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Surface organization of polyurethanes observed by static secondary ion mass spectrometry

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Static secondary ion mass spectrometry has been used to investigate orientation effects at the surfaces of segmented polyetherurethanes. The presence of hard segments at the polymer surface was found to be dependent upon the sample preparation method. Spin casting can produce a larger hard segment content than straightforward solvent evaporation, and films produced by spin casting slowly reorganize to remove hard segments from the top 10 Å or so. The occurrence of such effects is restricted to polymers with high polypropylene oxide content in the soft segment and a reasonably large (above about 2500) soft segment molecular weight.

(Keywords: polyurethane; s.s.i.m.s.; surface segregation)

INTRODUCTION

Segmented polyurethane surfaces demonstrate some intriguing orientation phenomena[1,2]. The nature of these polymers allows the bulk structure to bear little relationship to that expressed at the surface. Although these materials have manifold uses, we are concerned mainly with the medical applications of polyurethanes[3-6], where surface chemistry and surface interactions are of the utmost importance[7].

It is well known that polyurethanes separate into two distinct phases in the bulk[8]: a polyether-rich (also known as the soft segment) phase and a urethane-rich (hard segment) phase. The formation and size of these domains depend upon many factors, such as the molecular weight of the soft segment[9], the nature of the chain extender[10] and the thermal and solvent history of the sample[11]. The division of these components in the bulk is quite well understood, but less is clear about such effects at the polyurethane surface.

Previous studies have demonstrated that it is the soft segment which is expressed at the air/polymer interface[12]. This observation can be rationalized in terms of the surface energetics of the individual components. When the polyether has a lower characteristic surface energy than the urethane unit, it may be expected to concentrate at the polymer surface in air or under vacuum. Recent X-ray photoelectron spectroscopy (X.p.s.) and static secondary ion mass spectrometry (s.s.i.m.s.) studies indicate that urethane groups are still present within the top few monolayers of the polymer[13]. This may be due to the extension of hard segment phases into the top 10 Å (1 Å = 0.1 nm) of the polymer and/or a low but detectable concentration of urethane links in the soft segment phase. Additionally, the preparative methods employed (in most of the references, spin casting from a volatile solvent) may have some effect upon the surface chemistry. For analytical purposes it is convenient to examine thin polymer films which reduce problems associated with charge compensation. It has been shown, however, that 'bulk' phase separation is retarded in thin polyurethane films less than 20 nm thick[14]. Does this slow phase separation influence the surface chemistry? If it does, there are obvious implications for modelling bulk polymer surfaces with thin films.

In this paper we investigate the surface properties of novel polyurethanes which contain a soft segment consisting of a triblock polyether. The polyethers used have a middle block of poly(propylene oxide) (PPO) and two end-blocks of poly(ethylene oxide) (PEO) terminated with hydroxy groups. These polyethers have been shown to reduce protein adsorption and bacterial adhesion when adsorbed onto polystyrene films[15], and they enhance the stability of polystyrene colloids *in vivo*[16]. It is hoped that by forming polyurethanes from these compounds some of the resistance to protein adsorption will be retained in the resultant polymer. Indeed, polyurethanes which contain PPO/PEO copolymers as the soft segment do show a reduction in protein adhesion when compared with standard biomedical polymers[17].

Since protein adhesion is an interfacial process, it is essential to have a clear idea of the surface chemistry of the polyurethanes to gain an understanding of which factors may influence the adsorption mechanism. It is vital to know, for example, the concentration of urethane

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*To whom correspondence should be addressed units at the polymer surface and whether this will increase or decrease upon hydration[18], as a function of the polymer thickness or under any other set of conditions in which the materials might be employed. S.s.i.m.s. is able to probe the very near surface (approximately 10 Å deep[19]) of materials and may be used to gauge at least qualitatively the concentration of species within this depth[20,21].

EXPERIMENTAL

Materials

Synthesis of the polyurethanes was carried out at the University of Ghent, Belgium. All polymers were used as received. These materials possessed polyether soft segments capped with *N,N'*-methylenebis(phenyl diisocyanate) (MDI) and extended with butanediol. The polyether segment consisted of PEO and PPO homopolymers or block copolymers, which are detailed in *Table 1*.

Films of the polyurethanes were cast from 0.1% w/v solutions in dimethylformamide (DMF) onto sample stubs coated with aluminium foil. Thin films were prepared by spin casting, which involved dropping 50 μl of solution onto a stub spinning at 5000 rev min^{-1}. Thicker films were formed by evaporating 20 μl of solution onto a stationary stub, giving an average polymer thickness of approximately 170 nm (the polyurethane density was assumed to be 1.2 g ml^{-1}). Both preparations were repeated at least three times on all polymers used in this study. To investigate ageing effects in air, the polyurethane films were stored in a clean glass Petri dish at room temperature.

Surface analysis

S.s.i.m.s. spectra were obtained using a VG Ionex SIMSLAB 3B instrument equipped with a differentially pumped EX05 ion gun and a 12-12M quadrupole mass spectrometer. The main chamber routinely achieved a base pressure of better than 10^{-9} mbar, and during operation this rose to approximately 10^{-7} mbar (1 bar = 10^5 Pa). The ion gun was run in the fast atom mode. 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 less than 10^{13} atoms cm^{-2}, the threshold for s.s.i.m.s. experiments[22].

X.p.s. analysis was carried out on a VG Scientific ESCALAB Mk II electron spectrometer employing MgKα X-rays ($h\nu = 1253.6$ eV), the X-ray gun being operated at 10 kV and 34 mA. The spectrometer was run in the fixed analyser transmission mode with pass energies of 50 eV for survey scans and 20 eV for high resolution spectra of C_{1S}, N_{1S}, O_{1S} and Al_{2P}. No other elements were detected. Electron take-off angles of 45° and 75° were used to give a variation in sampling depth (approximately 5 nm and 20 nm, respectively).

Table 1 Compositions of polyurethane polyether soft segments

Diol composition PEO/PPO/PEO (monomer units)	Diol identity	Abbreviation	Source
7/54/7	Pluronic L101	L101	BASF (Ludwigshafen)
3/30/3	Pluronic L61	L61	BASF
13/30/13	Pluronic L64	L64	BASF
76/30/76	Pluronic F68	F68	BASF
45/0/0	PEG 2000	E2000	SERVA (Heidelberg)
91/0/0	PEG 4000	E4000	SERVA
0/34/0	PPG 2000	P2000	SERVA
0/69/0	PPG 4000	P4000	SERVA

RESULTS

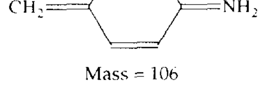
X.p.s.

In all of the polymers analysed, the drop-casting method (i.e. straightforward solvent evaporation) produced films thicker than the X.p.s. sampling depth. This is to be expected, as the sampling depth of X.p.s. for organic polymers is of the order of tens of angstroms[23]. Both the surface elemental composition and the shape of the C_{1S} envelope were in good agreement with those expected from the stoichiometry and structure of the polymer. These results will be published elsewere[24]. Spin-cast films appeared to be very thin or patchy. This was evident by the appearance of the Al_{2P} peak in the X.p.s. spectra. Attenuation of this substrate signal at different electron take-off angles can give some information on whether the polymer overlayer is continuous or uneven. X.p.s. spectra were taken at 45° and 75°, and only in a few cases (L64, L61 and E4000) did the Al_{2P} signal change in accordance with a thin, flat overlayer model[25]. All other polymers showed small decreases in relative aluminium content at 75°, indicating uneven film formation. S.s.i.m.s. of all samples under discussion suggested that the films were not patchy since there was no intense ion signal at m/z 27 (due to the Al^+ ion). It is thought that s.s.i.m.s. has an information depth of approximately 1 nm compared with 2–5 nm for X.p.s.: these results imply that thin, continuous but uneven films are generally formed.

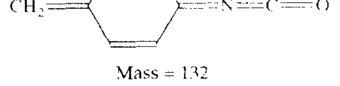
S.s.i.m.s.

Positive s.s.i.m.s. spectra of PEO and PPO have been reported previously[26]. The characteristic peaks from these materials have been assigned to ions which bear a close structural resemblance to their respective monomer units. In both cases the base peak corresponds to the protonated monomer, at m/z 45 for PEO and at m/z 59 for PPO. In addition, a series of prominent peaks are observed with the general formula $(n\mathrm{M}+\mathrm{H})^+$, where M is the polymer repeat unit. Other peaks within the PEO and PPO s.s.i.m.s. spectra also derive from simple fragmentations of the polymer chain. Spectra of pluronic block copolymers have also been measured and show no ion fragments other than those expected from the two polyethers[15]. These materials tend to give spectra typical of PPO rather than PEO, with the m/z 59 ion dominating. Whether this is owing to preferential orientation of PPO at the vauum/polymer interface or a greater secondary ion yield of PPO-derived fragments is unknown.

Ions that are particularly diagnostic of the MDI hard segment appear at m/z 106 and 132, the proposed structures of which are[27]



Mass = 106



Mass = 132

Polyethers do not produce ions at these masses, and thus the appearance of hard segments within the top 10 Å or so may be demonstrated by the presence of these ions.

The positive ion s.s.i.m.s. spectrum of spin-cast polyurethane P2000 is shown in *Figure 1*. Qualitatively, the results from the P4000 polymer are similar in that there are no ions of different masses observed. Below *m/z* 100 the full range of ions typical of PPO are observed. At higher masses, peaks typical of the diisocyanate unit may be seen, particularly at *m/z* 106. These results compare well with results obtained for similar polyurethanes[13]. *Figure 2* shows the s.s.i.m.s. spectrum of spin-cast E2000 which contains PEO as the soft segment. In this case the low mass peaks are characteristic of PEO homopolymer, with the *m/z* 45 ion dominating. The spectrum from the E4000 polyurethane is amost identical, and both have an ion at *m/z* 106.

Polyurethanes created from PPO/PEO triblock copolymers produce spectra with the dominant peak at *m/z* 59. The s.s.i.m.s. spectrum of spin-cast L61 is shown in *Figure 3*. Once again, below *m/z* 100 the spectrum is typical of the soft segment, the peaks and their relative intensities being indicative of PPO. As mentioned previously, this may be a result of preferential surface enrichment of the PPO component, or it may be an artefact of the s.s.i.m.s. process. The hard segment derived ion at *m/z* 106 was clearly present in all of the spin-cast films, except for polymer F68 where the signal was rather weak. It is possible that the high soft segment molecular weight in this polyurethane effectively reduces the hard segment concentration to a level close to the s.s.i.m.s. detection limit.

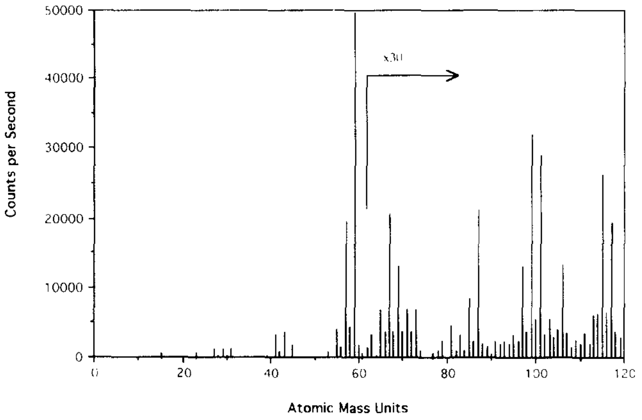


Figure 1 Positive ion s.s.i.m.s. spectrum of spin-cast polyurethane P2000

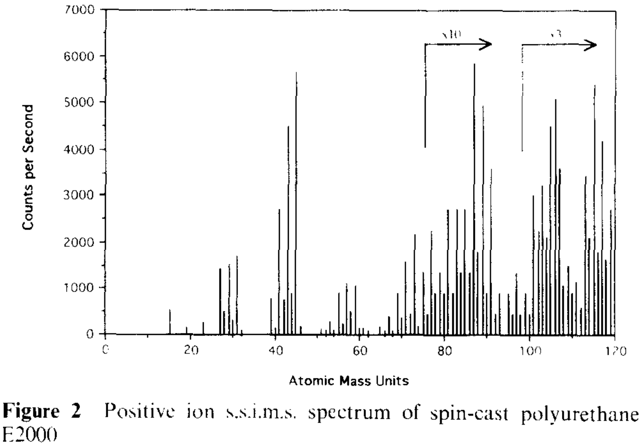


Figure 2 Positive ion s.s.i.m.s. spectrum of spin-cast polyurethane E2000

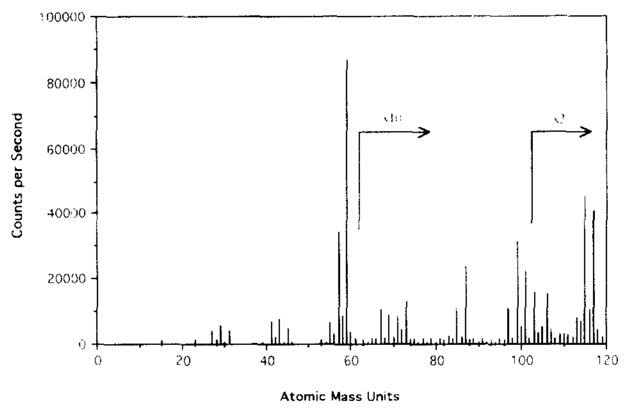


Figure 3 Positive ion s.s.i.m.s. spectrum of spin-cast polyurethane L61

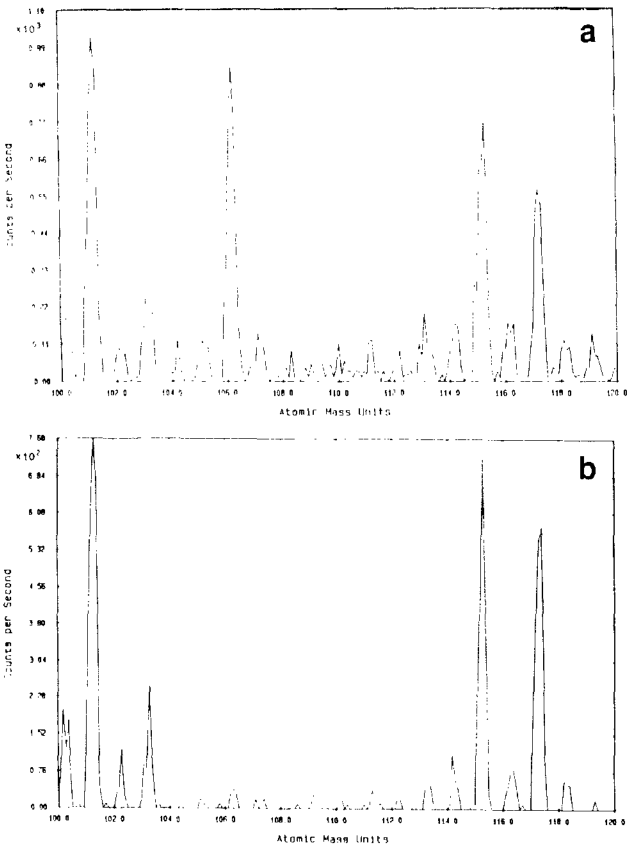


Figure 4 Comparison of s.s.i.m.s. spectra for (a) spin-cast and (b) drop-cast polyurethane L64

Influence of sample preparation

The relative intensity of the *m/z* 106 peak, diagnostic of MDI, was found to be sensitive in some cases to the preparative method. *Figure 4* shows the difference between spun and drop-deposited L64 in the *m/z* 100–120 range. To quantify this change, the peak area of the *m/z* 106 ion was compared with that of an ion appearing at *m/z* 103. This latter ion is present with moderately low intensity in both the PEO and PPO homopolymer s.s.i.m.s. spectra. *Table 2* lists the variations in the *m/z* 106 peak intensity obtained from spin-cast and drop-cast films. It can be seen that drop casting often produces a

Table 2 Variations in peak intensity for a characteristic hard segment ion with sample preparation method. Samples were aged for over 1 week. Standard deviations ($n = 3$) are given in parentheses

	$I(106)^a$			
	Spin-cast		Drop-cast	
Polyurethane	Fresh	Aged	Fresh	Aged
L101	0.38 (0.07)	0.36 (0.05)	0.15 (0.04)	0.12 (0.03)
L61	0.49 (0.10)	0.58 (0.02)	0.31 (0.08)	0.30 (0.05)
L64	0.63 (0.08)	0.20 (0.04)	0.27 (0.09)	0.16 (0.06)
F68	0.28 (0.07)	0.20 (0.05)	0.27 (0.09)	0.16 (0.06)
E2000	0.51 (0.06)	0.60 (0.05)	0.54 (0.07)	0.64 (0.03)
E4000	0.48 (0.02)	0.45 (0.07)	0.50 (0.06)	0.49 (0.05)
P2000	0.59 (0.08)	0.56 (0.07)	0.49 (0.04)	0.47 (0.03)
P4000	0.58 (0.10)	0.29 (0.04)	0.26 (0.05)	0.23 (0.05)

[a] Calculated by dividing the peak area of the m/z 106 ion by the combined peak areas of the m/z 106 and 103 ions

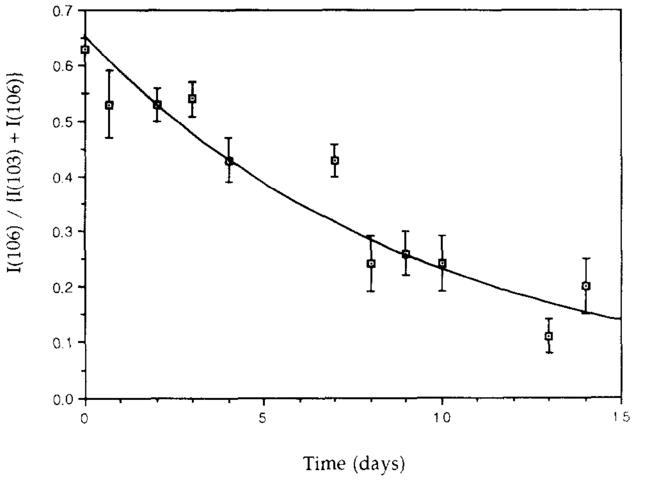


Figure 5 Time dependent change in m/z 106 ion intensity from spin-cast L64. Standard deviations are shown as error bars

lower intensity in the m/z 106 peak than spin casting. Significant differences were found for polymers L101, L64 and P4000 using the two preparative methods. Polyurethanes L61 and P2000 did not exhibit any statistically significant drop in m/z 106 relative intensity, and it is intersting to note that both of these polyurethanes have the lowest soft segment molecular weights of this polymer series (approximately 2000). The polyurethanes formed from PEO homopolymer showed no sensitivity to the method of film preparation. No change could be detected between spin-cast and drop-cast F68 polymer, which has a high PEO content. Both preparative methods produce spectra where the m/z 106 peak is extremely low in intensity.

Ageing of spin-cast films

Spin-deposited films of polyurethanes L64 and P4000 gave reduced hard segment ion signals when aged in air for over 1 week. Drop-cast films showed no change of this signal with time. This ageing phenomenon was followed over the course of 2 weeks for polymer L64. The results are illustrated graphically in *Figure 5*, and show a slow decrease in m/z 106 peak intensity. The process causing this change appears to be complete after 8 days, with no further significant variation in peak intensity occurring after that time. Only this polymer and P4000 exhibited ageing, the other materials being stable over the time periods employed (between 10 and 14 days). It is important to note that in these two cases the aged, spin-cast films give m/z 106 relative intensities similar to those of the drop-deposited films of the same polymers.

DISCUSSION

The relative intensity of the m/z 106 ion may be taken as indicative of the concentration of hard segments at the polymer surface. Other workers have found that the signal due to this ion decreases with an increasing soft segment molecular weight[13]. Such an effect may be noted between E2000 and E4000, and also between P2000 and P4000 after the films have been aged.

The polyurethanes which show the largest sensitivity to preparation method all have a soft segment composed mainly of PPO and a polyether mean molecular weight of roughly 2500 or above. It has been demonstrated that orientation at polyurethane/air interfaces favours the segment of lowest surface energy being uppermost[28]. Surface energies decrease in the order PEO > MDI hard segment > PPO, which suggests that there should be a surface excess of PPO in most of the polyurethanes discussed here[15]. Drop casting of polyurethanes in the manner described above seems to produce thick films with surfaces in a favourable low energy state. Spin casting creates thinner films which have high hard segment concentrations within the top few angstroms of the surface. These may then reorient to remove MDI-containing segments into the bulk.

It has been shown in the simple case of phase-separated symmetric diblock copolymers that only a small difference in surface energy is necessary to produce quite large segregation phenomena at the surface of solvent-cast films[29]. These and similar[30] studies demonstrate quite clearly the effect of drying time and annealing on the surface of polystyrene (PS)/poly(methyl methacrylate) (PMMA) copolymer films cast from toluene. It was found that fast drying of copolymer films tended to produce non-equilibrium surfaces with a high content of PMMA, whereas slower drying and anealing resulted in a surface excess of polystyrene, the excess depending on the inverse square root of the molecular weight of the copolymer. It has been shown both theoretically and experimentally that these ordering effects can be influential over quite a distance within copolymer films, with alternating lamellae of one and the other component forming parallel to the surface[31,32]. Triblock copolymers have also been investigated and found to form a 'hairpin' configuration between two dissimilar interfaces[33].

There are substantial differences that should be noted between these ideal systems and the polyurethanes under study here. The polyurethanes are not symmetric diblock copolymers, the soft segments have a much higher molecular weight than the hard segments, and the latter will tend to form themselves into spherical domains[34]. Annealing above 100°C of the PS/PMMA systems described previously was necessary to effect surface segregation and the formation of phase-separated structures. Both of the components in these copolymers have a glass transition temperature of about 100°C, whereas the soft segments used in our experiments are well above their glass transition temperatures under ambient conditions (T_g of PPO is −75°C, T_g of PEO is

−67°C)[35]. Therefore, one would expect reorganizations within the polyurethanes to be able to occur at room temperature. The speed of solvent drying may be an important factor in the retention of hard segments within the surface of these polyurethanes. It was noted, however, that even after spin casting, a layer of solution was visible on the sample stub that took up to an hour to dry. The drop-cast films took about 2 h to dry. DMF is a relatively involatile solvent (boiling point 153°C[36]), and further experimentation is necessary to determine whether the evaporation rate influences the surface chemistry of these systems.

The preferred conformation of these polyurethanes (with the exception of E2000 and E4000) is with the PPO segment at the polymer/air interface. This preference will tend to exclude the phase-separated urethane hard segments from the surface and to some extent the PEO part of the soft segment. The most stable conformations in *Table 2* are the drop-cast aged films, where it can be seen that the hard segment surface contribution depends to a large extent upon the molecular weight of the soft segment. The fresh drop-cast polymers are indistinguishable from drop-cast polymers that have been aged, indicating that they, too, are in a low energy state. Thin spin-cast films are shown to have higher hard segment contributions to the surface in some of these polymers. This may, as noted previously, be due to a solvent effect, but there is also substantial evidence that phase separation is drastically slowed in thin polyurethane films of similar compositions to the ones studied here[14]. If the hard segments in these systems are more homogeneously distributed (i.e. less segregated) in a thin film, then one may expect a higher population to reside at the polymer/air interface. Whatever the causes of the non-equilibrim surfaces are, it has been demonstrated that reorientation occurs over a period of several days to produce a more favourable surface.

CONCLUSIONS

Orientation in the topmost atomic layers of polyurethanes has been investigated using s.s.i.m.s. It was found that hard segment characteristic ions could be detected in almost all cases at the surface of spin-cast films. The influence of casting method upon surface chemistry has been demonstrated by comparison with much thicker films.

Spin casting is used as a common preparative technique for polymer surface analysis. We have shown that in some cases this method may produce surfaces which are not at equilibrium or are not representative of the surfaces of thicker samples. Substantial differences between spin-cast and drop-cast polyurethanes seem to occur when the soft segment has a high (above about 2500) molecular weight and substantial PPO character. This provides an interesting extension to earlier work where soft segments with molecular weights lower than 2000 were examined[1]. Such an effect is not evident when the soft segment consists solely of PEO.

In addition, a surface reorganization of spin-cast polyurethane films was observed to occur over a period of roughly 1 week. We believe that this is the first reported observation by s.s.i.m.s. of such a phenomenon at polyurethane surfaces. Two of the polyurethanes exhibited ageing, and in both cases there was also a difference between their spin-cast and drop-cast surfaces.

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REFERENCES

1 Ratner, B. D., Briggs, D., Hearn, M. J., Yoon, S. C. and Edelman, P. G. in 'Surface Characterisation of Biomaterials' (Ed. B. D. Ratner), Elsevier, Amsterdam, 1988, p. 317

2 Deng, Z. and Schreiber, H. P. *J. Adhes.* 1991, **36**, 71

3 Lelah, M. D., Stafford, R. J., Lambrecht, L. K., Young, B. R. and Cooper, S. L. *Trans. Am. Soc. Artif. Int. Org.* 1981, **27**, 504

4 Brunstedt, M. R., Ziats, N. P., Robertson, S. P., Hiltner, A., Anderson, J. M., Lodoen, G. A. and Payet, C. R. *J. Biomed. Mater. Res.* 1993, **27**, 367

5 Wabers, H. D., Hergenrother, R. W., Coury, A. J. and Cooper, S. L. *J. Appl. Biomater.* 1992, **3**, 167

6 Planck, H., Egbers, G. and Syré, I. (Eds) 'Polyurethanes in Biomedical Engineering', Elsevier, Amsterdam, 1984

7 Davies, M. C. in 'Polymer Surfaces and Interfaces II' (Eds W. J. Feast, H. S. Munro and R. W. Richards), Wiley, Chichester, 1993, p. 203

8 Blackwell, J. R., Quay, J. R., Nagarajan, M. R., Born, L. and Hespe, H. *J. Polym. Sci., Polym. Phys. Edn* 1984, **22**, 1247

9 Wilkes, G. L. and Abouzahr, S. *Macromolecules* 1981, **14**, 456

10 Blackwell, J. R., Nagarajan, M. R. and Hoitink, T. B. *Polymer* 1982, **23**, 950

11 Crystal, R. G., Erhardt, P. F. and O'Malley, J. J. in 'Block Polymers' (Ed. S. L. Aggarwal), Plenum Press, New York, 1970, p. 179

12 Yih, R. S. and Ratner, B. D. *J. Electron Spectrosc. Relat. Phenom.* 1987, **43**, 61

13 Hearn, M. J., Ratner, B. D. and Briggs, D. *Macromolecules* 1988, **21**, 2950

14 Meuse, C. W., Yang, X., Yang, D. and Hsu, S. L. *Macromolecules* 1992, **25**, 925

15 Bridgett, J. PhD thesis, Nottingham University, 1993

16 Norman, M. E., Williams, P. and Illum, L. *Biomaterials* 1993, **14**, 193

17 Braatz, J. A., Heifetz, A. H. and Kehr, C. L. *J. Biomater. Sci., Polym. Edn* 1992, **3**, 451

18 Lewis, K. B. and Ratner, B. D. *J. Colloid Interface Sci.* 1993, **159**, 77

19 Briggs, D. in 'Practical Surface Analysis' (Eds D. Briggs and M. P. Seah), Vol. 2, Wiley, Chichester, 1992, p. 390

20 Briggs, D. *Org. Mass Spectrom.* 1987, **22**, 91

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

22 Briggs, D. and Hearn, M. J. *Vacuum* 1986, **36**, 1005

23 Briggs, D. in 'Practical Surface Analysis' (Eds D. Briggs and M. P. Seah), Vol. 1, Wiley, Chichester, 1992, p. 443

24 Shard, A. G., Davies, M. C., Tendler, S. J. B., Jackson, D. E., Lan, P. N. and Schacht, E. unpublished results

25 Briggs, D. and Riviere, J. C. in 'Practical Surface Analysis' (Eds D. Briggs and M. P. Seah), Vol. 1, Wiley, Chichester, 1992, p. 134

26 Briggs, D., Brown, A. and Vickerman, J. C. 'Handbook of Secondary Ion Mass Spectrometry', Wiley, Chichester, 1989

27 Hearn, M. J., Briggs, D., Yoon, S. C. and Ratner, B. D. *Surf. Interface Anal.* 1987, **10**, 384

28 Yoon, S. C. and Ratner, B. D. *Macromolecules* 1986, **19**, 1068

29 Green, P. F., Christensen, T. M., Russell, T. P. and Jerome, R. *Macromolecules* 1989, **22**, 2189

30 Green, P. F., Christensen, T. M., Russell, T. P. and Jerome, R. *J. Chem. Phys.* 1990, **92**, 1478

31 Shull, K. R. *Macromolecules* 1992, **25**, 2122

32 Mayes, A. M., Russell, T. P., Satija, S. K. and Majkrzak, C. F. *Macromolecules* 1992, **25**, 6523

33 Russell, T. P., Mayes, A. M., Deline, V. R. and Chung, T. C. *Macromolecules* 1992, **25**, 5873

34 Garbassi, G., Morra, M. and Occhiello, E. 'Polymer Surfaces from Physics to Technology', Wiley, Chichester, 1994, p. 286

35 Brandrup, J. and Immergut, E. H. 'Polymer Handbook', Wiley, New York, 1966

36 Lide, D. R. (Ed.) 'Handbook of Chemistry and Physics', 74th Edn, CRC, London, 1993