical Surface Analysis', 2nd Edn, Vol. 1, Wiley, Chichester, 1990

12 Yasuda, H. 'Plasma Polymerisation', Academic Press, London, 1985

13 Ward, R. J., Munro, H. S., Davies, M. C. and Short, R. D. *Polymer* 1993, **34**, 2250