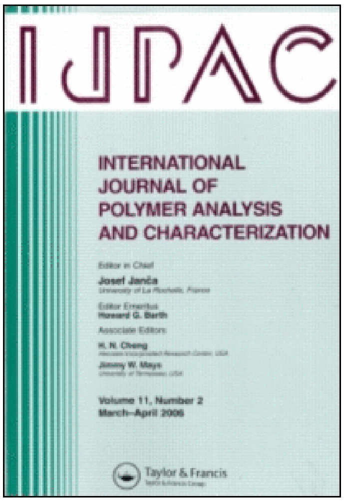

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Quantitative ToF SIMS Analysis of Spun-Cast and Solution-Cast Polymer Films

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Films of a series of monodisperse, moderately syndiotactic poly(methyl methacrylate) (PMMA) standards, with M_w ranging from 2,900–428,000, were solution-cast and spun-cast from chloroform onto clean aluminium substrates. The polymers were thoroughly characterized by conventional spectroscopic and chromatographic techniques. The films were studied using x-ray photoelectron spectroscopy (XPS) and time-of-flight secondary-ion mass spectrometry (ToF SIMS). The effects of molecular weight and film thickness on SIMS spectra were investigated thoroughly by unit-mass and high-resolution ToF SIMS. Film thickness had a pronounced effect on the negative SIMS spectra, particularly in films a few monolayers thick. This was seen in both the total negative ion counts (*m/z* 31–200) and the key negative ion intensity ratios. A parallel effect was observed with respect to the effect of molecular weight. These differences are attributed to (i) the original end-group concentration in the surface which decreases with increasing molecular weight and (ii) the original end-group concentration in the surface which increases as film thickness decreases.

Keywords: Time-of-flight secondary-ion mass spectrometry (ToF SIMS), poly(methyl methacrylate), molecular weight, film thickness

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INTRODUCTION

Time-of-flight secondary-ion mass spectrometry (ToF SIMS) is an established method for the analysis of polymer surfaces.[1] Many classes of polymers have been studied, such as polystyrenes,[2] polyamides,[3] polyurethanes,[4] polyglycols,[5] polymethacrylates,[6] *etc.* For most of these applications, SIMS has been used in a qualitative nature, that is to distinguish between polymer types by a so called 'fingerprint' spectra.

One polymer that has been well documented in the SIMS literature is poly(methyl methacrylate).[6–15] It is clear from examination of published spectra of PMMA that marked differences in relative ion intensities exists. These arise in part from use of different instrumentation (ToF vs. quadrupole), but also from the lack of standardization in material and preparation prior to analysis. While there has been some work on instrumentation parameters, there has been very little on sample related variables, that is additives, molecular weight, polydispersity, solvent, *etc.* The intrinsic sample properties and sample preparation method all contribute to the SIMS spectra. Their relative importances have not been systematically investigated. Hence, in this paper the effects of molecular weight and film thickness on SIMS spectra of PMMA are investigated.

EXPERIMENTAL

Polymer Evaluation

Four monodisperse poly(methyl methacrylate) standards were purchased from Polymer Laboratories (Church Stretton, England) with M_w values of 2,900, 12,700, 89,100, and 428,000. These will be referred to as samples PMMA-1, PMMA-2, PMMA-3, and PMMA-4, respectively. The polymers were extensively characterized by ^{1}H nuclear magnetic resonance spectroscopy (NMR), Fourier-transform infrared spectroscopy (FT-IR), and size exclusion chromatography (SEC). These were used to verify the polymer data as supplied, that is molecular weight, polydispersity, and tacticity, and to identify impurities present, if any. Matrix-assisted laser-desorption ionization time-of-flight mass spectrometry (MALDI ToF MS) was used to elucidate the end-groups of the samples.

Surface Analysis

Surface analysis was carried out by x-ray photoelectron spectroscopy (XPS) and ToF SIMS. XPS was carried out using a VG CLAM 2 photoelectron spectrometer (VG Scientific, East Grinstead, England). The operating conditions for XPS analysis using Mg K_α x-rays were 100W (10mA, 10kV). The take-off angle relative to the plane of the sample surface was 30°, which gave a typical sampling depth of 1.8nm for the C1s electrons.[16] Survey scan spectra were obtained using a pass energy of 100eV. Two narrow-scan spectra of carbon (C1s) and oxygen (O1s) core levels were taken using a pass energy of 20eV.

Unit-mass ToF SIMS was carried out on two VG Scientific IX23LS time-of-flight secondary-ion mass spectrometers (VG Scientific, East Grinstead, England). The primary ion source was a FEI liquid metal (Ga^+) ion source, which gave a beam current of 1nA. The analyzer was a Poschenreider type. For secondary ion extraction the sample was held at ±5kV, depending on whether positive or negative spectra were being acquired. Charge compensation for insulating samples was achieved by use of a low-energy electron flood gun. The sample bias was reduced to zero during the electron flood cycle to prevent sample damage. The mass information obtained by the detector was transferred to a Digital/PDP microcomputer via time-to-digital converters. The system was controlled by VGX7000T software.

High-resolution ToF SIMS were recorded on a Physical Electronics PHI 7200 instrument (Eden Prairie, Minnesota, USA). This instrumentation has been extensively described elsewhere in the literature.[17]

Film Preparation

HPLC-grade hexane, methanol, and chloroform were purchased from Aldrich Chemicals Co. (Gillingham, England) and used as supplied. The glassware used in the sample casting process underwent a rigorous cleaning procedure, which was required to minimise the amount surface contamination at the polymer surface. First, a mild abrasive detergent was applied and thoroughly rinsed with distilled water. The glassware was then immersed in 20% concentration nitric acid for 30 min and subsequently rinsed with distilled water. Finally, the glassware was rinsed by HPLC-grade methanol and dried in an oven at 50°C overnight.

For surface analysis, films of PMMA were (i) solution-cast into an aluminium pan and (ii) spun-cast onto aluminium, which was purchased from Fisons Chemicals (Loughborough, England). The aluminium substrate was found to have a hydrocarbon overlayer on the surface. A suitable cleaning procedure was determined for the aluminium substrate by ToF SIMS analysis. The criteria for selecting the cleaning procedure (Table I), was the one which produced the highest $Al^+/C_3H_5^+$ peak ratio, which was then used throughout the sample casting process. Hence, the aluminium substrate was cleaned by the following procedure: a 15 min soak in hexane, followed by a thorough rinse in distilled water and a 15 min soak in chloroform. The aluminium was subsequently dried in an oven at 50°C overnight.

For solution-cast films 200mg of PMMA sample was dissolved into 10ml of chloroform, that is 2% w/v. The solution was poured into an aluminium pan, partially covered and placed into a fume cupboard. Once the majority of solvent was removed, the aluminium pan was placed in a vacuum oven at 10^{-2} mbar for 24 h, at a preset temperature (50°C), which had previously been determined from XPS measurements.[18] The films were considered to be of constant thickness, which was calculated to be 66μm, based on the density of PMMA as $1.188 g/cm^3$.[19]

For spun-cast films, two concentrations were used, 2 and 0.2% w/v. Subsequent to casting, the films were placed in a vacuum oven at 50°C for 24 h. The thicknesses of the spun-cast films were 2μm and 2nm, respectively for the 2% and 0.2% concentrations. The former was calculated by a cut-and-weigh method, based on the density of PMMA as $1.188 g/cm,^3$[19] while the latter was calculated by signal substrate signal attenuation XPS.[20] The air/polymer interface was analyzed for all the films.

TABLE I Observe $Al^+/C_3H_5^+$ Peak Areas Ratios for Various Aluminium Pan Cleaning Procedures as Determined from ToF-SIMS

Aluminum pan cleaning procedure	*Peak area Al^+*	*Peak area $C_3H_5^+$*	*Area ratio $Al^+/C_3H_5^+$*
uncleaned	405807	221406	1.832
15 min soak in hexane	708992	289030	2.453
hexane/distilled water/methanol	1064902*,†	187323	5.684
hexane/distilled water/chloroform	1296202*,†	45329	28.595

* 15 min soak in hexane followed by thorough rinse in distilled water, with final 15 min soak in either methanol or chloroform.

† Dried in an oven at 50°C overnight.

RESULTS AND DISCUSSION

Polymer Evaluation

The results of polymer evaluation are shown in Table II. The tacticity of the samples was determined by ratioing the integrals of the methyl peaks in the ^1H NMR spectra. This showed that the samples are moderately syndiotactic. The molecular weight and polydispersity were determined using a polystyrene calibration curve. No presence of impurity was observed in the FT-IR or NMR spectra and no oligomeric species were present in the SEC chromatograms. Thus the samples were considered to be 'contaminant free'. The end-groups of the PMMA-1 and PMMA-2 were determined by MALDI ToF MS and were shown to be hydrogen-terminated, for example in the case of Figure 1, which shows the MALDI ToF MS for PMMA-1, *m/z* 2325 is interpreted as sodium cationized [H-(MMA)$_{23}$-H]. The end-groups for the other samples were obtained from the supplier.

X-ray Photoelectron Spectroscopy (XPS)

A survey scan XPS spectrum for a PMMA-2 is shown in Figure 2. The spectrum contains two primary peaks, C1s at *ca.* 285eV and O1s at *ca.* 533eV. Figure 3 shows a narrow scan spectrum of the C1s peak. The C1s curve was fitted with four contributions. The most intense is due to the carbon bound to carbon and/or hydrogen centred at 285eV. The other three peaks are due to $\underline{C}CH_2CH_3$, $O\underline{C}H_3$, and O-$\underline{C}$=O, which are shifted from the main peak by 0.8, 1.8, and 4.0 eV, respectively.[21] In the O1s narrow scan, two peaks of equal intensity were fitted at *ca.* 533.9eV for $\underline{O}$=C and the other for $\underline{O}$-C at *ca.* 535.5eV.

TABLE II Polymeric Data for PMMA Samples

PMMA Sample	M_w	*Polydispersity*	*mm**	*mr**	*rr**	*End Groups*
PMMA-1	2,900	1.14	55%	34%	11%	H-(MMA†)$_n$-H
PMMA-2	12,700	1.08	54%	38%	8%	H-(MMA)$_n$-H
PMMA-3	89,100	1.09	51%	44%	5%	$C_6H_5C(CH_3)_2$-(MMA)$_n$-H
PMMA-4	428,000	1.18	55%	40%	5%	$C_6H_5C(CH_3)_2$-(MMA)$_n$-H

*m and r refer to meso and racemic diads, respectively.

†MMA refers to methyl methacrylate repeat unit.

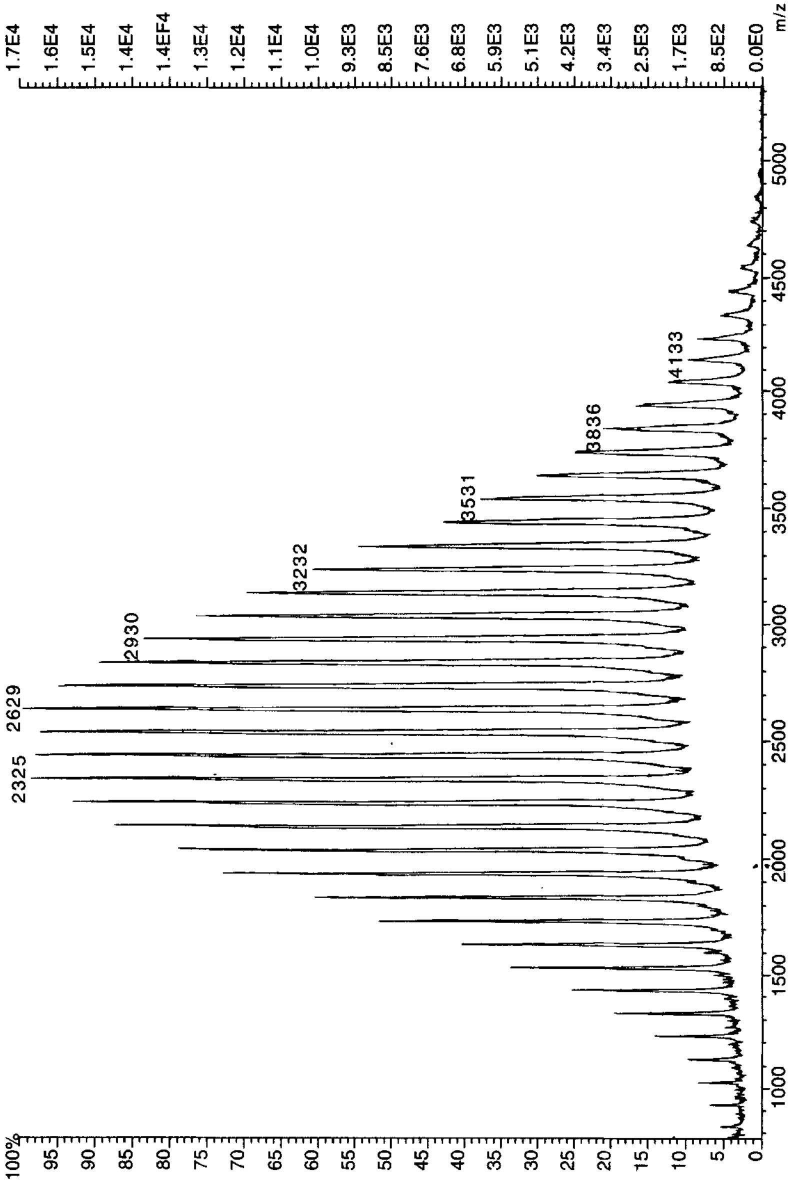

FIGURE 1 MALDI ToF MS of PMMA-1 for end-group determination.

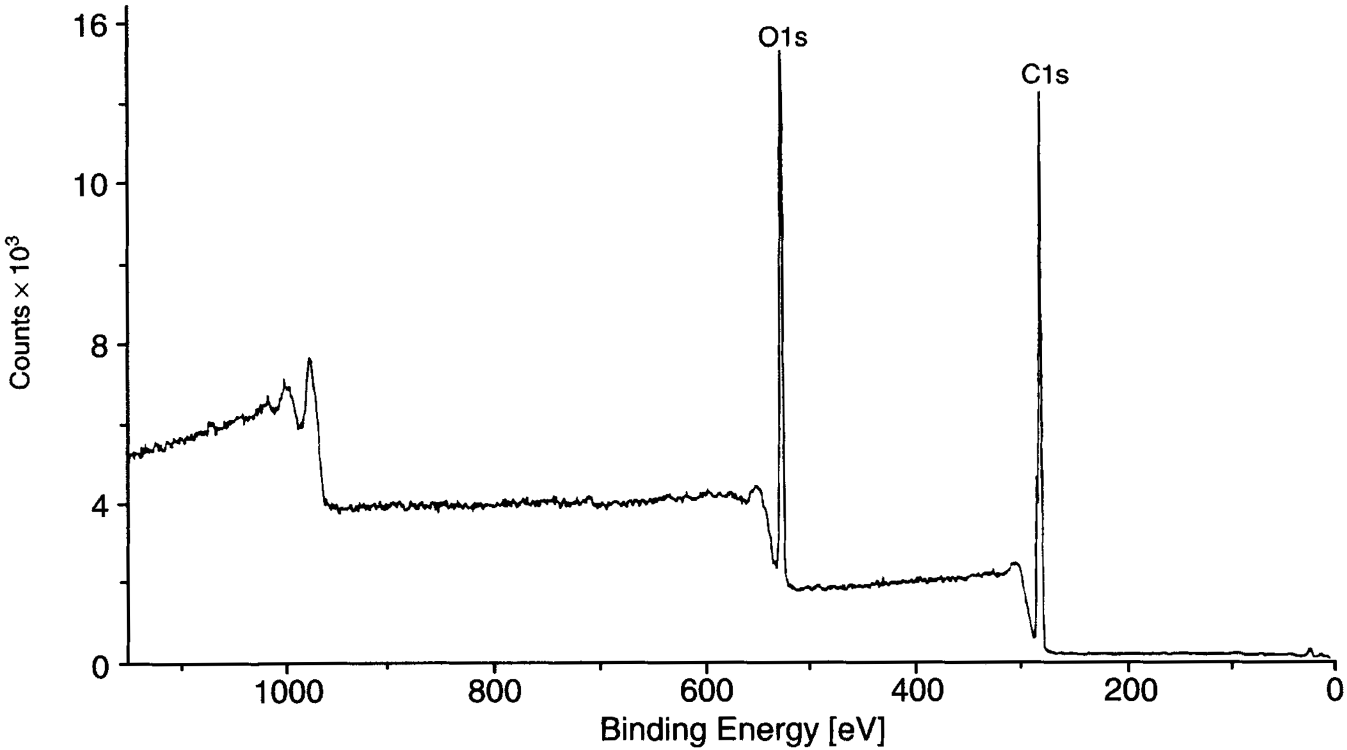

FIGURE 2 Wide-scan XPS spectrum of PMMA-2.

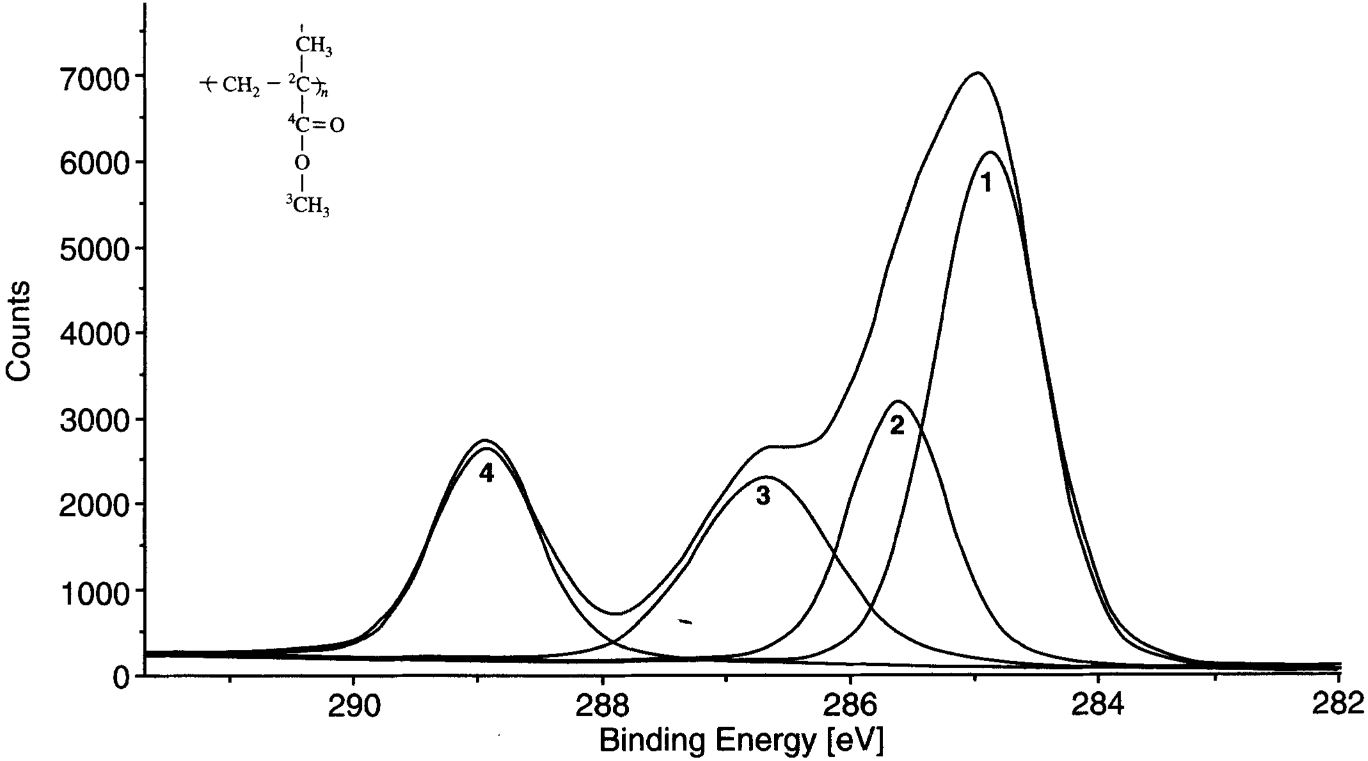

FIGURE 3 C1s curve fit for PMMA-2.

Time-of-Flight Secondary-Ion Mass Spectrometry

Polydimethylsiloxane was detected in some initial positive ion spectra with typical peaks at *m/z* 73, 147, and 207. This was effectively removed from the surface after the sample was ultrasonically cleaned for 1 min in HPLC-grade hexane. Hence, this process was adopted for all sample surfaces prior to analysis. The ultrasonic cleaning process has been thoroughly investigated,[18] and these results showed that this process does not degrade the polymer or have any effect on the quantification of SIMS data.

Positive and negative ion spectra of PMMA are shown in Figures 4a and 4b, respectively. At low mass in the negative ion spectra (<*m/z* 30), the peaks that dominate are of very high peak intensity, that is H^-, C^-, CH^-, O^-, OH^-, C_2^-, and C_2H^-, and give no chemical information relating to the structure of the polymer. Characteristic key ions of PMMA are observed at *m/z* 31, 41, 55, 85, 87, 101, 141, and 185. In the positive ion spectra, characteristic key ions are observed at *m/z* 59, 69, 115, 126, and 186. In addition, the positive ions *m/z* 139, 233, and 235 were selected on their prominence in their respective mass range. The structural formulae of the ions were unambiguously determined on the PHI 7200. These formulae are shown in Table III.

To allow us to identify differences in the samples, with respect to molecular weight and film thickness, the SIMS data were analyzed by the following methods:

1. Measurement of the absolute peak intensity.
2. Normalization- the absolute peak intensities of the peak of interest is normalized over a mass range (*m/z* 0–400 for positive ions and *m/z* 31–200 for negative ions). The criteria used in the selection of these ranges have been stated elsewhere.[18]
3. Ion intensity ratios. The absolute peak intensity is ratioed by the intensity of a base molecular-ion peak in the spectra (*m/z* 59 for the positive ions and *m/z* 31 for the negative ions).

Also, to establish the level of spectral reproducibility, standard errors were employed. The standard errors used have been calculated elsewhere.[18]

Effect of Molecular Weight

The effect of molecular weight on the SIMS spectra has been investigated quantitatively for all films and the absolute negative ion intensities are given in Table IV. Figure 5 shows a plot of the total negative ion counts

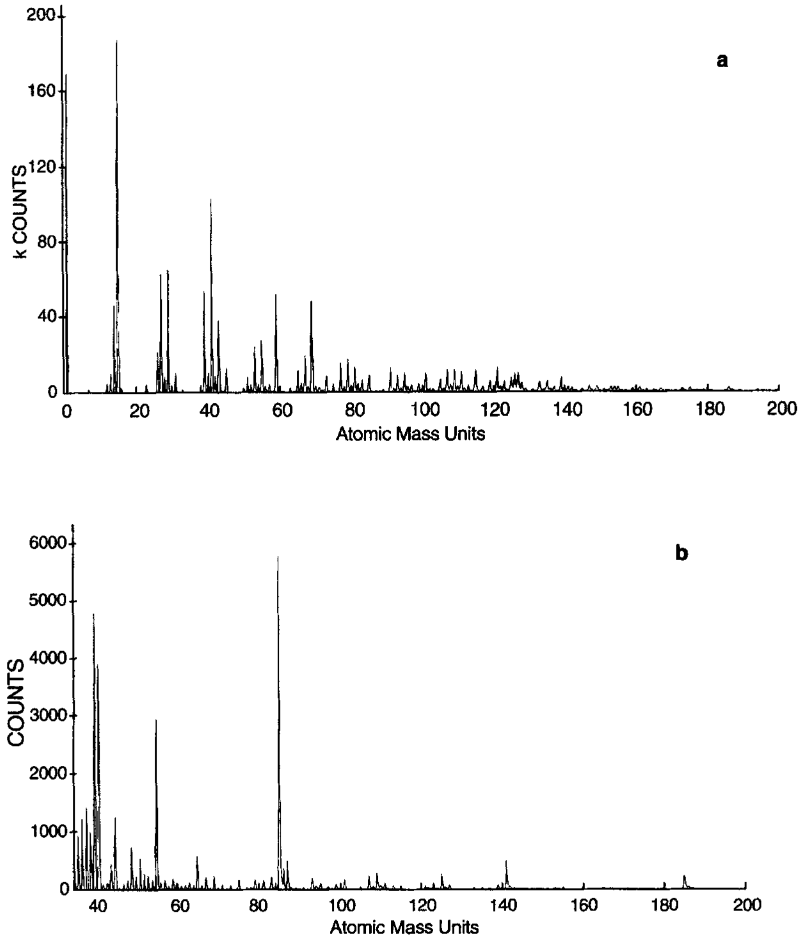

FIGURE 4 (a) Positive SIMS spectra (b) Negative SIMS spectra.

(*m/z* 31–200) vs. the log molecular weight of the PMMA sample. From this figure it can be seen that the total negative ion intensity decreases with increasing molecular weight. Figure 6 shows negative ion intensity ratios based on *m/z* 31, which are significantly affected by molecular weight, that is 85/31, 87/31, and 101/31. The ion ratios 41/31, 55/31, 141/31, and 185/31 were found to be constant over the molecular weight range and are ot shown. The figure shows that at molecular weights >90,000 the PMMAs are indistinguishable. No obvious trends were seen in the positive ion

TABLE III Prominent Peaks in the Positive and Negative Ion SIMS Spectra of PMMA

m/z	*Secondary positive ion structure*	*m/z*	*secondary negative ion structure*
59	CH_3OCO^+	31	CH_3O^-
69	$CH_2 = C(CH_3)CO^+$	41	C_2HO^-
115	$[(CH_3)^2C(COOCH_3)CH_2]^+$	55	CH_2CHCO^-
126	$[CH_2 = C(COOCH_3)CH_2CH = CH_2]^+$	85	$CH_2 = C(CH_3)COO^-$
139	$[C_8H_{11}O_3]^+$	87	$CH_3CH = C(OCH_3)O^-$
186	$[CH_3C(COOCH_3) = CHCH(CH_3)COOCH_3]^+$	101	$C = C(OCH_3)O^-$
233	$[C_{14}H_{17}O_3]^+$	141	$(CH_3)_2C = CHC(CH_3) = C(OCH_3)O^-$
235	$[C_{14}H_{19}O_3]^+$	185	$CH_3C(COOCH_3) = CHC(CH_3) = C(OCH_3)O^-$

TABLE IV Absolute Negative Ion Intensities for a Molecular Weight Series Cast from Chloroform

Sample	*Total Counts (m/z 31–200)*	*31*	*41*	*55*	*85*	*87*	*101*	*141*	*185*
PMMA-1 (66 μm)*	120939	56164	5126	3718	7849	2913	2985	6584	456
PMMA-2 (66 μm)*	91259	40384	3445	2037	3857	814	721	402	252
PMMA-3 (66 μm)*	72824	25604	2445	1274	2133	376	180	225	158
PMMA-4 (66 μm)*	60405	22322	2207	1074	1887	276	150	181	126
PMMA-1 (2 μm)†	151528	71902	6862	5270	9142	5040	4814	712	422
PMMA-2 (2 μm)†	112802	65104	5408	3140	6368	1402	1148	404	310
PMMA-3 (2 μm)†	82400	50721	3646	2270	4634	650	332	530	350
PMMA-4 (2 μm)†	90578	47376	4042	2064	4078	468	214	402	342
PMMA-1 (2 nm)†	245516	88168	10492	10056	27764	11148	11532	2164	1132
PMMA-2 (2 nm)†	106424	50828	5244	2712	6240	1320	992	516	448
PMMA-3 (2 nm)†	118012	57644	5612	3076	7776	832	384	668	568
PMMA-4 (2 nm)†	115044	60308	5428	3192	8060	900	268	636	304

*solution cast

†spun cast

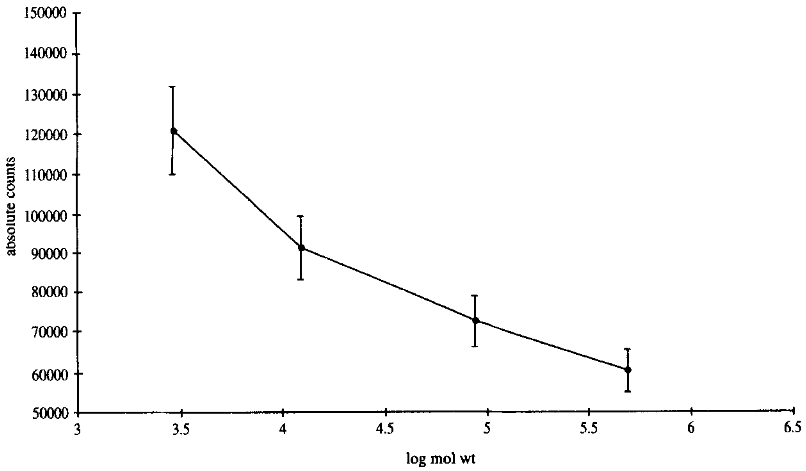

FIGURE 5 Total negative ion counts (*m/z* 31–200) for solution-cast PMMA films.

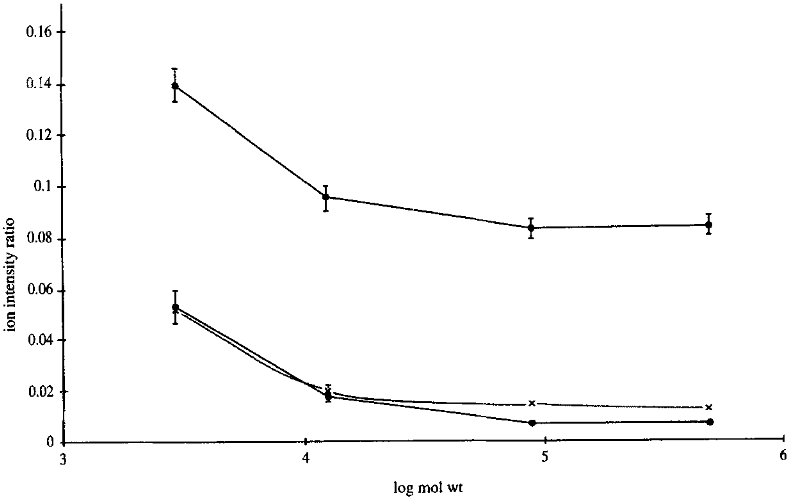

FIGURE 6 Negative ion intensity ratios based on *m/z* 31 for solution-cast PMMA films: 85/31 (♦), 87/31 (x), 101/31 (●).

spectra, which appear to remain constant with increasing molecular weight. This result is in good agreement with previous findings,[18,22] which speculate that the secondary ion yield for each ion is very similar. This result is attributed to the low probability of positive ions forming from original end-groups, that is positive ions originate from the polymer main chain.

The assignments of the *m/z* 87 and 101 were identified in a study of a low-molecular-weight PMMA oligomer (M_w ~ 1890) and originate from original polymer end-groups, that is fully saturated.[12] The end-groups of PMMA-1 and PMMA-2 have already been established to be hydrogen-terminated, hence it is anticipated that these end-groups produce the *m/z* 87 and 101 ions. From the observed decrease in the *m/z* 87/31 and 101/31 ion ratios, with increasing molecular weight (Fig. 5), it is proposed that this effect arises as a result of a decrease in the surface original polymer-end group concentration. Hence, at low molecular weight the largest contribution to the relative ion intensities would be predominantly from the original end-groups, with a small contribution from the fragmentation of the polymer main chain. As molecular weight increases, the contribution from the original chain-ends decreases, up to a point (M_w > 90,000) where the contribution is predominantly from polymer main chain with only a small contribution, if any, from original end-groups.

The origin of the *m/z* 85 ion has been assigned to a new polymer end-group, created as a result of a primary ion beam impact.[12] However, the contribution of this new end-group is not thought to be significant. Although these end-groups are seen in cationized fragments emitted from submonolayer films of low-molecular-weight PMMAs on silver, the situation here is very different. Chain entanglements will inhibit the emission of whole molecules. It is therefore proposed that the major contribution to the intensity of the *m/z* 85 ion at low molecular weight is predominantly from the original polymer end-groups, that is *m/z* 87-2H, with a minor contribution from the fragmentation of the polymer main chain. As the molecular weight increases, the contribution from the original chain-ends decreases, up to a point (M_w > 90,000) where the contribution is predominantly from polymer main chain with only a small contribution, if any, from original end-groups.

The original end-groups of the other PMMA samples, that is PMMA-3 and PMMA-4 are cumyl and hydrogen. There is no spectral evidence for the presence of the cumyl end-groups. The dominant contribution for *m/z*

85, 87, and 101 for these is from the polymer backbone with only a minor, if any, contribution from the original end-groups. Otherwise, the negative ion spectra of PMMAs with $M_w > 90{,}000$ are indistinguishable.

Effect of Film Thickness

The effect of thickness on the SIMS spectra of PMMA has been investigated quantitatively for all the samples. The absolute negative ion intensities for all the peaks monitored in the various films are shown in Table IV. Figure 7 shows the total negative ion counts (*m/z* 31–200) vs. the log molecular weight for all thicknesses. This data clearly indicates two distinct trends. Firstly, total negative ion counts decrease as molecular weight increases in all the films. This is in very good agreement with earlier work on the effect of molecular weight in solution cast films.[18] Secondly, within a molecular weight regime, the total negative ion intensity decreases as film thickness increases. This observation is also illustrated in Table V, which shows the negative ion ratios that displayed the greatest effect with respect to molecular weight based on *m/z* 31 for the film thicknesses studied.

From the observed trend it is proposed that the surface concentration of original polymer end-groups increases as the polymer film thickness

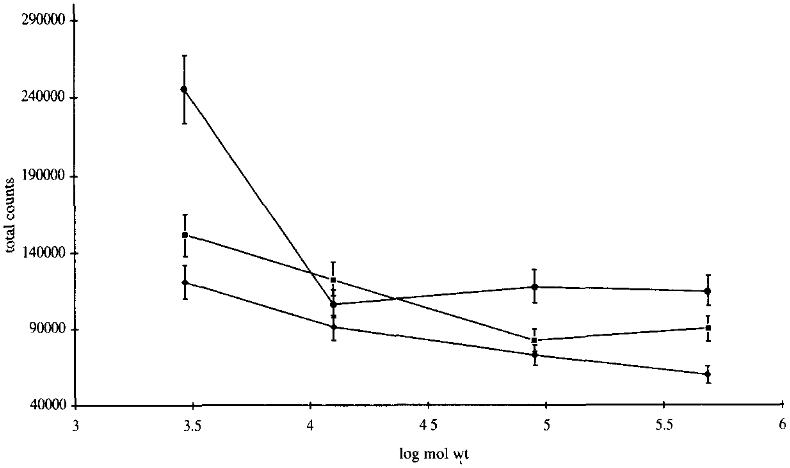

FIGURE 7 Total negative ion counts (*m/z* 31–200) for varying thicknesses of PMMAs: 66μm (♦), 2μm (■), 2nm (●).

TABLE V Negative Ion Ratios Based on m/z 31 for Varying Thicknesses of a Series of PMMAs Cast on to an Aluminium Substrate

Sample	*85/31*			*87/31*			*101/31*		
	2nm*,†	2μm*,‡	66μm‡,¶	2nm	2μm	66μm	2nm	2μm	66μm
PMMA-1	0.315	0.127	0.140	0.126	0.070	0.052	0.131	0.067	0.053
PMMA-2	0.123	0.098	0.096	0.026	0.021	0.020	0.020	0.018	0.018
PMMA-3	0.135	0.091	0.083	0.014	0.014	0.015	0.007	0.008	0.007
PMMA-4	0.134	0.086	0.085	0.015	0.001	0.012	0.004	0.005	0.007

*spun cast

†thickness calculated by signal substrate signal attenuation XPS.

‡thickness calculated by cut and weigh method

¶solution cast

decreases. Hence, at low molecular weight the largest contribution to the relative ion intensities, *m/z* 87 and 101, would be predominantly from the original end-groups, with a small contribution from the fragmentation of the polymer main chain (Fig. 8). As thickness increases, the surface concentration of original chain-ends decreases, probably up to a point where the contribution is no longer significant. Positive ion spectra were once again uninformative.

From this study, it is apparent that the negative ion intensity ratios and total ion counts are both molecular weight and thickness dependent. It is proposed that these factors can be explained by the following: (i) the surface end-group concentration decreases with increasing molecular weight and (ii) the surface end-group concentration increases as film thickness decreases. Theoretical models based on molecular dynamic and Monte-Carlo simulations of semicrystalline systems predict an excess of chain-ends at the surface.[23,24] This behavior has been proved in amorphous polymer surfaces.[25] Other recent work has also shown polymer surfaces enriched by chain-ends.[26,27] A 2-fold chain-end enrichment was observed in the top 1nm of isotopically end-capped polystyrene (M_w ~ 10,000) by high-resolution electron energy loss spectroscopy.[26] A static SIMS study of diblock and triblock copolymers of hydrogenous and deuterated

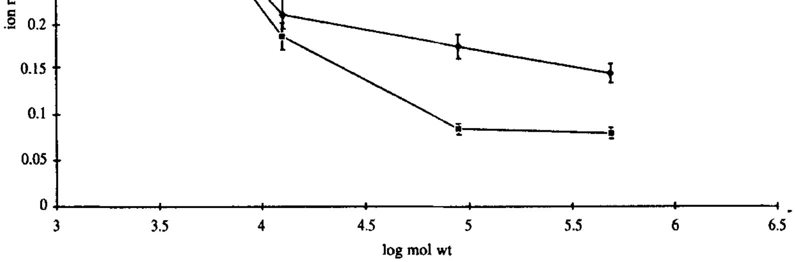

FIGURE 8 Negative ion intensity ratios *m/z* 87/85 (♦) and 101/85 (■) for solution-cast PMMA film.

polystyrene (M_w ~ 10,000) indicated the surface chain-end concentration was up to 400% of the bulk value This was found to be independent of any isotope effects.[27]

Recently, it was proposed that chain-end enrichment would significantly lower the surface glass-transition temperature (T_g).[25] This behaviour has been reported experimentally by Keddie *et al.*[28] They found that T_g was decreased with decreased thicknesses of polystyrene films. From these results it was postulated that a 'liquid-like' layer exists at the surface, which is independent of molecular weight.[28] This behaviour was observed in a subsequent study with PMMA on gold surfaces.[29] From our results we speculate that there is a large surface concentration of end-groups at low molecular weight. When the polymer chain length increases, the end-group concentration decreases, up to a point where this concentration becomes independent of molecular weight. Within a molecular weight regime, the surface concentration of original polymer end-groups decreases as the film thickness increases.

CONCLUSIONS

The effects of molecular weight and film thickness on ToF SIMS spectra have been systematically investigated for a series of poly(methyl methacrylates). Negative ion spectra were found to be susceptible to sample variables, but the positive ion spectra were very uninformative. Both molecular weight and film thickness had a pronounced effect on the SIMS spectra seen in both the total negative ion counts and negative ion intensity ratios, Figures 5, 6, and 7. The effects are explained as follows: (i) the original surface end-group concentration decreases with increasing molecular weight and (ii) the surface end-group concentration increases as film thickness decreases. These results obtained complement other SIMS studies of surface enrichment by polymer end-groups.[27,30,31]

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