Interaction of nitrogen and ammonia plasmas with polystyrene and polycarbonate studied by X-ray photoelectron spectroscopy, neutron activation analysis and static secondary ion mass spectrometry

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The interactions of NH_3 and N_2 plasmas with the surfaces of polystyrene (PS) and bisphenol-A polycarbonate (PC) have been studied with X.p.s. and SSIMS. Primary amino groups could be detected at the surfaces of both polymers after treatment with the NH_3 plasma but not with the N_2 plasma, with the aid of derivatization reactions with salicylaldehyde and 5-bromosalicylaldehyde. PC differs in its reactivity from PS with respect to its ease of undergoing chain scission during the plasma treatments, which results in modified structures of low molecular weight at the surface. The surface coverage of primary amino groups on PS after treatment with the NH_3 plasma was determined by means of neutron activation analysis after derivatization of these groups with 5-bromosalicylaldehyde and estimated to be approximately 0.5 amino groups per nm^2.
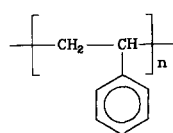
INTRODUCTION

The interaction of plasmas with polymeric material has been studied by various groups. One of the aims of this research is to improve the adhesion properties of this material without affecting the bulk properties. Analysis of the modified chemical structure of the polymer surface is normally performed by X-ray photoelectron spectroscopy (X.p.s.). The incorporation of new elements (O, N) into the surface can be detected by this technique. Furthermore, in some cases detailed spectra can be used to gain insight into the modified chemical structures (i.e. new functional groups) at the surface[1-3]. A more elegant method that can be used to study the appearance of new functional groups at the surface is to perform specific reactions on these groups with reactants containing elements (such as halogens) which are not present at the parent surfaces[4-7]. A lot of work has been done with oxygen plasmas. Results on plasmas containing nitrogen (N_2, NH_3) are more scarce. In principle such plasmas will be capable of incorporating amino groups into the surface. These groups give basic properties to the surface, which are supposed to be helpful for adhesion of coatings with acidic properties. Furthermore, amino groups are relatively reactive nucleophilic agents, suitable to perform subsequent reactions. In this way various functional groups may be formed at the surface. X.p.s. studies on N_2-plasma-treated polymers were done by Yasuda et al.[8] They showed that nitrogen can be incorporated into the surface of various polymers and that oxygen is incorporated too. By means of a chemical derivatization
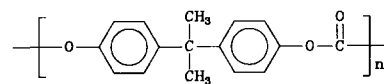
reaction, Everhart et al.[5,9] detected primary amino groups at the surface of polyethylene treated with a N_2 plasma.

In this paper we investigate the effect of N_2 and NH_3 plasmas on polystyrene (PS) and bisphenol-A polycarbonate (PC) with X.p.s. Both polymers contain aromatic groups which may have the same reactivity towards these plasmas. On the other hand, PC differs significantly from PS because it contains aromatic groups in the backbone of the polymer and furthermore it contains hetero atoms in its backbone, which may result in different reactivity. Our aim is to search for primary amino groups and this will be done by derivatization with 5-bromosalicylaldehyde (BSA) (Scheme 1). The imine formed after reaction is very stable and contains bromine which can be detected with X.p.s. and quantitatively with neutron activation analysis (NAA)[10].

In the last few years, static secondary ion mass spectrometry (SSIMS) has proved to be a very powerful technique for analysing the chemical structure of the surface of polymeric material[4,11-14]. Although few results on plasma-treated surfaces have appeared in the literature, it seems that marked spectral changes can be
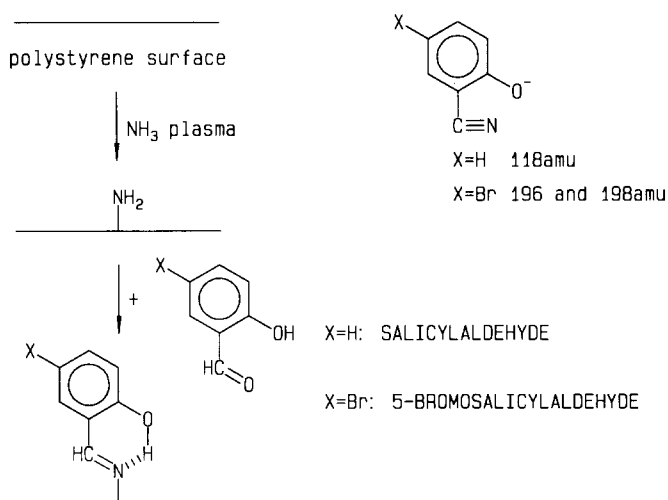

polystyrene

bisphenol-A polycarbonate

Scheme 1

polystyrene surface

NH₃ plasma

NH₂

X=H   118amu
X=Br   196 and 198amu

X=H: SALICYLALDEHYDE
X=Br: 5-BROMOSALICYLALDEHYDE

observed after the treatments[13,15,16]. Reduction and chain scission of PC by a H_2 plasma can be followed in a detailed manner with SSIMS[13].

To see what changes can be observed in SSIMS spectra of PS and PC treated with N_2 and NH_3 plasmas, a SSIMS study was performed parallel to the X.p.s. study.

EXPERIMENTAL

Bisphenol-A polycarbonate ($\bar{M}_w = 34\,000$), PS ($\bar{M}_w = 320\,000$) as well as all other chemicals were purchased from Aldrich. PC was spincoated at 2000 rev min^{-1} on silica supports from 3% solutions in chloroform and PS from 6% solutions in toluene. The thickness of these polymer layers was about 0.5 μm, which avoids surface charging during the SSIMS experiment.

The reactions with BSA and salicylaldehyde were performed in ethanol (1% solutions) for 10 min at room temperature. Longer reaction time did not improve the yields. After the reaction, the surfaces were thoroughly rinsed with ethanol.

The time-of-flight SIMS mass spectrometer used has been described before[17-19]. During the measurement a target area of about 1 mm^2 is bombarded by 12 keV Ar$^+$ ions with an average current of about 0.5 pA for 30 s. In this way, the maximum intensity of secondary ions varies between 10^4 counts and 10^5 counts, depending on the species analysed.

The X.p.s. measurements (wide scan spectra) were performed on a Leybold–Heraeus LHS-10 apparatus equipped with a non-monochromatized Al Kα source. The nitrogen content relative to the carbon content (X_N) was determined from the peak intensities (I) with the aid of the attenuation length which is proportional to the kinetic energy of the electrons (Ek), and the instrumental cross-sections (σ) according to[20]:

$$X_N = \frac{I_{N_{1s}}\sigma_{C_{1s}}\sqrt{Ek_{C_{1s}}}}{I_{C_{1s}}\sigma_{N_{1s}}\sqrt{Ek_{N_{1s}}}} \times 100\%$$

(i.e. $X_C = 100\%$). In the same manner the oxygen and bromine content were determined.

Plasmas were generated in an Edwards model 306 coating system. The gas pressure was about 10^{-1} mbar,

the plasma current 20 mA and the electrode potential 2.5 kV. The samples were kept in the dark (field-free) region during the plasma treatment. The gases used have a purity of more than 99.9%.

NAA measurements were performed by irradiating the samples with approximately 12×10^{15} neutrons cm^{-2}, followed by γ-spectrometry[21]. In this way 0.011 μg Br cm^{-2} could be determined on the treated surfaces and 0.003 μg Br cm^{-2} on the untreated surfaces.

RESULTS AND DISCUSSION

Interaction of nitrogen and ammonia plasmas on PS studied by X.p.s. and NAA

After treatment of a PS surface with one of the plasmas for 5 min, the incorporation of nitrogen and oxygen into the surface can be detected from the appearance of a N_{1s} signal with a binding energy (BE) of about 401 eV and an O_{1s} signal with BE $\simeq 533$ eV in the X.p.s. spectra of the modified surfaces. *Table 1* shows the percentages of nitrogen and oxygen relative to carbon calculated from the intensities of the N_{1s}, O_{1s} and C_{1s} (BE $\simeq 286$ eV) signals. *Table 1* does not pretend to give exact quantitative values but trends due to the different treatments. Comparison of the results of 5 min NH_3 plasma treatment and 5 min N_2 plasma treatment reveals that in the latter case much more oxygen incorporation is observed. The incorporation of oxygen in polymeric surfaces after or during treatment with a non-oxygen-containing plasma is a common phenomenon[3,5,8]. It is very well likely that during plasma treatments radical intermediates play an important role. Radicals react very fast with O_2 (peroxyradical formation). This means that small amounts of O_2 in the plasma have a great affinity to the treated surface even though the oxygen will not necessarily be excited in the plasma. Furthermore, after termination of the plasma treatment, radical centres may still be at the surface and will react with O_2 after bringing the surface under normal atmospheric conditions.

An important difference in the effect of both plasmas is that incorporation of Br (detected by the $Br_{3p1/2}$ and $Br_{3p3/2}$ signals with BE $\simeq 192$ and 185 eV, respectively) is only observed after reaction of BSA in ethanol with the NH_3 plasma-treated surface but not with the N_2-plasma-treated surface. This means that only after treatment with a NH_3 plasma primary amino groups are incorporated

Table 1 Percentage of elemental composition relative to carbon ($= 100\%$) of a PS surface after various treatments

Treatment	$X_N{}^a$	$X_O{}^b$	$X_{Br}{}^c$
No treatment	–	1.5^d	–
5 min NH₃ plasma	3.2	5.0	–
+ ethanol	2.9	5.5	–
+ BSA in ethanol	3.1	6.1	1.2
10 min NH₃ plasma	10.2	6.7	–
+ ethanol	5.1	7.2	–
+ BSA in ethanol	5.6	7.8	0.9
5 min N₂ plasma	5.0	16.0	–
+ ethanol	4.0	16.0	–
+ BSA in ethanol	3.3	19.0	0.0

^{a} Determined from the N_{1s} and C_{1s} signals
^{b} Determined from the O_{1s} and C_{1s} signals
^{c} Determined from the $Br_{3p1/2}$, $Br_{3p3/2}$ and C_{1s} signals
^{d} This oxygen is of unknown origin

into the surface. From the Br/N ratio it can be concluded that about 30% of the nitrogen in the NH₃-plasma-treated surface is present as primary amino groups or at least accessible for reaction with BSA.

To find out whether more primary amino groups can be incorporated, the NH₃ plasma treatment was performed for 10 min. *Table 1* shows that the nitrogen content indeed increased but after reaction with BSA the amount of bromine incorporated does not deviate much from the amount detected after the reaction of BSA with the surface treated for 5 min with the plasma. Furthermore, after reaction with BSA about 50% of the nitrogen disappeared from the surface. The same effect is observed after rinsing the plasma treated surface with ethanol. Probably low-molecular-weight species are formed which dissolve in ethanol. This effect is less or not observed afer 5 min NH₃ plasma treatment. When the plasma treatment was performed for 2 min followed by reaction with BSA, approximately 2% nitrogen and 1% bromine could be detected. It seems that there is a maximum in the amount of primary amino groups to be formed at the surface. These results can be explained by assuming at least four types of reactions:

(1) incorporation of primary amino groups;

(2) incorporation of nitrogen without the formation of primary amino groups;

(3) conversion of primary amino groups to other nitrogen-containing groups;

(4) formation of new functional groups accompanied by chain scission.

Processes 1 and 2 will be operative for short plasma treatment times. Processes 3 and 4 may be regarded as the effects of a plasma on an already plasma-treated surface. Oxygen may also play an important role in processes 3 and 4.

The amount of primary amino groups incorporated into the surface after treatment with the NH₃ plasma for 5 min was determined by NAA from the bromine content after reaction with BSA. A surface coverage of 0.5 ± 0.2 Br atoms nm^{-2} was found. With the aid of the Br/N ratio (obtained from *Table 1*) a surface coverage of about 1.3 N atoms nm^{-2} can be calculated. From the density of PS it can be estimated that the mean surface coverage of styrene units is 3.3 units nm^{-2}. Thus theoretically, after 5 min NH₃ plasma one of every three units would have reacted with nitrogen. However, the nitrogen does not necessarily have to be situated at the first monolayer. When the electron emission angle of the X.p.s. spectrometer is varied from 90 to 20° with respect to the sample surface, the X.p.s. information depth decreases by a factor of 3, which resulted in a 1.5-fold increase of the N_{1s}/C_{1s} intensity ratio of the surface treated with the NH₃ plasma for 10 min. This indicates that the nitrogen incorporation occurs at least in the uppermost layers of the material, as expected.

Interaction of nitrogen and ammonia plasmas on bisphenol-A polycarbonate studied by X.p.s.

Table 2 shows some X.p.s. data of the surface of PC before and after plasma treatments for 10 min with NH₃ and 5 min with N₂. The interaction of the NH₃ plasma with PC differs from that with PS because after reaction with BSA in ethanol no bromine could be detected and the nitrogen disappeared from the surface. Furthermore, the amount of oxygen, originally present in the carbonate

Table 2 Percentage of elemental compositions relative to carbon ($= 100\%$) of a PC surface after various treatments

Treatment	N[a]	O[b]
No treatment	–	18.3
10 min NH₃ plasma	6.0	14.7
+ethanol	<0.5	16.0
5 min N₂ plasma	5.7	23.6
+ethanol	<0.5	18.6

[a] Determined from the N_{1s} and C_{1s} signals
[b] Determined from the O_{1s} and C_{1s} signals

group thus forming part of the main chain, decreases significantly. Therefore the loss of oxygen means probably scission of the polymer main chain. This agrees with the observation that the modification can be 'washed away' by an alcohol rinse.

PC is known to react with amines to form urethane structures[13]. To see whether NH₃ reacts with PC under plasma conditions, PC was treated with NH₃ without switching on the plasma. The X.p.s. spectrum of PC had not changed after this treatment thus the changes in *Table 2* are due to the plasma treatment.

After treatment with the N₂ plasma, the chain scission effects also observed after treatment with the NH₃ plasma were observed. Contrary to the effect of the NH₃ plasma treatment, a significant amount of oxygen was incorporated, a difference in the effects of both plasma treatments also observed with PS.

It may be concluded that the incorporation of nitrogen into the surface of PC by plasma treatments without chain scission is difficult compared with PS. These chain scissions are also observed after treatment of PC with H₂ and O₂ plasmas[13]. The ease of chain scission is probably due to the relatively reactive and/or labile carbonate group.

Interaction of nitrogen and ammonia plasmas on polystyrene studied by SSIMS

Figure 1a shows the positive ion spectrum between 10 and 140 a.m.u. of the surface of PS. It contains peaks which are typical of aromatic material and which are of relatively low intensity in spectra of aliphatic compounds. The most important among them are observed at 26, 38, 50, 51, 77, 91 and 115 a.m.u.[13,22] Such typical ions can also be observed above 140 a.m.u., but they are of lower intensity. After treatment with an NH₃ plasma for 5 min, the spectrum changes completely as shown in *Figure 1b*. The peaks described above exhibit a lower intensity, relative to other peaks in the spectrum. Among the peaks that have increased in intensity are peaks at 28, 30 and 42 a.m.u. They have an even mass which points to the incorporation of nitrogen and are also observed in other nitrogen-containing material[13,16]. These peaks can be assigned to HCNH⁺ (28 a.m.u.), H₂CNH₂⁺ (30 a.m.u.) and CH₂CNH₂⁺ (42 a.m.u.). The spectrum did not change very much after the surface was rinsed with ethanol, which agrees with the results from the X.p.s. experiments.

Figure 1c shows the positive ion spectrum obtained after 5 min of N₂ plasma treatment. Although there are small differences between *Figures 1b* and *c*, nothing points to the fact that *Figure 1b* belongs to a surface containing more primary amino groups than the surface of *Figure 1c*.

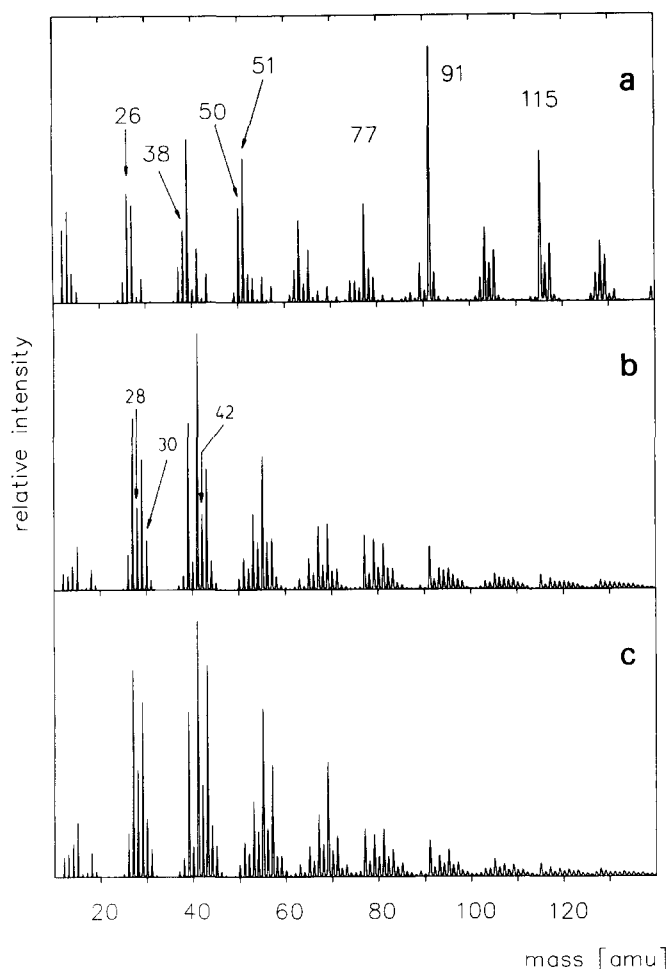PS does not contain oxygen to stabilize negative ions

Figure 1 Positive ion spectrum in the mass range 10–140 a.m.u. (a) Polystyrene, (b) polystyrene after 5 min NH₃ plasma treatment, (c) polystyrene after 5 min N₂ plasma treatment

Figure 2 Negative ion spectrum in the mass range 70–210 a.m.u. of polystyrene treated with an NH₃ plasma followed by reaction with 5-bromosalicylaldehyde

and is therefore not capable of forming negative ions providing structural information as observed in the negative ion spectra of for example PC and poly(ethylene terephthalate)[13,23]. The negative ion spectrum of PS shows only carbon cluster ions with structures C_n and C_nH ($n \geqslant 1$) observed at $n \times 12$ a.m.u. and $n \times 12 + 1$ a.m.u., respectively. These peaks are common to all polymers. After treatment with the NH₃ plasma, the incorporation of nitrogen can be detected from a new peak at 26 a.m.u. due to CN⁻. Furthermore, also oxygen can be detected from new peaks at 16 and 17 a.m.u. due to O⁻ and OH⁻, respectively. New peaks can also be found in the mass ranges of approximately 90–120 and 170–190 a.m.u. (*Figure 2*) of unknown origin. Due to the facts that probably several new structures are formed during the plasma treatment and that there is a lack of spectra of reference structures, it is very difficult to make peak assignments. After reaction with BSA the incorporation of bromine can be detected by peaks at 79 and 81 a.m.u. due to Br⁻, and at 158, 160 and 162 a.m.u. due to Br₂⁻. Furthermore, very weak peaks are found at 196 and 198 a.m.u., which can be assigned to the 2-cyano-4-bromophenolate anion (*Figure 2*). This anion contains part of the modified surface (namely the nitrogen atom in the cyanide group) and part of the original aldehyde. This gives extra proof for the formation of an imine at the surface as outlined in *Scheme 1*. More evidence for the fact
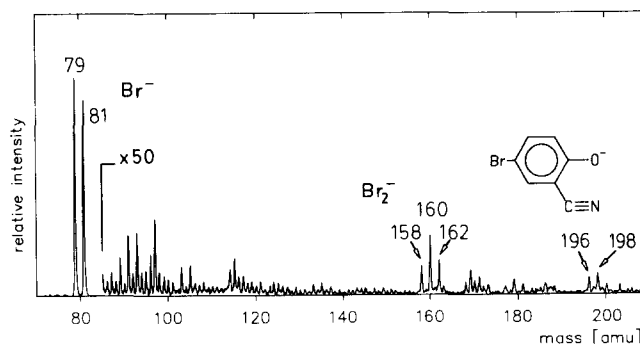
that this anion is formed from imine structures at the surface was obtained from the negative ion spectrum of the surface treated with salicylaldehyde. The 2-cyanophenolate anion (*Scheme 1*) was indeed detected at 118 a.m.u. (see also next section). Both anions could not be observed in the negative ion spectrum of the N₂-plasma-treated surface which was made to interact with one of the aldehydes. No effect of reactions with BSA or salicylaldehyde on the positive ion spectrum of the plasma-treated surfaces could be observed.

Interaction of nitrogen and ammonia plasmas on bisphenol-A polycarbonate studied by SSIMS

After treatment of PC with either plasmas for 5 min, changes were observed in the positive ion spectrum similar to those found with PS. After the modified surfaces had been rinsed with ethanol the original spectrum of PC was restored, which means that nearly all modified structures are washed from the surface. This observation was also made with X.p.s.

The negative ion spectrum of PC contains peaks due to characteristic ions formed from the repeating unit[13]. *Figure 3a* shows a part of the negative ion spectrum in which such ions at 117 and 133 a.m.u. are observed. The peak at 149 a.m.u. is due to the t-butylphenolate anion, originating from the polymer endgroup[13]. After treatment with the NH₃ plasma the spectrum becomes more complicated. Important new ions are observed at 119, 124, 126, 131 and 135 a.m.u. (*Figure 3b*). The ions observed at 119 and 135 a.m.u. are also found after treatment with an H₂ plasma and may arise after breaking of the bisphenol-A unit near the central carbon atom[13]. In this respect the NH₃ plasma resembles the H₂ plasma. Assignment of the peaks at 124, 126 and 131 a.m.u. is difficult. The first two peaks have an even mass which points to nitrogen-containing ions. *Figure 3d* shows marked spectral changes after treatment with the N₂ plasma, but formation of the above-mentioned ions is less pronounced in this case.

Only after treatment of the surface modified by the NH₃ but not the N₂ plasma with salicylaldehyde from the vapour phase (to avoid washing of modified structures from the surface by a solvent) did the peak at 118 a.m.u. (*Figure 3c*) increase in intensity due to formation of the 2-cyanophenolate anion (*Scheme 1*). This indicates that at least some primary amino groups are formed after treatment with the NH₃ plasma.

When PC reacts with amines, H₂ plasma or O₂ plasma, the carbonate bond is attacked, so that chain scission
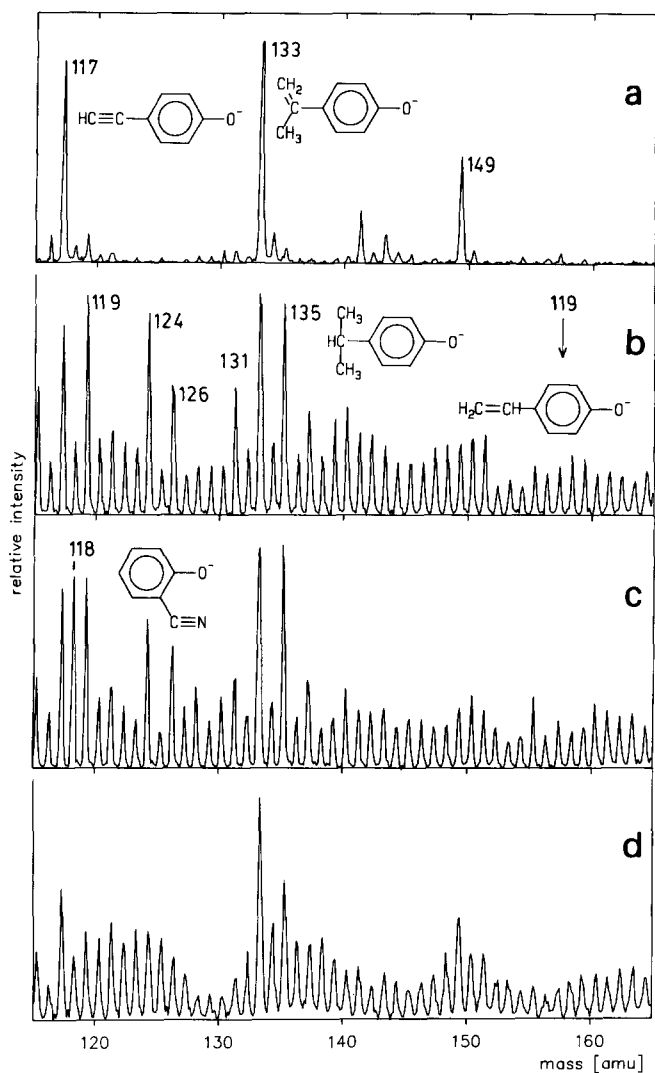
Figure 3 Negative ion spectrum in the mass range 115–165 a.m.u. (a) Bisphenol-A polycarbonate, (b) bisphenol-A polycarbonate after 5 min NH₃ plasma treatment, (c) bisphenol-A polycarbonate after 5 min NH₃ plasma treatment followed by a vapour phase reaction with salicylaldehyde, (d) bisphenol-A polycarbonate after 5 min N₂ plasma treatment

occurs and bisphenol-A terminated chains are formed. This new chain end gives rise to the formation of a peak at 227 a.m.u. (the bisphenolate-A anion) in the negative ion spectra. This peak is absent in the spectrum of untreated PC[13]. This form of chain scission is also observed under the influence of both nitrogen-containing plasmas as well. In these cases too, the newly formed peak at 227 a.m.u. disappeared almost completely upon rinsing the surface with ethanol.

It is expected that NH₃ will react in the same way as amines with the carbonate bond resulting in the formation of bisphenol-A terminated chains[13]. After the PC surface was treated with NH₃ gas without switching on the plasma, the peak at 227 a.m.u. was not observed, showing that this reaction does not occur under the plasma conditions.

A severe problem observed in the negative ion spectra of plasma modified polymer surfaces is their increased affinity for contaminants compared with the parent surfaces. The latter surfaces are rather stable even when they are left for some time in laboratory air.

Comparison of the X.p.s. and SSIMS results reveals

that chemical changes such as the formation of new endgroups during chain scissions can be detected with SSIMS and not with X.p.s. With the aid of known cross-sections for the elements, quantitative determinations can be made with X.p.s. independent of which functional group containing such an element is present at the surface. Such 'cross-sections' are still not known for SSIMS in which they are determined by ionization efficiency and ion stability. They can be determined with the aid of fully characterized surfaces as has been done for signals observed from alumina surfaces covered by *p*-bromobenzoic acid[24]. In principle, the nitrogen contents of the surfaces can be calculated using the CN⁻ peak at 26 a.m.u. in the SSIMS spectra. It is still not known whether the formation probability of this ion is independent of the structure (e.g. primary amine, amide, nitro) it originates from. A lot of work has to be done with model surfaces to establish this.

ACKNOWLEDGEMENTS

REFERENCES

1   Clark, D. T. and Dilks, A. *J. Polym. Sci., Polym. Chem. Edn.* 1979, **17**, 957
2   Salvati, L., Hook, T. J. and Gardella, J. A. *Polym. Eng. Sci.* 1987, **27**, 939
3   Clark, D. T. and Wilson, R. *J. Polym. Sci., Polym. Chem. Edn.* 1983, **21**, 837
4   Briggs, D. *Polymer* 1984, **25**, 1379
5   Everhart, D. S. and Reilley, C. N. *Anal. Chem.* 1981, **53**, 665
6   Gerenser, L. J., Elman, J. F., Mason, M. G. and Pochan, J. M. *Polymer* 1985, **26**, 1162
7   Pochan, J. M., Gerenser, L. J. and Elman, J. F. *Polymer* 1986, **27**, 1058
8   Yasuda, H., Marsh, H. C., Brandt, S. and Reilley, C. N. *J. Polym. Sci., Polym. Chem. Edn.* 1977, **15**, 991
9   Everhart, D. S. and Reilley, C. N. *Surf. Interface Anal.* 1981, **3**, 126
10   Van Velzen, P. N. T. *Surface Sci.* 1984, **146**, 319
11   Briggs, D. *Surf. Interface Anal.* 1986, **9**, 391
12   Lub, J., Van Vroonhoven, F. C. B. M., Van Leyen, D. and Benninghoven, A. *J. Polym. Sci., Polym. Chem. Edn.* in press
13   Lub, J., Van Vroonhoven, F. C. B. M., Van Leyen, D. and Benninghoven, A. *Polymer* 1988, **29**, 998
14   Lub, J., Van Velzen, P. N. T., Van Leyen, D., Hagenhoff, B. and Benninghoven, A. *Surf. Interface Anal.* 1988, **12**, 53
15   Lub, J. *Proc. SIMS VI* (Eds. A. Benninghoven, A. Huber and H. W. Werner), Wiley, London, 1988, p. 1033
16   van Ooij, W. J., Brinkhuis, R. H. G. and Newman, J. *Proc. SIMS VI* (Eds. A. Benninghoven, A. Huber and H. W. Werner), Wiley, London, 1988, p. 635
17   Steffens, P., Niehuis, E., Friese, T. and Benninghoven, A. in 'Ion Formation from Organic Solids' Vol. 25 (Ed. A. Benninghoven), Springer Verlag, Berlin, 1983, p. 111
18   Steffens, P., Niehuis, E., Friese, T., Greitendorf, D. and Benninghoven, A. *J. Vac. Sci. Technol.* 1985, **A3**, 1322
19   Bletsos, I. V., Hercules, D. M., van Leyen, D. and Benninghoven, A. *Macromolecules* 1987, **20**, 407
20   Bruninx, E. and van Eenbergen, A. *Spectrochim. Acta* 1983, **38B**, 821
21   de Sorte, D., Gijbels, R. and Hoste, J. 'Neutron Activation Analysis', Wiley Interscience, London, 1972
22   Briggs, D. and Wootton, A. B. *Surf. Interface Anal.* 1982, **4**, 109
23   Brown, A. and Vickerman, J. C. *Surf. Interface Anal.* 1982, **8**, 109
24   Van Velzen, P. N. T. *Proc. SIMS VI* (Eds. A. Benninghoven, A. Huber and H. W. Werner), Wiley, London, 1988, p. 1013