XPS and SSIMS Analysis Revealing Surface Segregation and Short-Range Order in Solid Films of Block Copolymers of PEO and PLGA

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ABSTRACT: The interfacial chemistry of solvent cast films of block copolymers of poly(ethylene oxide) (PEO) and poly(lactic and glycolic acid) (PLGA) have been investigated over a wide range of compositions. X-ray photoelectron spectroscopy (XPS) and static secondary ion mass spectrometry (SSIMS) were utilized to provide both elemental and structural data. In all cases it is found that the PLGA component preferentially resides at the copolymer surface, and this is demonstrated by the use of the variable electron takeoff angle XPS. SSIMS confirms the low concentrations of PEO at the copolymer surface. Radical cation intensities within the SSIMS spectra have been correlated to PLGA block compositions. It is demonstrated that these ion intensities may be used to estimate the PLGA surface chain sequence composition and its short-range order.

Introduction

Random copolymers of lactic and glycolic acids (PLGA) are of considerable interest as biomedical implants for the controlled release of drugs and in reconstructive surgery.[1−3] The ability to alter the *in vivo* degradation rate of PLGA devices is vital to the widespread applicability of these materials. One way of acheiving these goals is by creating a block copolymer of PLGA with another biocompatible polymer such as poly(ethylene oxide) (PEO). PLGA−PEO block copolymers have been shown to have quite different mechanical properties when compared to PLGA and are also thought to have enhanced degradation rates.[4,5] The bulk chemistry of these systems is reasonably well understood. However, little is known about the surface chemistry of PLGA−PEO block copolymers. It is important to know, for instance, whether one of the component blocks of the copolymer is preferentially expressed at the surface as this will ultimately determine the performance of the polymer *in vivo* and the biological response to its presence.[6]

X-ray photoelectron spectroscopy (XPS) and static secondary ion mass spectrometry have been employed to characterize the surface chemistry of biomedical biodegradable polymers.[7,8] Indeed, the surfaces of PEO and PLGA have previously been investigated by both XPS and SSIMS and spectra of both components have been published and interpreted.[9−11] In this paper, we examine the surface composition of a range of PLGA−PEO triblock copolymers currently under development for biomedical applications. The polymers have the following general structure:

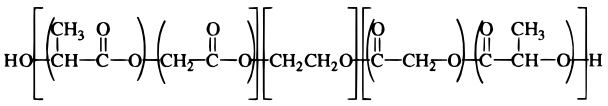

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Table 1. Copolymers of PLGA and PEO Used in These Studies

polymer	mol % PEO in polymer	mol % GA in PLGA block	M_w	M_n
69/0/31[a]	31	0	23 600	12 000
63/0/37	37	0	29 000	12 300
63/0/37[a,b]	37	0	22 400	9 900
58/0/42	42	0	36 000	19 700
42/8/50	50	16	13 000	5 300
51/12/37	37	19	17 000	7 900
53/14/33[a]	33	21	24 400	9 900
46/12/42	42	21	15 000	11 000
53/15/32	32	22	24 500	10 100
47/13/40	40	22	17 000	6 300
76/24/dext[c]	0	24	57 000	21 600
48/16/36[c]	36	25	12 700	2 330
45/18/37	37	29	18 000	8 500
46/23/31[c]	31	33	16 700	3 100
42/22/36	36	34	18 000	11 800
61/39/dext[c]	0	39	55 300	27 100
36/35/29[c]	29	49	16 400	2 410

[a] AB diblock copolymer. [b] Synthesized from D,L-lactide. [c] Stannous octoate used as catalyst.

Previously, we have shown that for pure PLGA spectral intensities in SSIMS may be related to the amount of glycolide in the polymer and to the short range polymer structure.[12] In the current study we show that this relationship also applies to block copolymers of PLGA and PEO and may be employed to determine the copolymer sequence in these complex copolymers. The demonstration of surface orientation in these copolymers is provided by XPS.

Experimental Section

Polymers. The synthesis of ABA triblock copolymers of PLGA and PEO, with PEO as the middle block has been described.[5] In essence, polymerization of a mixture of L-(+)-lactide and glycolide is initiated from both ends of hydroxy-terminated PEO. The polymers were characterized in the bulk as outlined previously.[5] A list of polymers used in these studies is provided in Table 1. Most copolymers were synthesized using aluminum isopropoxide as catalyst, the copolymers which were made using stannous octoate are noted in the table. Some AB block copolymers were analyzed, and one copolymer synthesized from D,L-lactide rather than L-lactide and these are also identified in the table. Two of the polymers were synthesized using dextran instead of PEG. These

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samples have a large PLGA content in comparison to dextran. However, the concentration of dextran could not be determined by NMR and is thought to be below 1 mol %.

Sample Preparation for Surface Analysis. Copolymer films were prepared from ~1% w/v solutions of the copolymers in HPLC grade chloroform (Fisons Scientific Equipment, Loughborough, UK). For SSIMS and XPS these solutions were cast onto aluminum-coated sample stubs (1 cm diameter) spinning at 5000 rpm. The films were then allowed to dry prior to analysis.

XPS. Samples were analyzed with an ESCALAB Mk 2 (VG Scientific, East Grinstead, West Sussex, UK.) utilizing the constant analyzer transmission mode of analyzer operation. An electron takeoff angle of 40° normal to the surface was employed, and most samples were also analyzed with an electron takeoff angle of 70°. The source was unmonochromatized Mg Kα radiation, and a pass energy of 20 eV was used to collect the narrow scans of the C 1s and O 1s core levels. Wide scans of the polymer films (pass energy 50 eV) did not reveal the presence of any other elements, which implies that the films are uniformly greater than ~7 nm in thickness and are free of inorganic contaminants. Data handling and analysis were performed on VGX900 V 5.01-C-MC software based on an IBM-PC compatible computer. Energy referencing is discussed later in the text.

SSIMS. Spectra were acquired using a SIMSLAB 3B (VG Ionex, East Grinstead, West Sussex, U.K.) equipped with a differentially pumped EX05 ion gun and a 12-12 M quadrupole mass spectrometer. Mass spectrometer ion optics were based upon the design of Wittmaack[13] (Peak Instruments Ltd, Buxton, U.K.). Argon atoms at 2 keV were used as the primary source with an equivalent current of 1 nA/cm^2. The polymer films were thin enough to eliminate the need for charge compensation. Positive and negative ion spectra were collected sequentially on the same sample, samples being exposed to atom bombardment for typically 15 min during an experiment. Positive ion spectra for quantification of radical ion intensities (m/z 155−205) were collected in triplicate on separate samples with a higher instrumental resolution than typically employed. These spectra took approximately 10 min to acquire. Data handling was performed on Spectra V 6.00-D-MS software based on an IBM-PC compatible computer.

Results and Discussion

(a) Evidence for Surface Segregation of PLGA in PLGA−PEO. XPS. The surface elemental compositions of the copolymers were calculated from the C 1s and O 1s peak areas with the use of appropriate sensitivity factors.[14] All of the polymer films had a surface concentration of 60 ± 2 atomic % carbon. The theoretical atomic % carbon of PEO is 66.7, and that of PLGA between 50.0 and 60.0 (depending upon composition: PLA = 60.0, PGA = 50.0) and in all of the copolymers the theoretical value based upon NMR data was in close accord with the XPS data. The similarity in carbon:oxygen ratios in the two blocks of the copolymers means that surface enrichment of one of the components will not result in a large change in the surface atomic % carbon. Examination of the C 1s envelope provides more sensitive information with regard to surface segregation.

There are four chemical environments evident in the high resolution scans in the C 1s region. These are outlined for polymer 58/0/42 in Figure 1, which demonstrates a typical fit to the raw data. The peaks are assigned to chemical groups found in the PLGA and PEO homopolymers. In decreasing order of binding energy, these are the carboxyl ester carbon (CO_2) from PLGA, the alcoholic ester carbon (C−O[PLA]) from PLGA, the ether carbon (C−O[PEO]) from PEO and the methyl carbon (CH) from the lactide units of PLGA.

The CO_2 peak is the most readily identifiable, and during the fitting procedure the position and area of this peak was used as a basis for other peaks from PLGA. By use of the known relative binding energy positions of the C-O[PLA] and CH peaks in pure PLA,[9,10] it is possible to constrain these peaks to acheive a chemically meaningful fit. The positions of these peaks are, respectively, ~2.0 and ~4.0 eV below that of the CO_2 peak. The first of these peaks (C−O) must be equal in area to the CO_2 peak, since there are equal numbers of both functionalities in PLGA, and the area of the latter peak (CH) may vary depending upon the PLGA block composition and the degree of hydrocarbon contamination within the polymer surface. The fourth peak, assigned to the PEO ether environment, was unconstrained in area and position. Constraints were used to achieve a reasonable fit and then removed during the final fit using the software minimization routine.

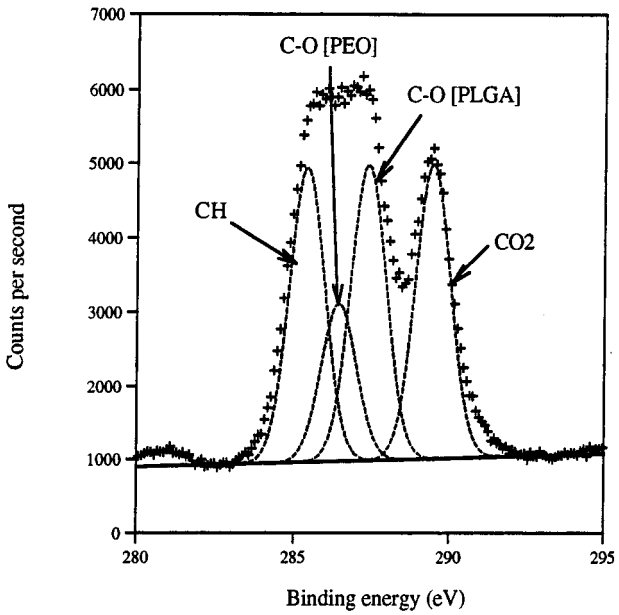


Figure 1. C 1s XPS spectrum of polymer 58/0/42 showing a typical peak fit.

It was found that the positions of the peaks relative to the CH peak were (in order of increasing binding energy) +1.0, +2.0, and +4.0 ± 0.1 eV. The PLGA peaks are in accord with the literature positions for the C 1s spectra of PLA; however, if the CH peak is assigned to 285.0 eV, then the PEO peak is significantly different than the reported literature position of 286.45 eV.[10] This would imply that either differential charging is occurring between the PLGA and PEO phases or that the binding energy of the methyl group in PLA is at ~285.4 eV and not at 285.0 eV. The consistency of the results between many different samples coupled with work that our group has performed on blends of PLA and poly(sebacic anhydride)[15] strongly indicates that the latter explanation is more valid. The binding energies of the CH, C−O, and CO_2 peaks in PLA then should be approximately 285.4, 287.4, and 289.4 eV. The latter two binding energies are atypical for the functional groups that are represented. Average values for a number of different polymers are 286.64 and 288.99 eV.[10] The large increases above the values expected are almost certainly due to secondary shifts induced by the close proximity of electron-deficient carbon atoms. It has been demonstrated beyond much doubt that carboxyl ester carbons can increase the binding energy of adjacent hydrocarbon carbon atoms by around 0.7 eV.[16] This is of the same magnitude as the β-shift we find here on the C−O group adjacent to the CO_2 group. The

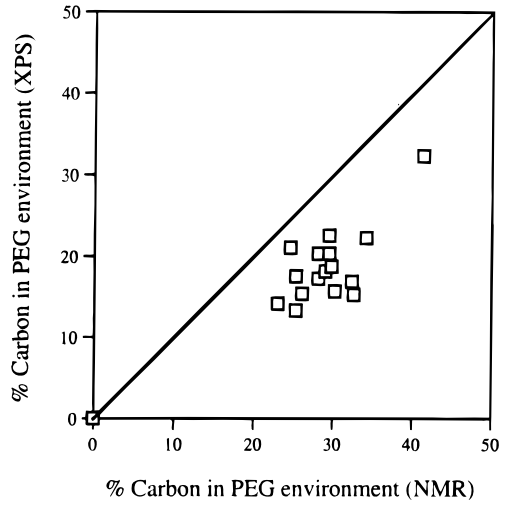


Figure 2. Surface PEG content of copolymers determined by XPS (electron takeoff angle 40°) vs bulk content determined by NMR. The line $x = y$ is also shown.

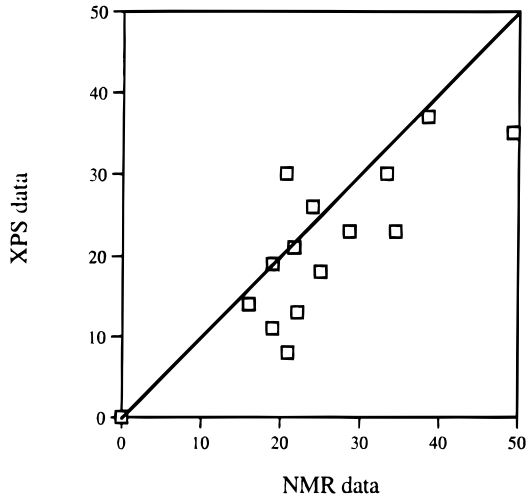


Figure 3. Comparison of mol % GA in PLGA block of copolymers calculated from XPS and NMR data. The line $x = y$ is also shown.

C−O atom itself is now highly electron deficient and may be expected to withdraw electron density from both the methyl and carboxyl functionalities, increasing both their apparent binding energies by (as it turns out) 0.4 eV. This value is almost the same as the secondary shift reported for carbonyl groups.[10]

In Figure 2 a comparison of PEG concentration, as determined by XPS, is made with values calculated from NMR data. In all of the polymers studied a marked depletion of PEO from the surface is evidenced by a lower than expected *C*−O[PEO] peak area. The polymer surface is richer in the PLGA block of the copolymers, presumably with the PEO blocks extending into the bulk of the material. The composition of the PLGA block may be calculated from the XPS data simply by dividing the *C*H peak area by the CO_2 peak area to obtain the PLGA mol % LA, and thus the mol % GA of the PLGA segment. Mol % GA values calculated from XPS data are compared with those calculated from NMR data in Figure 3. The correlation between bulk PLGA composition and that calculated from XPS is not good. In general, the XPS values are lower than the NMR, and this may be caused by a low level hydrocarbon contamination of the solvent cast films. If such contamination is present, the XPS mol % glycolic acid (GA) would be lower than expected since the apparent lactic acid (LA) content would be higher. An alternative explanation is that the PLGA block surface composition is different from that measured by NMR in the bulk. These results are discussed in more detail later, in the light of the SSIMS data.

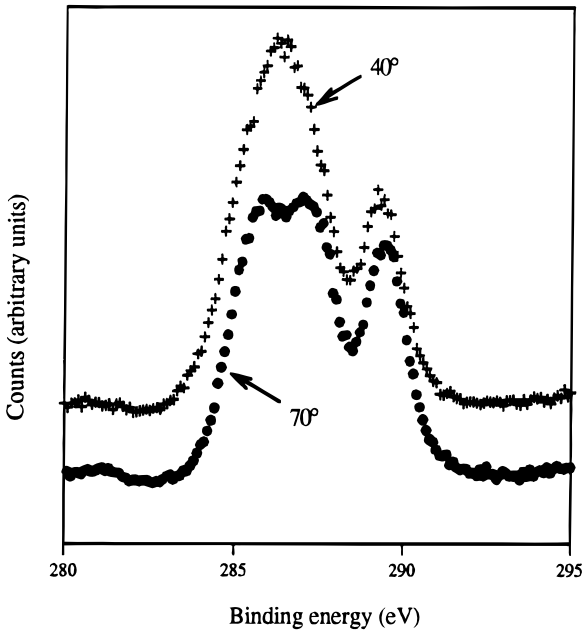


Figure 4. C 1s XPS spectra of polymer 42/8/50 taken at 70° (dots) and 40° (crosses) electron takeoff angles demonstrating different line shapes by changing the depth of analysis.

Variable electron takeoff angle studies were performed to investigate the surface enhancement of the PLGA block. The most distinctive results were obtained with the 42/8/50 copolymer, and the two C 1s spectra taken at different angles are shown as an overlay in Figure 4. The shape of the two spectra is remarkably different, and by comparison with the peak fit in Figure 1 it can be seen that at 40° takeoff angle the *C*−O[PEO] peak must be more intense relative to the other peaks than at 70° takeoff angle. At 70°, it is 15.1% of the total C 1s area, which is less than half the contribution at 40°, 32.3%. The sampling depth of the XPS experiment at 40° electron takeoff angle is approximately 7 nm and at 70° is about 3 nm.[17] All other PLGA−PEO copolymers demonstrated a decrease in the *C*−O[PEO] peak at glancing takeoff angle, but none were quite so dramatic as 42/8/50. No simple relationship appears to exist between the degree of PEO depletion and the polymer structure (molecular weight, PEO content or PLGA composition). It is known that PEO and PLGA are immiscible, and so one would expect discrete domains of both polymers to form in the bulk.[5] PEO domains obviously extend to the near surface, since in all of the polymers we observe contribution of PEO to the XPS spectra, but these domains appear to be covered by a thin PLGA overlayer. There have been many studies of block copolymer surfaces, with both XPS and SIMS,[18−20] and the results of those studies correlate well with theoretical treatments.[21] However, such treatments are not applicable in this case due to the lack of thermodynamic equilibrium, the solvent cast films under investigation have not been annealed, and it is probable that solvent effects will dominate.[18,19] However, in these studies, surface segregation of PLGA is observed, and we believe it is likely that at thermodynamic equilibrium this effect will still be evident.

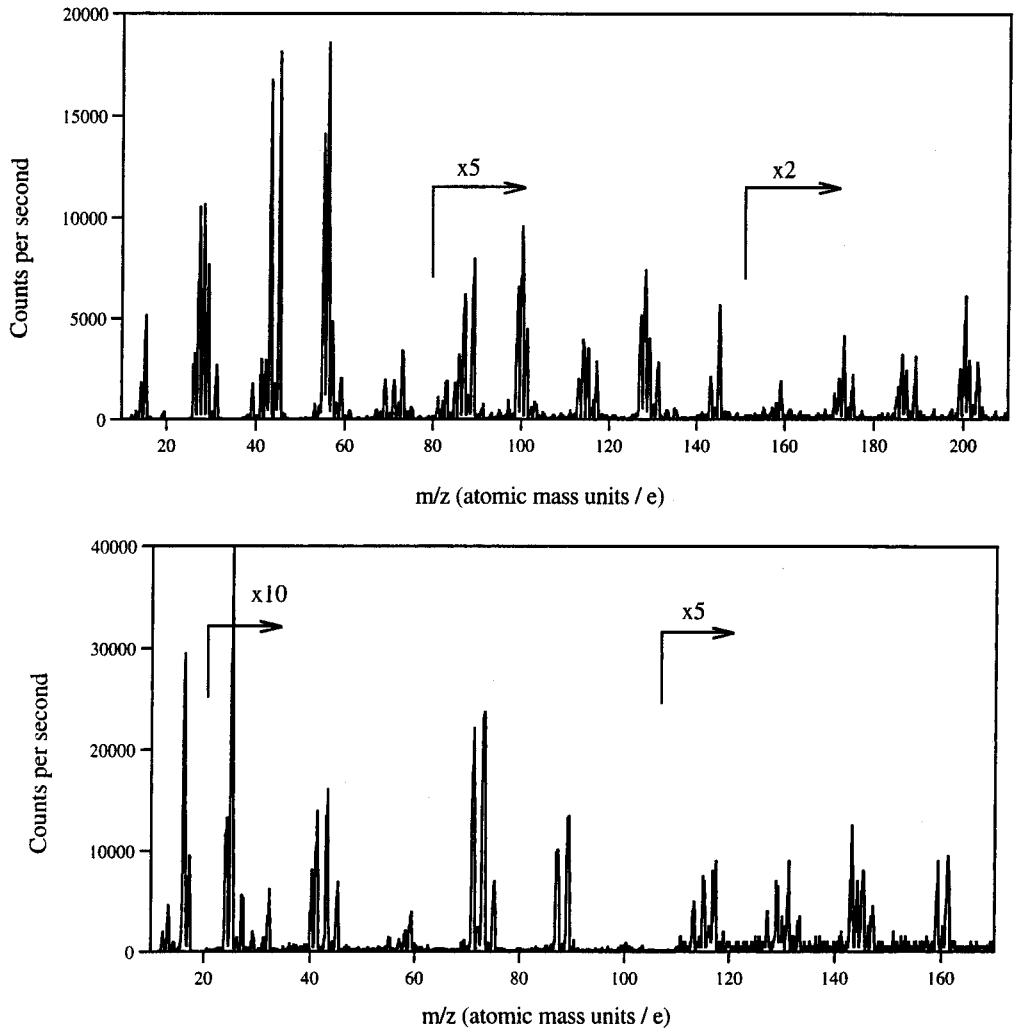
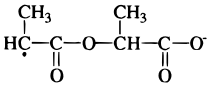


Figure 5. (a) Positive ion SSIMS spectrum of polymer 42/22/36. (b) Negative ion SSIMS spectrum of polymer 42/22/36.

SSIMS. Examples of positive and negative ion spectrum of PLGA−PEO copolymers are given in Figure 5. Despite the apparent complexity of some of the spectra, the positive ion assignments may all principally be based upon the spectra of PLA and PGA.[9] In PLA fragmentation processes produce ions of the type $[nM - O]^{\bullet+}$ and $[nM - O \pm H]^{+}$, which form intense peaks centred at m/z 56, 128, 200, and 272 for $n = 1-4$. Similar peaks are formed by the $[nM - CO_2]^{\bullet+}$ and $[nM - CO_2 \pm H]^{+}$ ions, but only for $n = 1$ and 2 at m/z 28 and 100. Other regularly repeating ions are the $[nM \pm H]^{+}$ doublets which appear at m/z 71/73, 143/145 and 215/217 for $n = 1-3$. Analogous ions can be found in the SSIMS spectrum of PGA.[9] PLGA is a random copolymer of lactic and glycolic acids; a difference in mass of 14 amu exists between these two monomers. This suggests that for every peak $[nM...]^{+}$ which appears in the pure PLA spectrum there will be $n + 1$ peaks in the PLGA spectrum due to sequential substitutions of a glycolic acid unit for a lactic acid unit in the fragment ion, and each of these peaks will differ in mass by 14 amu. For example, the series $[3M - O]^{\bullet+}$ in PLGA appears at $m/z = 158$, 172, 186, and 200 due to the $[3G - O]^{\bullet+}$, $[2GL - O]^{\bullet+}$, $[2LG - O]^{\bullet+}$ and $[3L - O]^{\bullet+}$ ions respectively where G is a glycolic acid repeat unit and L is lactic acid.[12]

The same method may be applied to interpretation of the negative ion SSIMS spectra, where the major ions in both PLA and PGA[9] are $[nM \pm H]^{-}$ and $[nMO \pm H]^{-}$. In our spectra only the $n = 1$ and 2 series were observable, and all ions from both series are present. In all of the spectra which were taken of these copolymers, two ions not noted in previous spectra of PLA or PGA[9] were detected at $m/z = 40$ and 144. Both of these are radical anions; the first may be assigned to the $C_2O^{\bullet-}$ ion, possibly deriving from PGA, and the second could be an analogue of the m/z 100 ion observed in the positive ion spectrum of PLA, with the addition of CO_2. The tentatively proposed structure of the m/z 144 ion is given as follows:



Typically, the SSIMS spectra of the copolymers investigated demonstrate little evidence of PEO. Although all of the major diagnostic peaks of PEO in the positive ion spectra (i.e. m/z 45, 87, and 89)[11] coincide with peaks typical of PLA, the relative peak heights and general shape of the spectra are similar to PLGA homopolymers[12] rather than PEO. In some of the copolymer negative ion SSIMS spectra a weak anion at m/z 58 is apparent which may be due to the $C_2H_2O_2^{\bullet-}$ ion from PEO.[11] This anion is not seen in PLA or PGA spectra.[9] The information provided by SSIMS is in agreement with that of XPS in that both spectroscopies strongly suggest that the uppermost surface of solvent cast PLGA−PEO films almost exclusively comprises of the PLGA portion of the copolymers.

(b) Evidence for Short-Range Order in the PLGA Chains of the Copolymers and Bulk-Surface Discrepancies in PLGA Composition. We have previously undertaken SSIMS studies of PLGA copolymers and shown that a relationship exists between the ion intensities of various radical cations and the short range structure of the copolymer.[12] In the spectra of PLGA copolymer, the relative intensities of $[n\mathrm{M} - \mathrm{O}]^{\bullet+}$ radical cations could be modeled using simple statistical methods. We applied the following assumptions to radical cation production and detection in the SSIMS of PLGA:

(1) Fragmentation, ionization, and sputtering occur with equal probability regardless of the type of monomer unit (lactic or glycolic acid) at the site or adjacent to the site of bond scission.

(2) All radical cations have the same stability regardless of the composition of the fragment ion.

Given these assumptions, for a truly random copolymer, the normalized spectral intensities of any given series n can be calculated from a binomial distribution. For the special case $n = 3$, where ions are observed at m/z 158, 172, 186, and 200, the normalized spectral intensities can be calculated as follows: $I\{158\} = p(\mathrm{G})^3$, $I\{172\} = 3p(\mathrm{G})^2p(\mathrm{L})$, $I\{186\} = 3\mathrm{p}(\mathrm{G})p(\mathrm{L})^2$, and $I\{200\} = p(\mathrm{L})^3$. Here $I\{\mathrm{x}\}$ is the normalized intensity of ion x calculated from the area of the peak at x and divided by the total areas of all the $[3\mathrm{M} - \mathrm{O}]^{\bullet+}$ peaks, $p(\mathrm{G})$ is the probability of finding a glycolic acid unit at any given site in the PLGA chain (i.e. the mol % of GA), and p(L) is the probability for finding lactic acid, $p(\mathrm{L}) + p(\mathrm{G}) = 1$.

In the case of PLGA produced from the dimeric lactide and glycolide, it was found that the ion intensities fell between two idealistic models, that of the truly random copolymer given above and a model based upon randomly distributed dimer units. This latter model was calculated for the $[3\mathrm{M} - \mathrm{O}]^{\bullet+}$ cluster by considering two adjacent dimeric units in the polymer and taking into account all the possible combinations of ions containing three repeat units which could be produced. The resulting normalized intensities were then as follows: $\mathrm{I}\{158\} = p(\mathrm{G})^2$, $I\{172\} = \mathrm{I}\{186\} = p(\mathrm{G})p(\mathrm{L})$ and $I\{200\} = p(\mathrm{L})^2$. The reason that the SSIMS spectral intensities of the dimeric polymer did not exactly match that of the model was ascribed to transesterification reactions during the synthesis of PLGA, and we use the term "scrambled dimeric" to describe this type of structure.[12]

The assumptions made above imply that the intensities of the individual peaks in each $[n\mathrm{M} - \mathrm{O}]^{\bullet+}$ series are proportional to the number of precursor groups in the copolymer. If this assumption holds for the copolymers under investigation here then it should be possible to calculate the mol % of GA in the PLGA block purely from SSIMS data. We analyzed the ion intensities of the $n = 3$ series of radical cations. The choice of the $n = 3$ series was one of convenience. The $n = 2$ series contains a coincident ion at m/z 100; both the ion $[2\mathrm{G} - \mathrm{O}]^{\bullet+}$ and the ion $[2\mathrm{L} - \mathrm{CO_2}]^{\bullet+}$ appear at this mass. The intensity of the $n = 4$, $n = 5$, etc. series in these copolymers were low. To calculate the GA mol % we used the following equation:

$$\text{GA mol \%} = 100(3I\{158\} + 2I\{172\} + I\{186\})/3$$

An example of the spectra used to calculate these values is given in Figure 6, the radical cations are marked with an asterisk. Interestingly, analysis of the data revealed that experimental values of GA mol % did not vary between repeat experiments by more than 3 mol % for any one polymer, and this was taken to be a crude measure of the level of error.

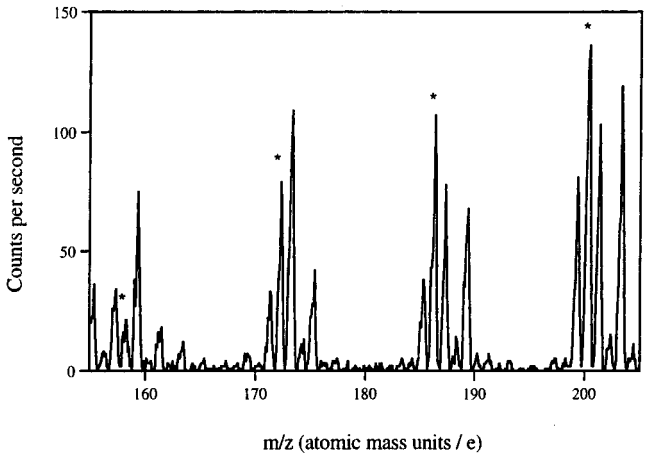


Figure 6. Positive ion SSIMS spectrum from m/z 155 to 205 of polymer 46/12/42 showing the $[3\mathrm{M} - \mathrm{O}]^{\bullet+}$ series labeled with asterixes.

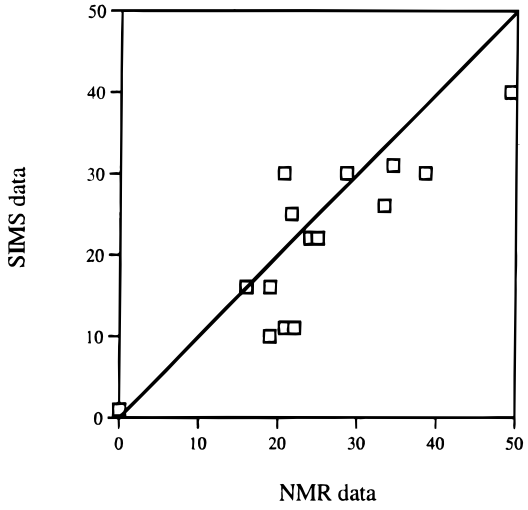


Figure 7. Comparison of mol % GA in PLGA block of copolymers calculated from SSIMS and NMR data. The line $x = y$ is also shown.

A comparison of GA mol % calculated values and the bulk, NMR values are shown in Figure 7. As with the XPS data, there is poor correlation between the bulk and surface values. The majority of the data points fall below the $x = y$ line, and this may indicate that the SSIMS calculation is inaccurate due to a failing of one of the assumptions outlined above. If the secondary ion yields of different structures and compositions are significantly variable, then our model would be expected to fail. The fact that most of the SSIMS mol % GA values are lower than the NMR data suggests that those ions which contain more LA units have higher secondary ion yields. It is not thought that hydrocarbon contamination will influence these values in any way. There are a few data points in Figure 7 which lie above the $x = y$ line, which implies that, for some of the polymers at least, the surface composition of the PLGA block is quite different from the bulk.

The correlation provided by the two surface techniques is very good, as shown in Figure 8. SSIMS and XPS give broadly similar values of mol % GA for the same polymers. Comparison with Figures 3 and 7, which plot surface against bulk data, shows that the NMR data is often at odds with the two surface techniques, particularly when there is a low mol % GA

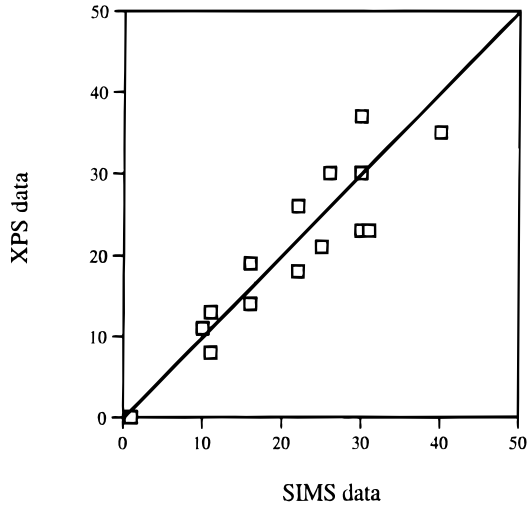


Figure 8. Comparison of mol % GA in PLGA block of copolymers calculated from XPS and SSIMS data. The line $x = y$ is also shown.

in the PLGA block. The agreement between XPS and SSIMS data strongly indicates that in many of these copolymers the surface PLGA block composition is different from the bulk. As noted previously, both techniques may underestimate the mol % GA of the PLGA block, either because of hydrocarbon contamination in XPS or because of a breakdown of assumptions made in the calculation of mol % GA in SSIMS. These processes are almost certainly independent of each other; if either were operating, one technique would tend to give consistently different mol % GA values from the other. The correlation between techniques could result from a coincidental operation of both processes, but such an event would not account for those polymers in which both XPS and SSIMS describe a larger surface mol % GA than the NMR. On the basis of these observations we suggest that there is, in many cases, a marked difference between the surface PLGA block composition in spin cast films of these copolymers and the bulk PLGA block composition determined by NMR. The reasons for this are unknown, but may result from variable surface energies, crystallinities, or molecular weights of PLGA blocks of differing compositions, resulting in a surface expression of blocks with mol % GA values dissimilar from the bulk.

By analysis of the individual ion intensities within the $[3M - O]^{\bullet+}$ series, we are able to probe the short range structure of the PLGA block. All of these polymers were synthesized from lactide and glycolide dimers and thus are expected to have the "scrambled dimeric" structure. This means that the SSIMS ion intensities for the $[3M - O]^{\bullet+}$ series should fall somewhere between those of the two models described above. Both of these cases have been calculated and compared to the experimental results. In Figure 9 some examples of this

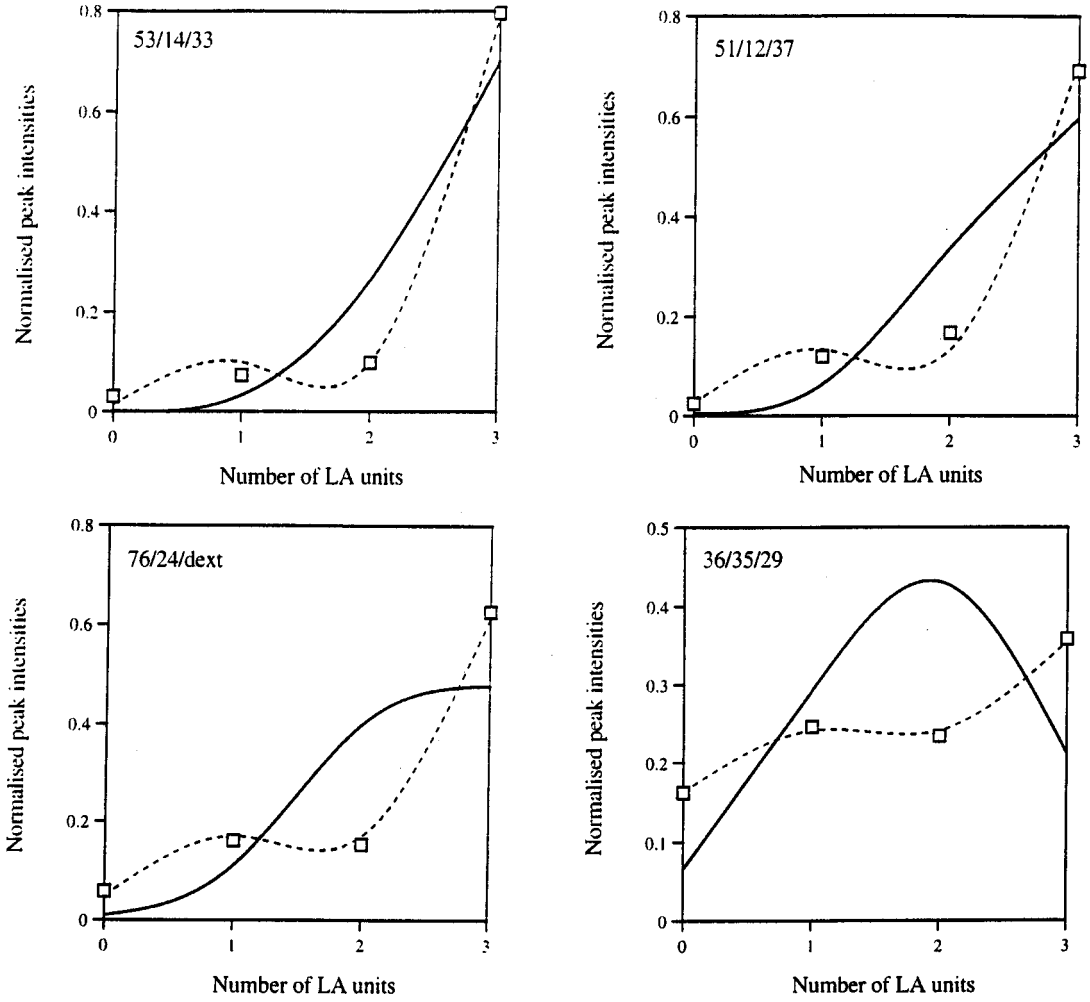


Figure 9. Normalized intensity of the four $[3M - O]^{\bullet+}$ spectral lines for selected copolymers. Number of LA units = 0, 1, 2 and 3 represent peaks at m/z 158, 172, 186, and 200 respectively. Comparison with statistical models is provided, solid lines represent random copolymers, and dashed lines represent random dimeric copolymers. Both lines are interpolated through calculated points.

comparison are shown. Values taken from the SSIMS data are plotted with the random (binomial, solid line) and "random dimeric" (dotted line) values calculated from the GA mol % determined by SSIMS. The data shown for each polymer are the mean of normalized intensities taken from the three spectra. In all polymers the level of variance between different spectra was suprisingly low; for any normalized intensity value the difference from the mean value over three repeats was less than 0.05.

The data points shown in the graphs in Figure 9 correspond to the random dimeric model rather than the random model. The figure shows a selection of the copolymers covered in this investigation, and without exception, all of the copolymers demonstrated excellent agreement with the dimeric model. This indicates that the level of transesterification in the PLGA block of these copolymers is very low, since a large amount of transesterification would result in the peak intensities, tending to reflect a more random composition. No significant differences could be found between polymers made with the aluminum catalyst and those synthesized from the tin catalyst. This is interesting because Kricheldorf *et al.*[22] reported that the sequence of PLGA synthesized by tin catalysis is closer to random than PLGA synthesized using aluminum isopropoxide. The former catalyst was reported to induce a greater degree of transesterification during polymerization, and the aluminum catalyst produced a copolyester with a more blocky nature. Since the SSIMS data suggest that there is little transesterification in either type of polymer we forward two possible explanations for this observation. First, the introduction of PEG into the polymerization causes a change in mechanism which results in a similar transesterification level for polymers produced from both catalysts. Second, the surface of these materials can be atypical of the bulk, as noted previously, and blocky PLGA material could preferentially reside at the polymer/air interface.

Conclusions

We have used XPS and SSIMS to study the surfaces of a series of solvent cast films of ABA and AB block copolymers of PEO (B) and PLGA (A). To our knowledge this is the first time that such experiments have been reported. Peak fitting the C 1s spectra reveals that the binding energy shifts for PLA are probably ~0.4 eV higher than previous reports in the literature, and this is explained in terms of β-shifts between electron-deficient carbon atoms within the polymer. The most important feature of the investigation is the clear existence of a surface-enriched layer of PLGA, as demonstrated by XPS with the use of variable electron takeoff angles and the lack of any strong signals from PEO in the SSIMS spectra.

The calculation of glycolic acid mol % in the PLGA segment can be performed both from SSIMS and XPS data. The values obtained are consistent; however there is a discrepancy between the surface techniques and the bulk determination of this value in some of the polymers. Modeling of SSIMS ion intensities within the $[3M - O]^{\bullet+}$ ion series confirms that the PLGA block has a "scrambled dimeric" structure, which is consistent with previous investigations on PLGA homopolymers.

We have shown that the approach of combining SSIMS and XPS is useful in characterizing complex biomaterials. The application of both techniques can provide insight into the polymer surface heirarchy and the polymer composition. Biomaterial systems are being developed for specific functions, and the elucidation this type of information can assist in their evolution and also help understand and interpret their behavior.

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