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XPS and SIMS characterisation of segmented polyether polyurethanes containing two different soft segments

Yves Deslandes^{a,*}, Gerald Pleizier^a, David Alexander^a and Paul Santerre^b

^a*Institute for Chemical Process and Environmental Technology, National Research Council, Ottawa, Ontario K1A 0R6, Canada*

^b*Department of Biomaterials, Faculty of Dentistry, University of Toronto, 124 Edward Street, Toronto, Ontario, M5G 1G6, Canada*

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Angle dependent X-ray photoelectron spectroscopy (XPS) and static secondary ion mass spectrometry (SSIMS) were used to study the surface composition of two polyether polyurethane block copolymers. Both were synthesised with 2,4-toluene diisocyanate and ethylene diamine as the hard segment, but different soft-segment compositions were used. In one case, the soft segment was polytetramethylene oxide (PTMO) while, in the other case, it was a mixture of PTMO and polyethyleneoxide (PEO). The selection of the two oligomers for the soft segments allowed for an investigation of the influence of an elastomer's polar character on the nature of chemical groups detected at the surface. By following the C1s signal and the atomic concentration of nitrogen with respect to take off angle, it was shown that the surface of the films were depleted in nitrogen containing hard segments. The study also showed that the sample having both PTMO and PEO soft segments displayed a tendency for the PTMO to segregate from the PEO and migrate to the top surface, resulting in a depletion of the top layer in PEO. Static SIMS of this sample confirmed this observation. Canadian Crown Copyright © 1998 Published by Elsevier Science Ltd. All rights reserved.

(Keywords: X-ray photoelectron spectroscopy (XPS); time-of-flight secondary ion mass spectrometry (TOF-SIMS))

INTRODUCTION

Segmented polyurethanes are multi-block copolymers made by one-step or two-step reaction of diisocyanates with hydroxyl-terminated, low molecular weight polymers (macroglycols) and diamines or glycols chain extenders¹. The segments containing the diisocyanates and chain extender are usually rigid and called 'hard' segments, while the macroglycol segments are usually quite flexible and hence called 'soft' segments.

Morphologic studies of segmented polyurethanes have shown that these polymers separate into two phases, leading to domains composed of hard segments and domains composed mostly of the soft segments^{2,3}. It has also been reported that, not only does the segregation take place in the bulk but, based on studies using surface analysis techniques such as X-ray photoelectron spectroscopy (XPS) and secondary ions mass spectrometry (SIMS), the surface of these polyurethanes is enriched in the soft segment with respect to the bulk composition of the polymers^{4–13}. The exact distribution of soft and hard segments near the very top surface is not precisely known. It has been reported that, based on angular dependant XPS, there may be very little or no hard segment present at the uppermost surface^{7,8}. On the other hand, Hearn and collaborators showed, using SIMS, that the surface is interspersed with small quantities of hard segments¹⁰.

X-ray photoelectron spectroscopy is probably the most

popular and accessible method to analyse the surface chemistry of materials⁴. However, when the modifications are small and found at the very top surface, XPS alone cannot provide much information on the changes in surface chemistry. XPS probes a layer of about 7.5 nm thick and the presence of only a few additional functional groups on the top layer will not be detected. Angle resolved XPS is a technique where, by tilting the sample, thereby changing the angle of the surface with respect to the detector, a thinner layer can be probed¹⁴. It is possible to obtain information on the top 1.5–2.0 nm of a surface. However, the intensity of the peaks decreases significantly at high take-off angle and it becomes difficult to interpret small differences in the shape of the envelopes.

Time-of-flight secondary ions mass spectrometry (TOF-SIMS) is a technique that can be used to probe an even thinner layer on the surface of polymers^{15–18}. The technique has been successfully applied to characterise the surface of polymers and it has been suggested that, when used in the static mode, it is capable of analysing the first 0.5 nm of a surface. In the SIMS experiment, a beam of ions is used to sputter materials off the surface and generate charged and neutral fragments. By controlling the current of the impinging beam, it is possible to minimise excessive surface degradation while generating enough molecular fragments to acquire a reproducible spectrum. This is called 'static' SIMS.

Our interest in this study lies in the search for information about the behaviour of polyurethanes when two different soft segments are used within the same polymer chain. In

* To whom correspondence should be addressed

this paper we report the study, using XPS and SIMS, of the surface of two polyurethanes having the same 'hard' segment but where the soft segment is polytetramethylene oxide (PTMO) in one case and a mixture of PTMO and polyethylene oxide (PEO) in the other case.

EXPERIMENTAL

Materials

The materials used for the synthesis included toluene 2,4 diisocyanate (TDI) (Eastman Kodak, Rochester, USA), polytetramethylene oxide (PTMO) of average molecular weight 1000 (Dupont, Wilmington, DE, USA), polyethylene oxide (PEO) of molecular weight 1000 (Aldrich Chemical Company, Milwaukee, WI, USA) and ethylene diamine (ED) (Aldrich Chemicals Company, Milwaukee, WI, USA). Prior to use, TDI was vacuum distilled at 70°C and 0.025 mmHg. PTMO and PEO were degassed for 24 h at 40°C and 0.5 mmHg. ED was distilled under atmospheric pressure. The two polymers were synthesised using a standard two step solution polymerisation, carried out in a Labconco Controlled Atmosphere glove box containing dried nitrogen gas and the solvent was dimethylsulfoxide (DMSO), distilled within 24 h of the synthesis.

Details for the synthesis have been published elsewhere¹⁹. The stoichiometry of the reaction was 2:1:1 of TDI:PTMO:ED and 2:0.5–0.5:1 for TDI:PTMO–PEO:ED respectively. In the first step of the synthesis, an approximate 15% wt/vol solution of TDI in reaction solvent (DMSO for PTMO and dimethylacetamide for PTMO/PEO) were mixed with an approximate 25% wt/vol solution of diol in the respective reaction solvent. This mixture was allowed to react at 50–60°C for a period of 3 h. Following this, the solution was cooled to 25°C and a 4% vol/vol solution of ED was added dropwise to the reaction mixture with stirring. After the reaction was complete, the polymers were precipitated in distilled water, finely chopped and further washed in distilled water with vigorous agitation in order to remove unreacted monomers. The polymers were then redissolved in their reaction solvent and the resulting solution centrifuged at 1500 G (Sorvall model number RT6000B, Dupont Instruments) for 10 min, in order to remove any non-soluble polymer gels. This solution was then precipitated in distilled water, chopped and washed three times. The polymers were dried in a vacuum oven at 50°C for 48 h. Molecular weights were determined by size exclusion chromatography¹⁹. The molecular weight data are reported as calibration grade polystyrene molecular weight equivalents.

Film preparation

The polymer samples were cast onto a clean aluminum pan, at 20–25°C. The concentration of casting solution was 20% wt/vol in dimethyl acetamide (DMAc). Solutions were centrifuged at 1500 G for 10 min and then filtered through glass wool sheets. The solvent was allowed to evaporate overnight in an oven at 50°C then further dried under vacuum at 50°C. All films were optically transparent, and about 0.3 mm thick.

XPS analysis

The surface of the samples was analysed using a KRATOS AXIS HS X-ray photoelectron spectrometer (Kratos, Manchester, UK). The size of the analysed area was about 1 mm². Monochromatised Al K_α radiation was used for excitation and a 180° hemispherical analyser with a

three channel detector was employed. The X-ray gun was operated at 15 kV and 20 mA. The spectrophotometer was operated in Fixed Analyser Transmission mode (FAT) throughout the study using electrostatic magnification. Survey and high resolution spectra were collected using 160 and 20 eV pass energy respectively. The pressure in the analyser chamber was 10^{−8} to 10^{−9} torr. An electron flood gun was used to neutralise the charge during the experiment. In order to verify that the surfaces were not damaged during angle dependent studies, the surfaces were scanned at zero degree take-off angle both before and after the angle dependence measurements. Binding energies were referenced to the carbon–carbon bond which was assigned a binding energy of 285 eV. Atomic composition was estimated using standard software provided with the instrument and using the following sensitivity factors: 0.25 for C1s, 0.66 for O1s and 0.42 for N1s relative to F1s at 1.00.

For the angular-dependant experiments, an 8° solid angle aperture was placed in the electron lens system. The measurements were made with the experimental geometry shown in Figure 1. In our instrument, the angle between the X-ray source and the electron collection optics is fixed at 65°. The sample was tilted in such a way as to change the angle Θ between the normal to the sample and the analyser. At $\Theta = 0$, the sample was perpendicular to the detector, leading to the maximum sampling depth. The effective sampling depth, z , was derived by

$$z = 3\lambda \cos \Theta \quad (1)$$

where λ is the effective mean free path for electrons to escape the surface and was set to the value of 2.5 nm based on previous studies^{20,21}. Therefore at $\Theta = 0$, $z = 7.5$ nm and at $\Theta = 80$, $z = 1.3$ nm.

The TOF-SIMS spectra were obtained by using a KRATOS PRISM instrument (Kratos, Manchester, UK). The sample was bombarded with 25 keV Ga⁺ ions with a current less than 1×10^{-9} A. Data acquisition required between 60 and 200 s. The total primary ion dose was always less than 10¹² ions/cm², which is within the 'static'

Figure 1 Geometry of angular-dependent experiments

Table 1 Molecular weight and polydispersity of the two polyurethanes studied

Polymer	Mw	Mn	Polydispersity
TDI–ED–PTMO	1.3×10^5	6.3×10^4	2.0
TDI–ED–PTMO/ PEO	7.3×10^4	4.1×10^4	1.8

limit for SIMS experiment. Charge neutralisation by means of a beam of electrons synchronously pulsed on every primary gun cycle, in antiphase with the ion extraction voltage, was used.

RESULTS AND DISCUSSIONS

The molecular weights and dispersity of the samples (*Table I*) are representative of conventional polyurethanes. The bulk chemistry characterised by FTIR spectroscopy

Figure 2 Sequence of the two copolymers and chemical structure of their components

Figure 3 XPS survey spectrum of TDI-ED-PTMO showing the peaks corresponding to oxygen, nitrogen and carbon

depicted the characteristic urethane/urea chemistry that has been described by Dillon²². The two copolymers studied have the same hard segment, made of 2,4-toluene diisocyanate and ethylene diamine, but have different soft segments. The basic chemical structure of the constituents and their theoretical sequence are shown in *Figure 2*.

Figure 3 shows the XPS survey spectra of TDI-ED-PTMO. Peaks corresponding to carbon, nitrogen and oxygen are detected. A quite similar spectrum was obtained for TDI-ED-PTMO/PEO but with slightly different peak intensities. High resolution spectra of the carbon signal shows an envelope that can be curve fitted into a series of peaks corresponding to different functional groups (see Figure 4). The peak usually at the lowest binding energy (285 eV) is assigned to carbon atoms that are linked only to carbon (C-C) and/or hydrogen atoms (C-H). The peak shifted by approximately 1.5 eV corresponds to carbon atom linked to carbon/hydrogen atoms and one oxygen atom via a single bond (C-O). Carbon peaks corresponding to carbonyl (C=O) and N-C=O functions appear shifted by about 2.5 and 4 eV respectively from the C-C peak. Because of the complexity of the polymers and the large number of possible ways to curve fit the envelope, we have

Figure 4 High resolution XPS spectra showing the deconvoluted C1's envelope for the TDI-ED-PTMO sample at 0° and 80° take-off angles

Table 2 Tabulation of the theoretical number of different atoms contributing to the XPS signal for each segment and the resulting 'bulk' composition (in atomic %) for the homogenous polymers, based on the stoichiometry shown in Figure 1: (a) $[-\text{TDI}-\text{ED}-\text{TDI}-(\text{PTMO})_{14}-]$

	TDI segment	ED segment	PTMO	'Bulk'
$\text{C}-\text{C}$	10	—	28	38
$\text{C}-\text{O}$, $\text{C}-\text{N}$	4	2	28	34
$\text{O}=\text{C}-\text{N}$	4	—	—	4
N	4	2	—	6
O	4	—	14	18

Table 3 Tabulation of the theoretical number of different atoms contributing to the XPS signal for each segment and the resulting 'bulk' composition (in atomic %) for the homogenous polymers, based on the stoichiometry shown in Figure 1: (b) $[-\text{TDI}-\text{ED}-\text{TDI}-(\text{PTMO})_{14}-\text{TDI}-\text{ED}-\text{TDI}-(\text{PEO})_{23}-]$

	TDI segment	ED segment	PTMO	PEO	'Bulk'
$\text{C}-\text{C}$	20	—	28	—	24
$\text{C}-\text{O}$, $\text{C}-\text{N}$	8	4	28	46	43
$\text{O}=\text{C}-\text{N}$	8	—	—	—	4
N	8	4	—	—	6
O	8	—	14	23	23

Table 4 Experimental atomic compositions calculated from the XPS intensities as a function of take-off angle (TO angle) for the polyurethane $[-\text{TDI}-\text{ED}-\text{TDI}-(\text{PTMO})_{14}-]$

TO angle	$\text{C}-\text{C}$	$\text{C}-\text{O}$, $\text{C}-\text{N}$	$\text{O}=\text{C}-\text{O}$	O	N
0°	45	31	2.3	18	3.4
20°	45	31	2.5	17	3.5
40°	48	30	1.7	17	3.0
60°	52	27	1.7	17	2.6
80°	56	24	1.3	17	1.1

Table 5 Experimental atomic compositions calculated from the XPS intensities as a function of take-off angle (TO angle) for the polyurethane $[-\text{TDI}-\text{ED}-\text{TDI}-(\text{PTMO})_{14}-\text{TDI}-\text{ED}-\text{TDI}-(\text{PEO})_{23}-]$

TO angle	$\text{C}-\text{C}$	$\text{C}-\text{O}$, $\text{C}-\text{N}$	$\text{O}=\text{C}-\text{O}$	O	N
0°	34	40	3.2	20	3.8
20°	34	41	3.0	19.5	2.6
40°	35	40	2.6	20	2.8
60°	39	38	2.2	18	2.2
80°	42	39	1.4	18	0

ignored secondary neighbour effects and we have considered $\text{C}-\text{O}$ and $\text{C}-\text{N}$ as having a similar chemical shift with respect to the $\text{C}-\text{C}$ peak.

Table 2 and Table 3 show the theoretical number of different types of chemical groups that actually contribute to the XPS signal based on the chemical formula for the hard and soft segment and the resulting 'bulk' composition for the homogeneous polymer. This is simply based on the average stoichiometry of the polymers. Note that both the nitrogen peak and the component of the C1s envelope assigned to the $\text{O}=\text{C}-\text{N}$ groups solely belong to the hard segment. Consequently, these peaks will allow the discrimination between the hard and soft segments. In addition, it is possible to differentiate between the PTMO and the PEO by following the $\text{C}-\text{O}$ peak. In the case of PEO, all the carbons atoms in the backbone of the chain are linked to one oxygen atom while for PTMO, there is an equal amount of carbon atoms linked to carbon/hydrogen only ($\text{C}-\text{C}$) and carbon linked to a carbon/hydrogen and an oxygen via a single bond ($\text{C}-\text{O}$). Therefore any variation in the relative intensity of the peaks corresponding to these groups (285

and 286.5 eV), as the angular resolved experiment is performed, can be related to the location of the PTMO and PEO segments with respect to each other.

Figures 4 and 5 show the curve fitted C1s envelopes for the TDI-ED-PTMO and the TDI-ED-PTMO/PEO respectively, recorded at take-off angle of 0° (thickness probed of about 7.5 nm) and 80° (thickness probed <1.5 nm). Clearly, differences in the intensity of the peaks are observed, particularly the contribution of the $\text{O}=\text{C}-\text{N}$ group at about 290 eV. The variation of the atomic concentration as a function of take-off angle for both samples are given in Table 4 and Table 5. Both samples showed a reduced nitrogen concentration at the immediate surface (i.e. 80° take-off angle) as well as a continuous depletion of nitrogen as the take-off angle increases.

In order to verify that no damage due to the irradiation took place during the experiments, we have recorded another spectra at zero take-off angle after completing the angle dependent measurements for both samples. The spectra were identical to the one obtained before the experiments, therefore indicating minimal changes were

induced to the surface throughout the collection of data and that the differences in intensities observed between the spectra recorded at 0° and 80° take-off angle were genuine.

It is apparent that changes in the types of chemical function at the surface occur within the XPS sampling depth. Examination of the data for TDI-ED-PTMO (Table 4) showed that the intensity of the nitrogen peak, attributed to the diisocyanate (hard segment), decreases from 3.4 atomic % at 0° take-off angle to about 1 atomic % at the uppermost surface (80° take-off angle). Correspondingly, the carbon peak centred on 289.2 eV is reduced from 2.3 to 1.3 atomic %. These data are indicative of a hard segment depletion at the surface. However, the presence of these two signals at the 80° take-off angle suggest that, although depleted, there exists a small quantity of hard segment in the outer 1.3 nm.

Some contamination of the surface by adventitious carbon or by impurities generated during film casting is probably present on the surface of the sample. However, the relatively constant oxygen signal, even at the largest take-off angle, suggests a low level of contamination by carbonaceous materials. The O/C ratio of 0.22, which is reasonably close to the value that would be expected for pure PTMO (O/C = 0.25) supports this assumption.

For the polymer with both types of soft segments, TDI-ED-PTMO/PEO, results of the angle resolved experiment (Table 5) are similar to TDI-ED-PTMO. As the take-off angle increases, the signals for nitrogen and O=C-N functions decrease. This depletion of hard segments at the surface is expected based on the similarities of the chemistry of the two polymers. In this case however, nitrogen is barely detectable at 80° take-off angle, although the signal for the

O=C-N groups at 289.0 eV is observed and account for about 1.4 atomic %. The decrease in the N1's peak at 400 eV from 3.0% at 0° to being almost undetectable at 80° again could suggest an almost complete hard segment surface depletion. However, because of the relatively low intensity of the signal at high take-off angle, the signal to noise ratio decreases, and the estimate of low concentration of carbamate groups is not accurate. We believe that some hard segments are present in the top 1.5 nm of the sample. This is consistent with previous results reported in the literature for similar copolymer systems^{23,24}.

It is interesting to observe that changes in the relative intensities of the C-C and C-O peaks of TDI-ED-PTMO/PEO occur as the thickness of the probed layer diminishes. Comparison of the carbon envelopes recorded at 0° and 80° take-off angle (Figure 5) indicates that the peak associated with C-O (286.5 eV) has significantly diminished in intensity compared to C-C (285 eV). This suggests that the PEO segments, for which all carbon atom are linked to one oxygen (C-O) is in relatively lower concentration at the very top layer. The very top layer is enriched in PTMO segments. Therefore we can propose a model for this particular polymer in which a PTMO rich layer is actually present at the very top surface of the sample. PEO segments will be found somewhat buried under PTMO and finally even deeper, the majority of the hard segments will be found. Note that a small quantity of hard segments is present in the top 1.5 nm.

SIMS analysis

Figure 6a and b show the positive ions SIMS spectra of the TDI-ED-PTMO and the TDI-ED-PTMO/PEO

Figure 5 High resolution XPS spectra showing the deconvoluted C1's envelope for the TDI-ED-PTMO/PEO sample at 0° and 80° take-off angles

Figure 6 Positive ions time-of-flight static SIMS spectra of: (a) TDI-ED-PTMO, (b) TDI-ED-PTMO/PEO, and (c) pure PEO

samples respectively. There are many similarities between them. For both samples, the base peak is at 55 ($C_4H_7^+$). Peaks at 27 ($C_2H_3^+$), 41 ($C_3H_5^+$), 43 ($C_3H_7^+$ and $C_2H_3O^+$) and 71 ($C_4H_7O^+$) are also very intense, although there are some differences in the relative intensity of each of them. These peaks are characteristics of the SIMS spectrum of PTMO as reported by Hearn *et al.*¹⁰.

The strong peaks mentioned above are not observed in the spectrum of PEO alone (Figure 6c). Surprisingly, the spectrum of the sample containing both PTMO and PEO segments does not show the presence of any significant quantity of fragments usually observed in the SIMS of pure PEO. The positive SIMS of PEO is characterised by a base peak at 45 amu ($C_2H_5O^+$) with very weak peaks above this value. Notice that the peak at 45 amu is very weak in the TDI-ED-PTMO/PEO sample (Figure 6b).

These findings are in agreement with those from Burrell *et al.* who studied copolyether-esters containing mixed polyether²⁴. Their study showed an enrichment of PTMO relative to PEO at the top surface. However, contrary to the case reported herein, they were able to detect a significant peak at 45 amu, suggesting that, although depleted with respect to PTMO, there was a significant quantity of PEO segments at the very top layer. One can speculate about the reasons for this discrepancy. First it can be the result of sample preparation techniques. Their films were either moulded plates or cast films from fluorinated solvents. Our films were cast (1 mm thick) from DMAc. These different methods of preparation can certainly lead to different morphologies in the bulk as well as at the surface. Differences in surface composition from polymers having the same chemistry but prepared differently have been reported in the scientific literature²⁵.

Another possible explanation for the discrepancies can be related to the difference in the length of the hard segment. In fact, the hard segments of the samples reported on in this paper are quite short (one or two monomers) compared to the samples studied by Burrell's group²⁴. Their hard segments contained approximately 11 monomers. This implies that, in this case, there are much longer hard segments linking two soft segments, making the whole macromolecular chain significantly less flexible and hindering the movement of the soft segments which cannot migrate as easily as when linked by short hard segments. Consequently, the short hard segments of our polymers can actually be visualised as acting as 'swivels' between two relatively long flexible chains, allowing for an increased freedom of movement for the soft segments relative to the corresponding materials reported on by Burrell²⁴, having longer hard segments. As a result of the longer hard segments' restrictive effect on the mobility of the soft chains, the coexistence of PEO/PTMO segments would eventually be forced into the top surface since the PEO segments could not migrate away from the surface so readily. These observations are interesting because they actually suggest that one could modify the soft segment nature at the surface of these polymers by proper selection of, not only the chemical nature and length of the soft segment, but also the dimensions of the hard segments.

CONCLUSION

In conclusion, angular dependent XPS measurements revealed a surface composition which decreased in nitrogen and carbamate signals as the thickness of the probed layer decreased and correspondingly an increase in carbons belonging to the soft segments. These findings indicate an enrichment in soft segments at the uppermost surface of these segmented polyurethanes when compared with the expected bulk composition. The study also showed that, for the polymer having both PEO and PTMO soft segments, the segment with the lower surface energy, PTMO, was preferentially found on the uppermost layer suggesting a significant depletion of PEO in the very top surface. Time-of-flight static SIMS analysis of the surfaces confirmed these observations.

REFERENCES

1. Ultee, A. J., in *Encyclopedia of Polymer Science and Technology*, John Wiley Interscience, New York, 1986, Ch. 6.
2. Cooper, S. L. and Tobolsky, A. V., *J. Appl. Polym. Sci.*, 1966, **10**, 1837.
3. Cooper, S. L., Estes, G. M., *Multiphase Polymers*, Adv. Chem. Ser. No. 176, American Chemical Society, Washington, DC, 1979.
4. Clark, D. T., Dilks, A., Peeling, J. and Thomas, H. R., *J. Chem. Soc., Faraday Discuss.*, 1975, **60**, 183.
5. Thomas, H. R. and O'Malley, J. J., *Macromolecules*, 1979, **12**, 323.
6. O'Malley, J. J., Thomas, H. R. and Lee, G. M., *Macromolecules*, 1979, **12**, 996.
7. Yoon, S. C. and Ratner, B. D., *Macromolecules*, 1986, **19**, 1068-1079.
8. Yih, R. S. and Ratner, B. D., *J. Electron Spectrosc. Relat. Phenom.*, 1981, **43**, 61.
9. Schmitt, R. L., Gardella, J. A., Magill, J. H., Salvati, L. and Chin, R. L., *Macromolecules*, 1985, **18**, 2675.
10. Hearn, M. J., Ratner, B. D. and Briggs, D., *Macromolecules*, 1988, **21**, 2950.
11. Green, P. F., Christensen, T. M., Russell, T. P. and Jerome, R., *Macromolecules*, 1989, **22**, 2189.
12. Bathia, Q. S. and Burrell, M. C., *Polymer*, 1991, **32**, 1948.
13. Burrell, M. C., Bathia, Q. S. and Michael, R. S., *Surf. Interface Anal.*, 1994, **21**, 553.
14. Fadley, C. S., *Prog. Solid State Chem.*, 1976, **11**, 265.
15. Briggs, D., *Surf. Interface Anal.*, 1986, **9**, 391.
16. Briggs, D., *Br. Polym. J.*, 1989, **21**, 3.
17. Briggs, D., Brown, A. and Vickerman, J. C., *Handbook of Static Secondary Ion Mass Spectrometry*, Wiley, New York, 1989.
18. Short, R. D., Ameen, A. P., Jackson, S. T., Pawson, D. J., O'Toole, L. and Ward, A. J., *Vacuum*, 1993, **44**, 1143.
19. Santerre, J. P., Labow, R. S., Duguay, D. G., Erfle, D. J. and Adams, G. A., *J. Biomed. Mater. Res.*, 1994, **28**, 1187.
20. Clark, D. T. and Thomas, H. R., *J. Polym. Sci., Polym. Chem. Edn.*, 1977, **15**, 2843.
21. Szajman, J., Liesegang, J., Jemkin, J. G. and Leckey, R. G. G., *J. Electron Spectrosc. Relat. Phenom.*, 1978, **14**, 247.
22. Dillon, J. G., *Infrared Spectroscopic Atlas of Polyurethanes*, Technomic Publ. Co. Inc., Lancaster, PA, 1989.
23. Santerre, J. P., Labow, R. S. and Adams, G. A., *J. Biomed. Mater. Res.*, 1993, **27**, 97.
24. Burrell, M. C., Bathia, Q. S. and Michael, R. S., *Surf. Interface Anal.*, 1994, **21**, 553.
25. Tyler, B. J., Ratner, B. D., Castner, D. G. and Briggs, D., *J. Biomedical Mater. Res.*, 1992, **26**, 273.