Surface Characterization of Methyl Methacrylate–Poly(ethylene glycol) Methacrylate Copolymers by Secondary Ion Mass Spectrometry and X-ray Photoelectron Spectroscopy

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ABSTRACT: Surface analysis of methyl methacrylate/poly(ethylene glycol) methacrylate copolymers has been carried out using X-ray photoelectron spectroscopy (XPS) and static secondary ion mass spectrometry (SSIMS). Both techniques confirm that solvent-cast films of these random copolymers present a surface that is very similar in composition to the bulk. A slight excess of methyl methacrylate units at the polymer/vacuum interface was noted in the XPS spectra. SSIMS reveals that the top few monolayers of the copolymer films are typical of the bulk material and also confirm the presence of a methoxy end cap in the poly(ethylene glycol) methacrylate macromonomer structure.

Introduction

Reduction in protein adsorption and cell adhesion on a polymeric material can be affected by the surface attachment of poly(ethylene glycol) (PEG).[1] It is thought that the water soluble PEG chains provide a steric barrier which slows protein deposition.[2] There are numerous medical applications for biologically inert surfaces, especially in the field of implants and medical devices. It is important therefore to investigate methods of generating PEG rich surfaces, and there are a variety of approaches to achieve this goal. Examples of strategies which have been employed are the physical adsorption of PEG-containing surfactants,[3] plasma immobilization,[4] and surface grafting.[5] Techniques such as these have the advantage that cheap, commercially available polymers with the necessary bulk physical properties for specific applications may be easily tailored to provide nonfouling surfaces. Unfortunately, the modified surfaces are often susceptible to chemical or physical degradation, and this will limit the period of time over which they will be effective.[4]

Another approach to immobilize PEG is to graft a water insoluble polymer with pendant PEG side chains. Such materials may be employed in the bulk, providing they have the necessary physical properties, or as coatings. In this work we investigate a range of methyl methacrylate/PEG methacrylate copolymers. The PEG methacrylate macromonomer has previously been used to produce graft copolymers with vinyl chloride[6] and acrylonitrile[7] to produce materials with demonstrable antithrombogenic properties. In another study, poly(ethylene terephthalate) was grafted photochemically with this macromonomer specifically to enhance wettability and antistatic properties.[5] Copolymers of alkyl methacrylates and PEG methacrylate have also been investigated,[8,9] and these compounds have proven to be resistant to protein adhesion as coatings[8] or in the bulk.[9]

Our interest is in the expression of the PEG side chains at the polymer surface. We have utilized X-ray photoelectron spectroscopy (XPS) and static secondary ion mass spectrometry (SIMS) to gain an understanding of the interfacial behavior of a range of alkyl methacrylate–PEG methacrylate copolymers. Both of these techniques have found increasing use in the field of biomaterials since it was recognized that a grasp of surface chemistry is vital to the production of effective biocompatible materials.[10] Some alkyl methacrylate–PEG methacrylate copolymers have previously been studied using XPS[8] but no investigation has, to our knowledge, been published on SIMS of these materials. Here we present a comparison of data from both techniques.

Experimental Section

Materials. The synthesis of methyl methacrylate (MMA)–poly(ethylene glycol (MW = 1000)) methacrylate (PEGMA) random copolymers was carried out using an automated reactor system, where temperature control was ±0.5 deg. The reaction vessel was a 500 mL flask, equipped with a water condenser, mechanical stirrer, and nitrogen inlet. The monomers and initiator (azobis(isobutyronitrile), AIBN) were added to the toluene with stirring. The mixture was purged with nitrogen for ~15 min before heating to 60 °C. The reaction was continued for 10 h under a nitrogen blanket. The polymer was isolated by precipitation into cold petroleum ether (40/60, 10 times excess by volume), redispersing in toluene and reprecipitating in cold petroleum ether as before. The resulting polymer was then vacuum dried overnight. Molecular weight determination was carried out by GPC, with DMF as the solvent with added lithium nitrate. PMMA standards were used with molecular weights ranging from 1.4 million to 1210.

A general copolymer structure is shown in Figure 1. Five copolymers were analyzed which had 12.5, 30, 40, 50, and 80% weight PEGMA monomer in the reaction vessel, the remainder being MMA. In addition, the pure homopolymers MMA (MW 25 000, Polysciences Inc., Warrington, PA) and PEGMA (ICI Paints, Slough, U.K.) were analyzed by SIMS.

Films of the methacrylate copolymers were spun cast from 1% w/v solutions in chloroform; 50 μL of these solutions was dropped onto aluminum foil coated sample stubs spinning at 5000 rpm. The films were then allowed to dry for 30 min prior to analysis.

Surface Analysis. Static SIMS spectra were obtained using a VG Ionex SIMSLAB 3B instrument equipped with a

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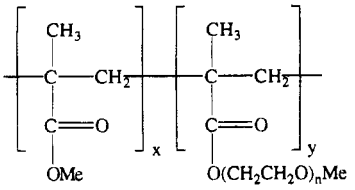


Figure 1. General structure of random MMA–PEGMA copolymers.

Table 1. Carbon Content and Molecular Weights of MMA–PEGMA Copolymers

% PEGMA	% carbon (XPS)	% carbon (theory)	M_w
12.5	70.0	70.8	62 600
30	68.5	70.1	74 700
40	68.3	69.6	82 300
50	67.6	69.2	94 000
80	65.6	67.8	114 600

differentially pumped EX05 ion gun and a 12-12M quadrupole mass spectrometer. Argon atoms at 2 keV were used as the primary source with an equivalent current of 0.8 nA. The total dose per sample was approximately 5×10^{12} atoms/cm^2, which is within the regime of the static SIMS experiment.[11]

XPS analysis was carried out on a VG Scientific ESCALAB Mk II electron spectrometer employing Mg Kα X-rays ($h\nu$ = 1253.6 eV) with an electron takeoff angle of 45°. The X-ray gun was operated at 12 kV and 20 mA. Survey spectra (0–1000 eV binding energy) were run, followed by high-resolution spectra of the C 1s and O 1s regions. Acquisition and analysis of data were handled using a VGS 5000S data system based on a DEC PDP 11/73 computer. Peak fitting was carried out with a linearly subtracted background and Gaussian peaks with 30% Lorentzian character. The typical full width at half-maximum was found to be 1.6 eV in the case of components in the C 1s spectra and 1.8 eV in the O 1s.

Results and Discussion

XPS. All of the polymer films demonstrated the presence of only two elements, oxygen and carbon. No signal from the aluminum substrate could be detected, indicating that polymer films were uniformly more than ~100 Å thick. Taking into account sensitivity factors, the relative areas of the C 1s and O 1s peaks were close to those expected from MMA–PEGMA copolymers. These data are tabulated, along with molecular weight information, in Table 1.

Peak fits of the C 1s and O 1s envelopes are shown in Figure 2. The carbon spectra were fitted with five component peaks representing different chemical environments. Four of the peaks are typical of the PMMA homopolymer. It is now generally accepted that a peak representing an inductively shifted atom, as proposed by Pijpers and Donners,[12] should be included when peak fitting PMMA. In the initial peak fitting routine, three of these peaks (not the hydrocarbon peak) were constrained to be equal in area, as would be expected from the structural repeat unit of PMMA. The fifth peak, which represents carbon atoms in a poly(ethylene glycol) type environment was unconstrained in both position and area. The position of this peak was found to differ in binding energy from the methyl methacrylate *C*–O by only ~0.3 eV (see list below). While the instrumental resolution of the equipment used to acquire these spectra is not sufficient to warrant suggesting that we can distinguish between these two environments, the peak is included to clarify the PEG concentration at the copolymer surface.

Chemical shifts of the component peaks, referenced to the hydrocarbon peak at 285 eV, were (±0.1 eV) *C*–COO 285.6 eV, *C*–O (PEG) 286.5 eV, *C*–O (MA) 286.8 eV, and *C*OO 288.9 eV. These values compare well with those obtained for poly(methyl methacrylate) and poly(ethylene glycol) homopolymers using high-resolution instrumentation.[13] The O 1s spectra peak fits also demonstrate good agreement with literature values. The two peaks due to the ester groups in the methacrylate moiety occur at C=*O* 532.1 eV and *C*–O 533.8 eV (±0.1 eV), referenced to the hydrocarbon peak at 285 eV and the ether oxygen from poly(ethylene oxide) appears at 532.7 eV (±0.1 eV). The spectra for the 12.5% PEGMA copolymer is very similar to that of pure PMMA, the C 1s region has only a small contribution from the PEG environment and the O 1s line shape is typical of a doublet with equal intensity in each of the respective component peaks. The spectra are shown in order of increasing PEGMA content from top to bottom and the rise of the PEG environment in both the C 1s and O 1s spectra can clearly be seen. Since the area of each peak in the fit is proportional to the number of atoms in that environment, we can quantify the surface composition of these copolymers.

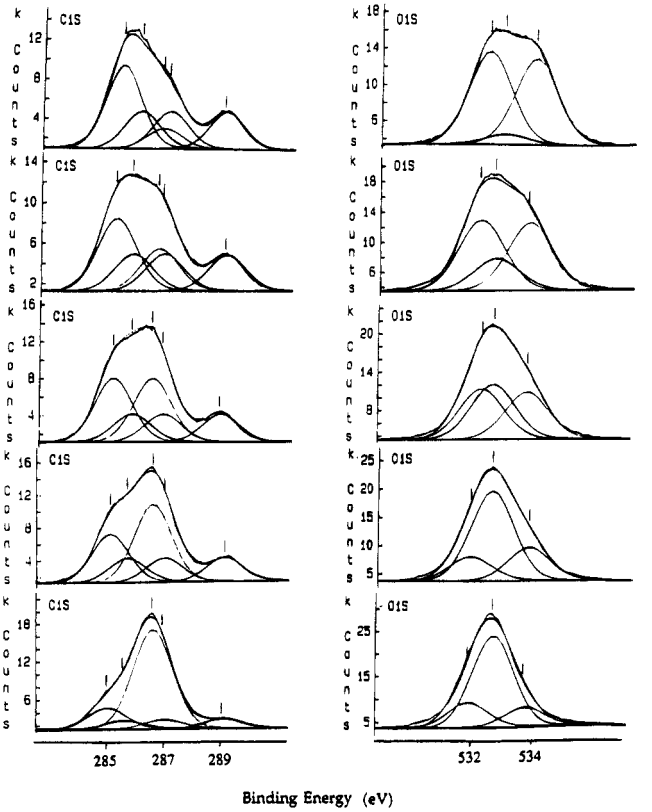


Figure 2. Peak fits of the C 1s and O 1s envelopes for copolymers containing (top to bottom) 12.5, 30, 40, 50, and 80% PEGMA.

Component peak areas for the C 1s spectra are plotted in Figure 3, the solid lines representing the theoretical compositions of these polymers. Generally, there is good agreement between the experimental data and the expected values, the maximum deviation in area of components in any of the copolymers being 5%. It can be seen that there are always less carbon atoms in a poly(ethylene glycol) type environment than predicted, which may be due to preferential orientation of MMA to the air surface. There also appears to be low levels of hydrocarbon contamination on the copolymer surfaces, but this is not unusual for solvent cast polymer films.[14]

Static SIMS. Positive Spectra. SIMS spectra from the 12.5% PEGMA and the 80% PEGMA copolymers are

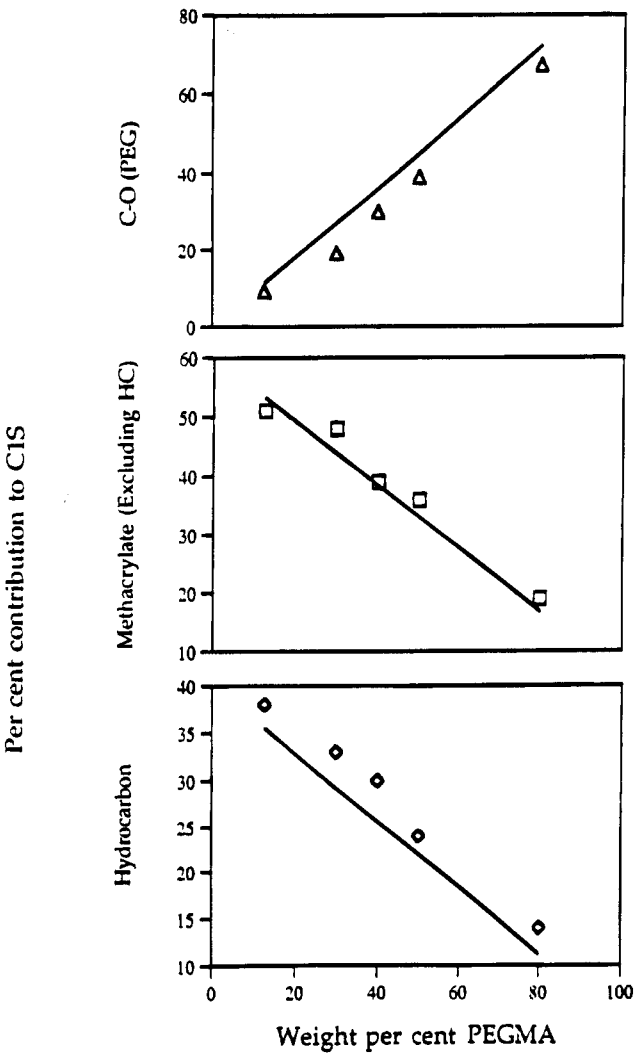


Figure 3. Experimental (points) versus theoretical (solid lines) relative areas for various components in the C 1s peak fits.

given as examples in Figure 4. The positive ion spectrum of the 12.5% PEGMA copolymer is almost identical to literature examples of PMMA homopolymer.[14,15] The similarity between SIMS results for this copolymer and poly(methyl methacrylate) suggests that there is little expression of PEG chains at the air/vacuum interface. Although the SIMS spectrum of PMMA is well documented, the structural assignment of ions has been a matter of some discussion.

Within the mass range m/z 0–100 most of the peaks in the positive ion spectra of PMMA were initially assigned to hydrocarbon fragments derived from the polymer backbone, following a loss of the pendant ester group.[16] Some of these assignments were erroneous, as SIMS studies with perdeuterated PMMA were able to demonstrate.[17] A few of the peaks, such as those at m/z 29, 43, and 69 contain a significant contribution from oxygen-containing fragment ions, as shown in Table 2. The multiplicity of ions which appear at masses above m/z 69 are difficult to unambiguously assign, with the exception of the radical cations appearing at m/z 126 and 128 which are respectively due to $C_7H_{10}O_2^{\bullet+}$ and $C_{10}H_8^{\bullet+}$, the latter probably being a naphthalene-like aromatic fragment.[17]

In contrast, the 80% PEGMA copolymer gives a relatively simple SIMS spectrum which is similar to the PEG homopolymer.[18] Diagnostic ions derive from (nM + H)$^+$ fragments, where M is the monomer repeat unit. There are, however, intense signals that do not derive from either PEG or PMMA homopolymer. One such ion appears at m/z 103 and is the strongest ion above m/z 100. In this spectra there are also peaks at m/z 59 and 147 which, although they are present in the PMMA spectra, are far more intense than would be expected, given the low yield of other ions typical of PMMA. These three ions are all 14 mass units higher than the diagnostic PEG ions at m/z 45, 89, and 133. It is highly likely that this series of peaks is due to fragments which contain the terminal methyl end caps from the PEG side chains; see Table 3. The intensity of these peaks are roughly equivalent to those of analogous ions which do not contain the methyl end cap. Since the PEG side chains are, on average, 22 repeat units in length it may be expected that the diagonstic PEG ions would be more intense than the end group derived ions. The enhanced intensity of these fragments is thought to be due to a

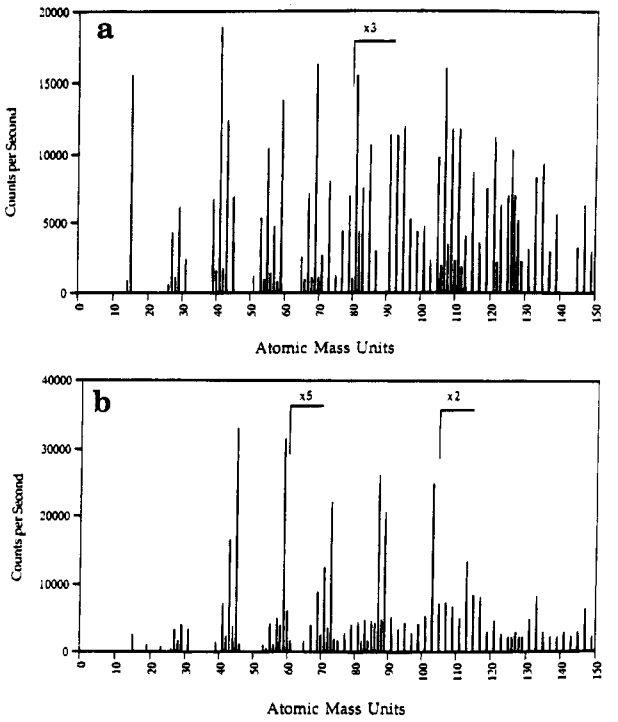
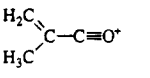
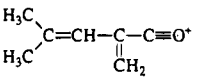
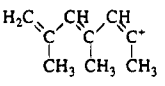
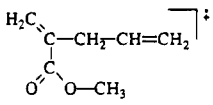


Figure 4. Static SIMS spectra of (a) 12.5% PEGMA copolymer and (b) 80% PEGMA copolymer.

Table 2. Assignments for Some Typical Ions Observed in the Positive SSIMS Spectrum of PMMA

29	COH^+	43	$C_2OH_3^+$
55	$C_4H_7^+$	59	$H_3C-O-C\equiv O^+$
69		109	
121		126	

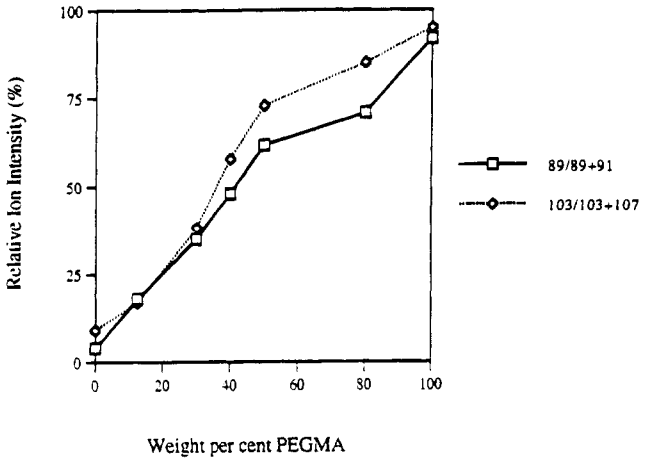


Figure 5. Variation of the relative ion intensities of PEGMA-derived ions with changing copolymer compositions.

Table 3. Masses of Major Ions Deriving from the PEGMA Macromonomer

n	$[(CH_2CH_2O)_n + H]^+$	$[(CH_2CH_2O)_n + CH_3]^+$
1	45	59
2	89	103
3	133	147

higher secondary ion yield of fragments derived from the terminal groups.

The three other copolymers exhibit spectra that are intermediary between these two extremes. Figure 5 plots the relative ion intensity of two peaks associated with the PEGMA macromonomer (m/z 89 and 103) against the copolymer composition, values obtained from the pure homopolymers are also plotted for comparison. The relative ion intensity is calculated by dividing the area of the relevant peak by the combined areas of that peak and another typical of PMMA, the result being expressed as a percentage. The two peaks typical of PMMA were at m/z 91 and 107. These are sufficiently close in mass to the PEGMA diagnostic ions to make any problems associated with mass dependent sensitivity negligible. Their absolute intensities within the spectra of the 12.5% PEGMA copolymer are similar to those of the PEGMA diagnostic ions in the 80% PEGMA copolymer, a condition which is necessary for this type of comparison to be meaningful. The values plotted in the graph are averages taken from three individual spectra of different samples of each copolymer. Remarkable consistency was acheived, the variation between these values for different spectra being typically ±5%.

As the values for the homopolymers show there is little contribution from PMMA to ion intensity at m/z 89 and 103, and conversely from poly(PEGMA) to ions with m/z 91 and 107. If the absolute ion yield of the m/z 91 ion from PMMA was identical to the absolute ion yield of the m/z 89 ion from poly(PEGMA) and assuming that ion yield is directly related to the surface concentration of the parent polymer, then one would expect a plot such as that in Figure 5 to give a straight line. Comparison of the ions at m/z 89 and 91 can be seen to display almost a linear relationship between the copolymer composition and ion intensity. A similar argument should be applicable to the ions appearing at m/z 103 and 107; however, some deviation from linearity is noted. This effect is possibly caused by a nonequivalence of the absolute ion yield of the m/z 103 ion from poly(PEGMA) and the m/z 107 ion from PMMA, with the PEGMA derived ion having the higher yield. Alternatively, the environment of the parent species within the copolymer may influence resulting ion intensities[19] (for example, if the polymer is in a crystalline or amorphous state). These matrix effects are difficult to quantify, but on the basis of the m/z 89 relative intensity results, they are not thought to be occurring.

Negative Spectra. The negative ion SIMS spectra demonstrated the full complement of ions associated with both PMMA and PEG. The dominant ions deriving from PMMA were observed at m/z 55, 85, and 185, which are respectively assigned to $C_3H_3O^-$, $(M - CH_3)^-$, and $(2M - CH_3)^-$ where M is the PMMA repeat unit.[20] These, and other ions typical of PMMA, were most intense in the spectra of the 12.5% PEGMA copolymer and decreased in intensity as the concentration of the macromonomer was increased. Conversely, the negative ions associated with the PEG homopolymer increased in intensity with a greater percentage of PEGMA in the copolymer. Peaks appearing at m/z 43, 58, 59, and 61 typify the PEG negative ion SIMS spectra, these signals have been respectively ascribed to the $C_2H_3O^-$, $C_2H_2O_2^{\bullet -}$, $C_2H_3O_2^-$, and $C_2H_5O_2^-$ ions.[18] No ions of similar masses and intensities were present for a meaningful comparison of relative ion intensity versus copolymer composition to be made.

Conclusions

Surface chemical analysis of MMA/PEGMA copolymers of varying compositions has been carried out, XPS reveals that solvent cast films of these materials present surfaces with a composition very similar to that of the bulk material. In all cases slightly less PEG was found at the polymer/vacuum interface than expected, indicating that a preferential migration of MMA rich material to the surface was occurring. The chemical shifts of components within the C 1s and O 1s spectra were found to be almost identical to those previously recorded on PEG and PMMA homopolymers using high-resolution equipment.

Ions present within the SSIMS spectra of the copolymers were entirely consistent with the XPS data. The spectra revealed a mixture of MMA and PEG within ~1 nm of the surface. Also a relationship between the intensity of PEG-derived ions and the bulk concentration of PEG was demonstrated. Bulk compositional changes in this series of copolymers have been shown to extend to the top few monolayers of the material.

The presence of the methyl-capped PEG chain ends was readily detectable by SSIMS, and a series of ions containing this group could be easily distinguished. Such features cannot be resolved from XPS data, and this observation further demonstrates the highly complementary nature of the SSIMS technique to XPS.

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