Static secondary ion mass spectrometry analysis of polycarbonate surfaces. Effect of structure and of surface modification on the spectra

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The positive and negative ion mass spectra of the surfaces of polycarbonate derived from bisphenol A and polycarbonate derived from the bisphenol of acetophenone, and of bisphenol A and the bisphenol of acetophenone are presented. The spectra were obtained with a time-of-flight static secondary ion mass spectrometer. Comparison of the spectra of the four mentioned compounds made it possible to deduce the structures of characteristic ions. The interaction of amines with the surface of polycarbonate derived from bisphenol A could be analysed in a very detailed manner with the aid of the negative ion spectra. Some aspects of the interaction of hydrogen and oxygen plasmas with this polymer are discussed with reference to the spectra. Chain scissions were one of the processes occurring during the plasma treatments.

(Keywords: polycarbonates; static secondary ion mass spectrometry; ion formation; chemical surface modification; plasma treatment)

INTRODUCTION

The chemical structure of polymer surfaces can be analysed in great detail by means of static secondary ion mass spectroscopy (SSIMS). In the case of carbon chain polymers like poly(alkyl methacrylates), ions formed in the SSIMS experiment originate to an important extent from substituents linked to the carbon chain (e.g. ester groups in the case of poly(alkyl methacrylates))[1,2]. Ions formed from polymers in which hetero atoms form part of the main chain originate to an important extent from repeating units (e.g. poly(ethylene terephthalate) and polycarbonate)[3–5].

In order to gain more insight into the structure of the ions which are formed from polycarbonate derived from bisphenol-A I_A, a technologically important polymer, the positive and negative ion spectra of this polymer are compared with those of polycarbonate derived from the bisphenol of acetophenone I_B. In this way information about the chemical structure of typical ions can be obtained by comparing the difference in mass units of the ions originating from the two different polymers with the difference in chemical structure of both polymers. Furthermore, the spectra of these polymers are compared with the spectra of the corresponding bisphenols, which can be regarded as part of the repeating units. In this way one can discriminate between ions that are due to the structure of the repeating units and ions due to the polymer structure.

Because of its high surface sensitivity, SSIMS is a very suitable method for analysing chemically modified surfaces[5,6]. To determine the changes that occur in the spectrum of polycarbonate derived from bisphenol-A I_A after chemical modification of the surface, a reaction must be performed which produces well defined products that make interpretation of the spectra straightforward. Reaction with alkylamines is used for this purpose. Two new end groups are formed at the surface, one containing the bisphenolate-A moiety, the other containing the alkyl carbamate moiety[7,8].

Interaction of a plasma with a polymer surface is another way to modify the chemical structure of this surface. For example, a polymer surface brought into contact with an oxygen plasma will be oxidized. New, oxygen-containing groups are introduced at the surface. Much has been done to analyse the oxidized surfaces of polymers with X-ray photoelectron spectroscopy (X.p.s.)[9–11]. A lot of questions still remain about the chemistry involved in these plasma reactions. Plasma reactions with polymers with a relatively complex structure like polycarbonate derived from bisphenol A are less extensively investigated than reactions with polymers like polyethylene and polypropylene which have less complex chemical structures. This paper presents the spectra obtained from the surfaces of polycarbonate derived from bisphenol A treated with an electrode glow discharge in O_2 and in H_2. These spectra are compared with the spectra of the untreated surface in order to estimate which ions indicate oxidation (O_2 plasma) or reduction (H_2 plasma) of polycarbonate. An effort is made to deduce chemical changes due to the plasma treatments with information from the spectra.

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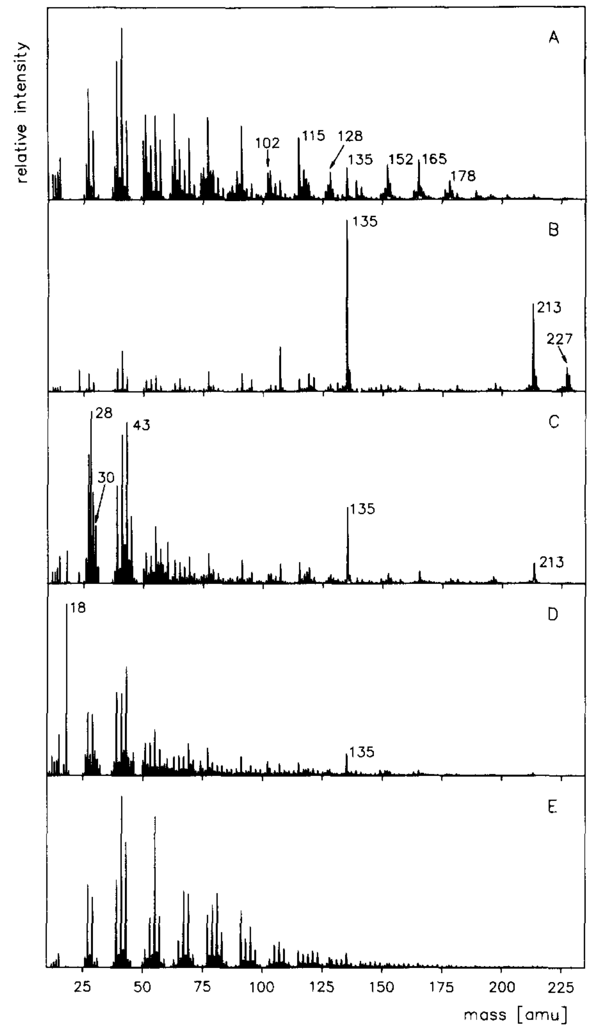


Figure 1 Positive ion spectra in the range 10–235 a.m.u. of polycarbonate I_A (A), bisphenol-A IV_A (B), polycarbonate I_A treated with n-propyl amine (C), polycarbonate I_A treated with an O_2 plasma for 2 min (D), and polycarbonate I_A treated with an H_2 plasma for 10 min (E)

EXPERIMENTAL

Materials. Polycarbonate derived from bisphenol A tert-butylphenol terminated ($\bar{M}_w = 34\,000$) was purchased from Aldrich Chemical Company. The iso-octyl-terminated polymer (Macrolon, $\bar{M}_w = 20\,000$) and the polycarbonate derived from the bisphenol of acetophenone were purchased from Bayer. Bisphenol A and the bisphenol of acetophenone were kindly provided by Mr G. Werumeus Buning of our laboratory. All other chemicals were purchased from Aldrich Chemical Company and used as such.

Sample preparation. The polymers were spin-coated at 2000 rev min^{-1} on copper or silica supports from 3% solutions in chloroform. The thickness of these polymer layers was about 0.5 μm, which avoids surface charging during the SIMS experiment. The bisphenols were spin-coated in the same way from 6% solutions in ethanol.

The reactions with n-propylamine and n-butylamine were performed by leaving the coated layer for 45 min in a 2% hexane solution of the amines at room temperature. Subsequently, the samples were thoroughly rinsed with hexane or ethanol and spun dry.

Instrumental. The time-of-flight SIMS mass spectrometer used has been described before[12–14]. 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 were performed on a Leybold Heraeus apparatus equipped with an Al Kα source.

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

RESULTS AND DISCUSSION

The positive and negative ion spectra of both polymers and their corresponding bisphenols. Figures 1A and *2A* show the positive spectra of polycarbonate derived from bisphenol-A I_A and polycarbonate derived from the bisphenol of acetophenone I_B, respectively. Both spectra are dominated by peaks which are typical of a polymer that contains aromatic groups. These peaks are found at 25, 26, 37, 38, 50, 51, 77 and 91 a.m.u. in the lower mass range. The other peaks in the lower mass range are due to carbon- and hydrogen-containing ions which are found in the positive spectra of nearly all polymers. In the higher mass range, signals due to aromatic ions are found, some of which are outlined in *Scheme 1*. These peaks are also found in the positive spectra of polystyrene but not in non-aromatic polymers like polyethylene or poly(methyl methacrylate)[2,15]. Although the relative intensities of these ions differ in the spectra of both polycarbonates,

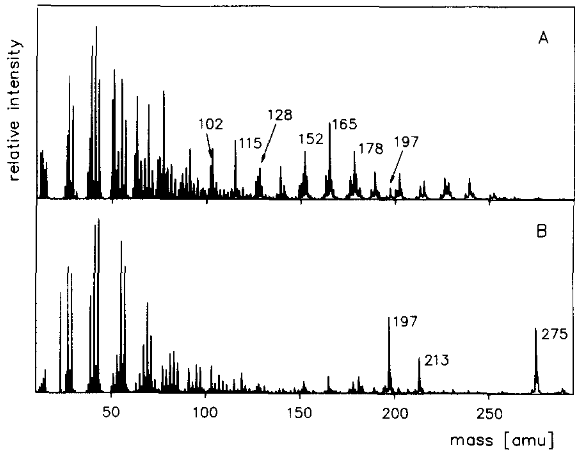
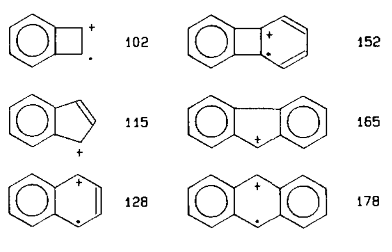
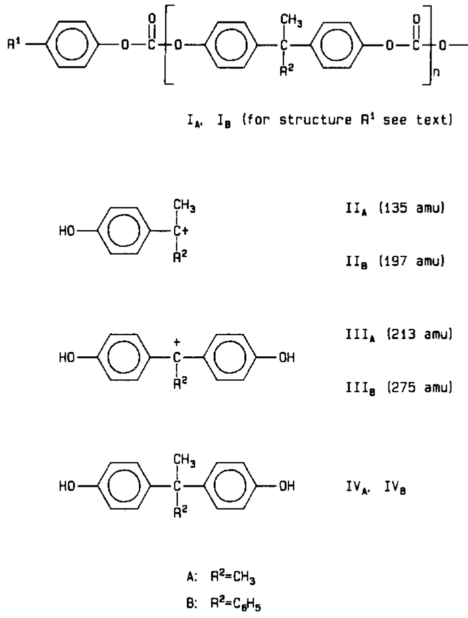


Figure 2 Positive ion spectra in the range 10–295 a.m.u. of polycarbonate I_B (A), and the bisphenol derived from acetophenone IV_B (B)



Scheme 1



Scheme 2

they are not very useful to determine the chemical structure of both polymer surfaces.

In the spectrum of polycarbonate I_A a peak of moderate intensity is found at 135 a.m.u. which can be attributed to ion structure II_A (*Scheme 2*). Also ion II_B can be detected as a peak at 197 a.m.u. in the spectrum of polymer I_B. These ions are characteristic for the structure of the repeating units of both polymers (see below).

The positive ion spectra of the two bisphenols IV_A and IV_B, which are used to prepare the two corresponding polymers I_A and I_B by reaction with phosgene or diphenylcarbonate[16], are shown in *Figures 1B* and *2B*, respectively. By comparison of both spectra it is very easy to determine the structure of most ions in the relatively high mass range, taking into account the mass difference between a methyl group and a phenyl group of 62 a.m.u. In both spectra peaks are found that are due to the molecular cation and the molecule minus hydride: at 228 and 227 a.m.u. from bisphenol IV_A and at 290 and 289 a.m.u. from bisphenol IV_B. When these molecular cations lose one methyl group, ions III_A (213 a.m.u.) and III_B (275 a.m.u.) are formed. When the molecular cation of IV_B loses a phenyl group, again ion III_A is formed. Finally, when both molecular cations lose a 4-hydroxyphenyl group, ion II_A (135 a.m.u.) is formed from IV_A and ion II_B (197 a.m.u.) from IV_B. These two ions had already been detected in the spectra of the two corresponding polymers.

Comparison of the results from *Figures 1A* and *2A* with those of *Figures 1B* and *2B* shows that in the case of the polymers the positive spectra are almost entirely formed from peaks due to ions outlined in *Scheme 1*, whose structures are independent of the polymer structure, while both bisphenols give rise to relatively intense peaks due to ions whose structure depends on the bisphenol structure and peaks of relatively low intensity due to the ions of *Scheme 1*. Two reasons are proposed for these differences:

(1) Cations formed from the bisphenols can desorb immediately from the surface while cations on the polymer surface are still linked to the non-volatile polymer backbone and desorb only when at least one bond is broken, which may occur with rearrangements.

(2) The ions with structural information about the repeating unit of the polymer (*Scheme 2*) contain at least one phenolic hydroxyl group. The hydrogen atom of this hydroxyl group is not present in the parent polymers which means that the latter ions are also rearrangement products when they are formed from the polymer. This makes their probability of formation less than in the case of the bisphenols.

The negative spectra were recorded beginning from 60 a.m.u. because below this value only relatively intense signals are observed from O^-, OH^-, C_n^- and C_nH^-, which do not contain structural information.

Figure 3A shows the negative ion spectrum of polymer I_A. Comparison of this spectrum with that of the corresponding bisphenol IV_A shown in *Figure 3B*, reveals some similarity. The spectra contain the same peaks at 93, 117, 133 and 211 a.m.u. Apart from these peaks, the deprotonated molecular ion V_A is found as an intense peak at 227 a.m.u. in the spectrum of the bisphenol. The same similarity is found when the negative ion spectrum of polymer I_B (*Figure 4A*) is compared with the spectrum of its corresponding bisphenol IV_B (*Figure 4B*). *Scheme 3* gives the structures of the most important negative ions.

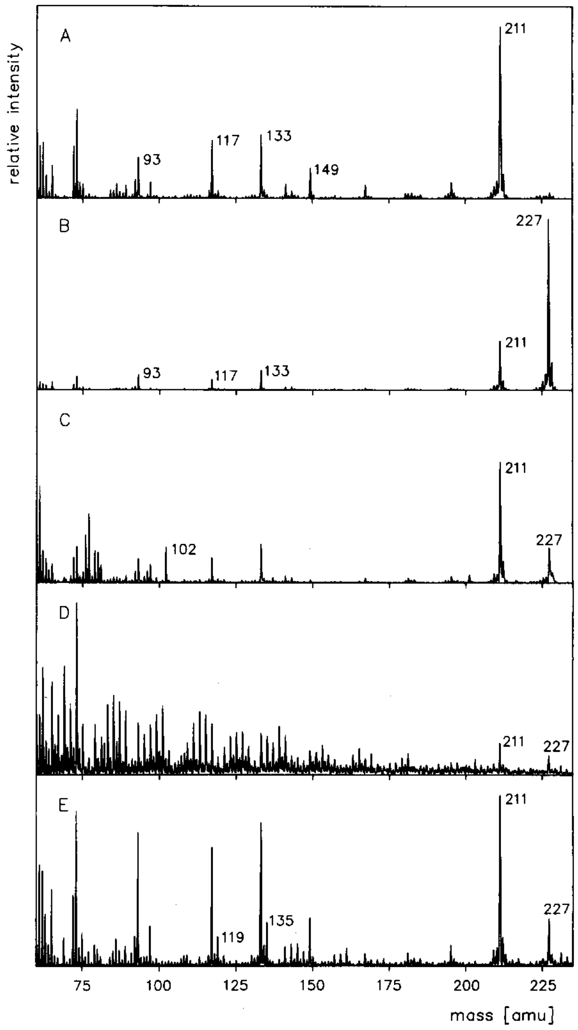


Figure 3 Negative ion spectra in the range 60–235 a.m.u. of polycarbonate I_A (A), bisphenol-A IV_A (B), polycarbonate I_A treated with n-propyl amine (C), polycarbonate I_A treated with an O_2 plasma for 2 min (D), and polycarbonate I_A treated with an H_2 plasma for 4 min (E)

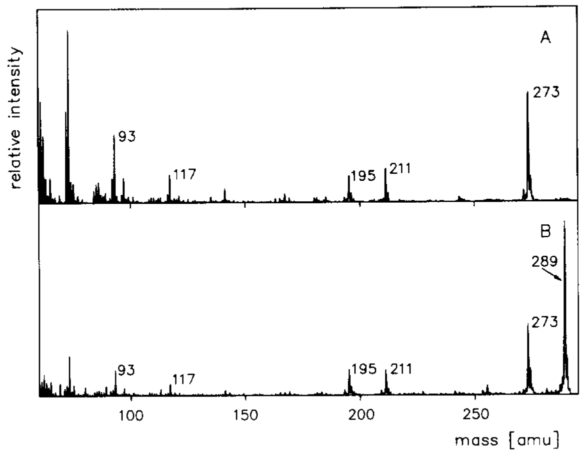
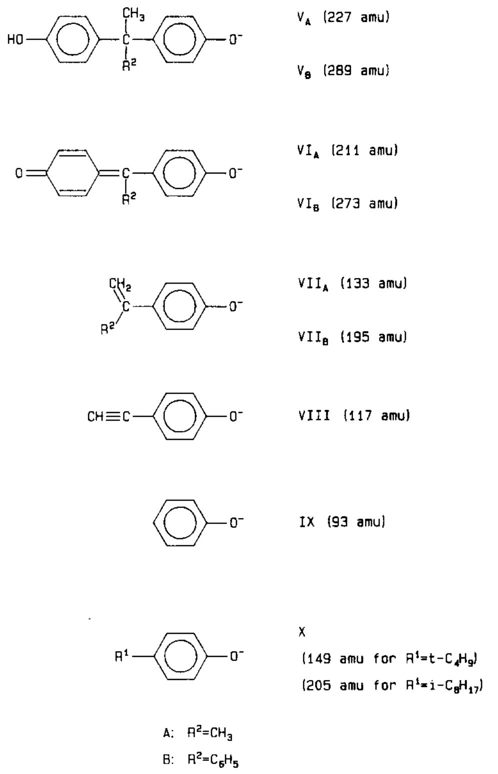


Figure 4 Negative ion spectra in the range 60–295 a.m.u. of polycarbonate I_B (A), and the bisphenol derived from acetophenone IV_B (B)



Scheme 3

The results for polycarbonate I_A are similar to those found by Briggs[5]. In that study, the peak at 117 a.m.u. was attributed to the 4-isopropylidenephenyl anion. If this were true, one would expect a peak at 179 a.m.u. due to the phenylethylidenephenyl anion in the spectrum of polymer I_B. This is not the case, in fact a peak at 117 a.m.u. is again found due to the oxygen-containing anion VIII. All the ions outlined in *Scheme 3* contain at least one oxygen atom which stabilizes the negative charge. Unstabilized anions have little or no intensity in the negative ion spectra, as was also concluded from the negative ion spectra of poly(alkyl methacrylates)[1].

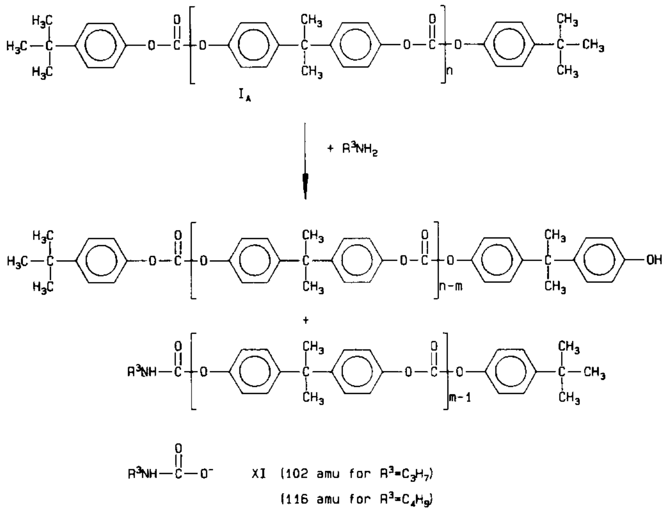
The peak at 149 a.m.u. in *Figure 3A* is due to the t-butylphenolate anion (X). This ion is formed from the end groups of the polymer chain ($R^1 = C_4H_9$ in *Schemes 2* and *3*). If a negative ion spectrum is taken from polycarbonate I_A, which contains end groups made from *p*-iso-octylphenol ($R^1 = C_8H_{17}$ in *Schemes 2* and *3*), a peak is detected at 205 a.m.u. in accordance with the mass of the *p*-iso-octylphenolate anion (X). The end groups of polycarbonate I_B are formed from phenol ($R^1 = H$ in *Scheme 2*). The phenolate anion (93 a.m.u.) which might be formed from this end group cannot be distinguished from the phenolate anion already formed from the bisphenol structure.

In contrast to the positive ions formed from both polymers, rearrangement reactions do not play an important role in the formation of negative ions. The absence of the anions V_A and V_B in the spectra of polymer I_A and polymer I_B, respectively, shows that even a surface reaction or rearrangement during ion formation to form a hydroxyl group from a carbonate group does not occur. In the following sections use will be made of this observation. The formation of the phenolate anion IX found at 93 a.m.u. in the negative ion spectra of all species, shows that in this case rearrangement with the formation of a C–H bond is possible. It is not yet clear which factors determine whether hydrogen shifts occur or not.

From comparison of the negative as well as the positive spectra of the polymers with their corresponding bisphenols, it must be concluded that there are no ions containing the carbonate group itself. The difference between the spectra of the bisphenols and the polycarbonates is determined by a difference in fragmentation of the bisphenol units free or linked by carbonate groups.

It can be concluded that negative ion spectra of polycarbonates are more reliable for analysis than the positive spectra, a conclusion which holds for more polymer systems[1,4,5].

Reactions of polycarbonate derived from bisphenol-A with alkylamines. Figure 1C shows the positive spectrum of polycarbonate I_A treated with a dilute solution of n-propylamine in hexane. The reaction that occurs is outlined in *Scheme 4*. If n-butylamine is used instead of n-propylamine, nearly the same spectrum (not shown) is obtained, only the peak at 43 a.m.u. due to the propyl cation ($R^3 = C_3H_7$) is less intense and the peak at 57 a.m.u. due to the butyl cation ($R^3 = C_4H_9$) is more



Scheme 4

intense. The incorporation of nitrogen in the surface is clearly apparent from the appearance of a peak at 28 a.m.u. due to H_2CN^+ and a peak at 30 a.m.u. due to $CH_2NH_2^+$. The intensity of the peak at 135 a.m.u., due to ion II_A is greatly enhanced. Furthermore, a peak at 213 a.m.u. is observed, due to ion III_A which has a very low intensity in the spectrum of the untreated surface (*Figure 1A*). In *Scheme 4* it is shown that hydroxyl groups are formed as new end groups of the scissored polymer chains. This means that ion II_A can be formed without rearrangement and consequently its intensity is high. The extra hydrogen needed for the formation of ion III_A from the new end group is probably obtained by the same mechanism as for the formation of ion II_A from the untreated polymer. In fact, if the reaction proceeds, these ions may also arise by formation of pure bisphenol A (IV_A). This is not believed to be the case here because the nitrogen content is very low; it could not be detected with X.p.s. Furthermore, after the surface was rinsed with ethanol, a good solvent for bisphenol A, the spectrum did not change.

The negative spectrum of polycarbonate I_A treated with n-propylamine is shown in *Figure 3C*. Comparison of this spectrum with that of the untreated polymer (*Figure 3A*), reveals two new peaks at 102 and 227 a.m.u. Furthermore, a new peak at 26 a.m.u. (not shown in *Figure 3C*) due to CN^- is observed. If the reaction is performed with n-butylamine, a peak at 116 a.m.u. instead of 102 a.m.u. is detected. The structure of the ions which give rise to these peaks with even mass is shown in *Scheme 4* (structure XI). They provide direct evidence for the formation of the urethane bond at the surface. The new end group with a hydroxyl group formed after reaction causes the formation of ion V_A resulting in the peak at 227 a.m.u. This peak will only arise when the carbonate group is broken and thus indicates chain scission at the surface. The intensity of the peak at 149 a.m.u. (ion X, $R^1 = C_4H_9$) due to the original end group decreases after reaction with the amines. This is probably caused by the fact that reactions on the carbonate group near this end group will result in the formation of low molecular weight species containing this end group, which may dissolve during the reaction or disappear when the surface is rinsed with solvent after the reaction. Because the end groups are more mobile than the rigid polymer chain at the surface, it is not unlikely that the carbonate groups next to these end groups will be more accessible for reaction than the carbonate groups further in the polymer chain. In that case the end groups will be cut preferentially from the polymer chain.

It can be concluded that the 'reaction products' of the reaction outlined in *Scheme 4*, which in fact is an organic synthesis on very small scale, can be analysed by means of SSIMS. The negative ion spectra in particular are very informative about the structure of the newly formed chemical groups.

Effect of oxygen plasma. After polycarbonate I_A was brought into contact with an electrode-oxygen discharge for 0.5 or 2.0 min, the SIMS spectra shown in *Figures 1D* and *3D* were obtained from the modified polymer surface. Comparison of the positive spectrum (*Figure 1D*) with the spectrum of the unmodified surface (*Figure 1A*) reveals two important effects. First, a relatively strong signal at 18 a.m.u. is observed and second, the structural characteristic ions II_A at 135 a.m.u. and III_A at 213 a.m.u. are more abundant. The latter two masses may point to chain scission (see previous section).

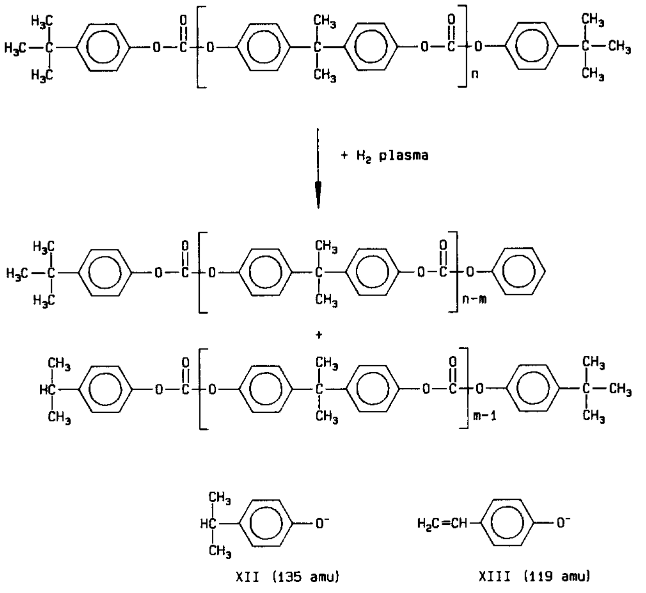
The mass at 18 a.m.u. (H_2O^+) might be due to water adsorbed to the surface or to some oxygen containing functional group which may be formed by oxidation of the polymer by the plasma. After the sample was dipped in water or ethanol, the signal at 18 a.m.u. decreased in intensity as well as the signals at 135 and 213 a.m.u. Therefore it is difficult to distinguish whether the signal at 18 a.m.u. is due to adsorbed water or to some new structure at the surface. In fact after the water or ethanol treatment the spectrum looks more like the spectrum of the untreated surface (the spectrum of this surface was not changed after a water treatment). Probably some of the modified structures have been washed from the surface. This effect is common to polymers modified by oxygen plasmas or corona treatments[10,17].

In the negative spectrum of the modified surface (*Figure 3D*) two important effects can be noticed when this spectrum is compared with that of the unmodified surface (*Figure 3A*). It is observed that the few peaks which form the negative spectrum of the parent polymer are now surrounded by a variety of peaks. From the masses of these peaks it is not easy to deduce ion structures, let alone a structure for the modified polymer surface. Probably a lot of oxygen-containing functional groups are formed on the surface. Results of this kind are also found with polycarbonate and a variety of polymers by means of X.p.s. analysis[11]. Fragmentation products of these structures may result in the large amount of new masses in *Figure 3D*.

A new peak is found at 227 a.m.u. (ion V_A) which points to chain scission at the carbonate group (see previous section). It is not unlikely that under the influence of the plasma treatment and subsequent reactions, the carbonate bond will be broken and bisphenol A terminated material of low molecular weight may be formed. The changes in the negative spectrum due to the plasma treatment disappeared partly after a water or ethanol dip, just as in the positive spectrum. Probably, low molecular weight material that was formed as described above, or by other reactions which cleave the polymer chain, may have been washed from the surface.

Effect of hydrogen plasma. Different stages of surface modification of polycarbonate I_A can be distinguished by varying the treatment time with an electrode-hydrogen discharge. After 2–4 min an increase is observed in the intensities of the peaks at 135 (ion II_A) and 213 a.m.u. (ion III_A) in the positive spectrum (not shown). This may point to chain scission (i.e. formation of bisphenolate A containing end groups; see previous sections).

In the negative spectrum a peak at 227 a.m.u. is observed (*Figure 3E*), probably due to ion V_A, which agrees with the observations in the positive spectrum concerning chain scission. In addition, two new peaks are found at 119 and 135 a.m.u. If polycarbonate I_B is treated with a hydrogen discharge, two new peaks are found at 119 and 197 a.m.u. It seems that the ions with masses of 135 and 197 a.m.u. have some structural resemblance with ions VII_A (133 a.m.u.) and VII_B (195 a.m.u.), respectively. The same may be true of the ion with mass 119 a.m.u. which can be related to ion VIII (117 a.m.u.). In all cases a mass difference of 2 a.m.u. is found. These new ions may be reduced forms of ions VII_A, VII_B and VIII originating from hydrogenated aromatic rings in the



Scheme 5

polymer. However, no reduced forms of ions VI_A and VI_B are found. This may be explained by assuming that such ions have a low formation efficiency and/or stability, but this is not very likely. A second explanation for mass differences of 2 a.m.u. may be another form of chain scission that is operative during the plasma treatment. Scission at the isopropylidene moiety will result in end groups containing phenolate and isopropylphenolate (*Scheme 5*). The latter end group will give rise to formation of the isopropylphenolate anion XII (135 a.m.u.). This ion may lose hydrogen, hence forming ion VII_A (133 a.m.u.), or lose methane with the formation of ion XIII (119 a.m.u.). In this case it is clear that an ion with a mass of 2 a.m.u. higher than that of ion VI_A will not be formed.

Spectra of selected model compounds should be recorded to find a definitive explanation.

After more than 10 min plasma treatment, the positive spectrum of *Figure 1E* was recorded. The intensity of the ions that are typical of an aromatic polymer (as discussed earlier) have decreased, probably due to hydrogenation of the aromatic rings. The negative ion spectrum (not shown) shows that nearly all characteristic ions have disappeared without the new ones appearing. Various processes probably occurring simultaneously may explain these observations:

(1) If the bisphenol-A units of the polymer were hydrogenated completely, a new polymer should be obtained which would form alkanolate anions instead of the substituted phenolate anions (V, VI, VII, VIII and IX) during the SIMS experiment. The former ions are less stable or are formed less easily, as could be estimated from SIMS experiments with selected polymethacrylates[18].

(2) The hydrogenation may not be complete, hence a lot of ions with various mass units will be generated, resulting in an overall low intensity of peaks.

(3) Other reactions may play a role; for example deoxygenation. Deoxygenated species will not form intense peaks in the negative ion spectra, as shown by the spectra of polystyrene and polypropylene[15]. The oxygen atom is necessary to stabilize the negative charge.

When the surfaces treated with hydrogen plasma were dipped in ethanol, nearly all effects of this treatment disappeared. The positive spectrum of this 'cleaned' surface is identical with that of the untreated surface and only the negative ion spectrum differs from that of the untreated surface by a small peak at 227 a.m.u., possibly a remnant of the chain scission.

It is clear that plasma treatments are not easily understandable forms of changing the chemical structure of the polycarbonate surface. At least, the treatment with hydrogen reveals molecular information (end group determination) indicating chain scission and thus the surface properties. Such results cannot or only with difficulty be obtained with other analytical techniques[6].

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