Surface modification of polycarbonate by u.v. light as studied by TOF-SIMS

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(Received 25 June 1992)

In this paper time-of-flight secondary ion mass spectrometry is used to study the chemical modification, upon exposure to u.v. light of 185 and 254 nm in an Ar atmosphere, of the surfaces of polycarbonate derived from bisphenol-A (PC-A) and from the bisphenol of acetophenone (PC-B). On irradiation with u.v. light, the polycarbonates show main chain scissions and photo-oxidative reactions. By this treatment hydroxyl groups are introduced on the polycarbonate surface, which is confirmed by chemical derivatization reactions. In addition, evidence is presented for the occurrence of a Photo-Fries rearrangement.

(Keywords: time-of-flight secondary ion mass spectrometry; polycarbonate; photodegradation)

INTRODUCTION

Chemical surface modification is an important method for obtaining desired surface properties of a particular material without changing the surface morphology and bulk properties[1].

For polymeric materials these properties, for example the ability of the material to adhere to or detach from another material, have been changed by a large number of different techniques, e.g. plasma and corona treatment or oxidation via wet chemical treatments[1,2]. Chemical modification by u.v. light is a less frequently used technique[3–5]. The use of far-u.v. light in particular gives the opportunity of limited penetration depth of the light due to a high absorption by polymers at these wavelengths and a high quantum yield for bond breaking[3,5].

In the last decade a number of studies have been performed on the photodegradation of polycarbonate derived from bisphenol-A (PC-A)[6,7]. Upon irradiation with wavelengths of 254–365 nm in vacuum, PC-A degrades by the Photo-Fries reaction shown in *Scheme 1* and by chain scission[6–9]. By this degradation phenylsalicylate, dihydroxybenzophenone and, together with loss of CO or CO_2, mono- or dihydroxybiphenyl, hydroxydiphenylether groups and phenolic end-groups are generated. Below 240 nm chain scission is the major pathway[5]. In the presence of oxygen the photo-products are easily oxidized[6,7].

In the previous studies, u.v., *F*Ti.r. and X.p.s. have been used for analysis of the u.v. irradiated polycarbonate surfaces. In the present study the photochemistry of PC-A and the polycarbonate derived from the bisphenol of acetophenone (PC-B) is studied with the more surface-sensitive technique of static secondary ion mass spectrometry (static-SIMS) to provide additional information on the chemical changes upon u.v. light exposure in the upper molecular layers of the polymer surface. Static-SIMS, particularly when used in combination with a time-of-flight (TOF) mass analyser, has proved to be a very versatile technique for characterizing the upper molecular layers of almost every material[10–15]. Recently, polycarbonate surfaces after plasma treatments and reactions with alkylamines have been studied with TOF-SIMS[10,16,17]. Detailed information about the chemical structure of the polymer and its end-groups after the modifications could be given.

EXPERIMENTAL

Sample preparation

Solutions (6% w/v) of polycarbonate derived from bisphenol A (t-butylphenol terminated; $M_w = 34\,000$) and from the bisphenol of acetophenone (PC-A and PC-B, respectively) in chlorobenzene were spin-coated at 2000 rev min^{-1} on a silicon wafer with a 20 nm thermal oxide surface layer. PC-A was obtained from the Aldrich Chemical Company and PC-B was kindly provided by Mr G. Werumeus Buning of our laboratory. All other chemicals were purchased from the Aldrich Chemical Company and used as received. The silicon wafer was cleaned by treatment with u.v./ozone for 10 min[10,11]. The polymer layer thickness was about 0.5 μm. In the same way a thin PC-A layer ($\sim$1 nm) on Ag (freshly prepared by vapour deposition on a silicon wafer) was prepared from a solution (0.05% w/v) of PC-A in chlorobenzene.

The samples were irradiated with u.v. light with a low pressure quartz–mercury vapour lamp which generates u.v. emissions at wavelengths of 185 and 254 nm with an intensity of 1.5 mW cm^{-2} and 15 mW cm^{-2}, respectively, at a distance of 2.54 cm. The distance from the samples to the lamp was about 2 cm. The irradiations were performed in argon and air atmospheres in a closed vessel

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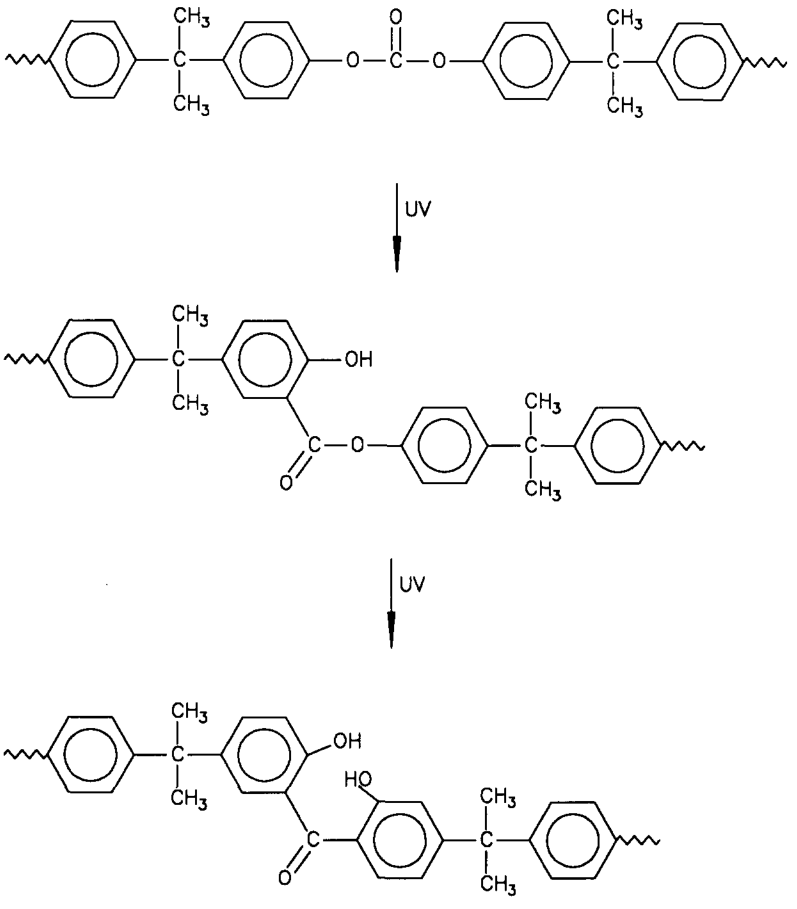


Scheme 1 Photo-Fries reaction of PC-A

with a quartz window. Before the irradiations the samples were exposed to a vacuum ($<10^{-6}$ mbar) for several hours to evaporate solvent remnants.

The corona-discharge treatment was performed with the Tantec Model HV05-2 system, composed of a power supply (max. 350 W operating in the 20–30 kHz frequency range), a transformer (14 or 28 kV) and an electrode. The samples were laid on an insulated ground plate (counter-electrode) and the corona-discharge (with maximal power) was applied by moving a wire loop electrode over the sample surface for a particular time.

TOF-SIMS

The chemical composition of the outermost monolayers of polymer substrates is analysed with a static-SIMS apparatus obtained from Ion TOF GmbH[11]. During the measurements, ions are generated from these surfaces by bombardment of the surface with a beam of primary Ar^+ ions of low ion dose (10^{12} ions cm^{-2}) and an energy of 10 keV. The spot diameter of the primary ion beam is approximately 50 μm. The secondary ions are accelerated to a few kilo-electron-volts and mass-separated in a Reflectron-type TOF mass analyser described elsewhere[11,18,19]. Under these conditions the SIMS instrument operates within the static limit, i.e. the probability that an ion will hit a previously bombarded area is negligible. The analysis depth of this technique is in the order of a few monolayers (about 1 nm), its sensitivity is in the range of parts per million of a monolayer. The mass accuracy for the experiments is in most cases better than 50 ppm.

RESULTS AND DISCUSSION

Static-SIMS spectra of non-modified polycarbonate surfaces have been discussed in previous papers[16,17,20,21]. These previous studies were performed with a low mass resolution TOF instrument. The structures proposed in those papers for the static-SIMS fragment ions and the Ag^+ cationized neutral fragments[20] are in agreement with the accurate masses of the peaks due to these ions obtained in this study with the Reflectron-type mass spectrometer with higher mass resolution. The spectra and some of the main static-SIMS fragment ions for PC-A are shown in *Figures 1a* and *2a*.

Thick polycarbonate layers on silicon wafers

From the static-SIMS spectra of PC-A before and after u.v. irradiation in Ar, the following changes due to the 20 min u.v. irradiation are observed (see *Figures 1* and *2* for the spectra and the most probable ion structures).

In the positive spectra:

(a) the detection of new peaks at m/z 121 and 161;
(b) an intensity increase of the peaks at m/z 43 (CH_3CO^+) and 135 relative to the aromatic $C_xH_y^+$ peaks in the positive spectra.

In the negative spectra:

(a) the detection of a new peak at m/z 135;
(b) an intensity increase of the peaks at m/z 92, 108, 109, 121 and 227 relative to the characteristic PC-A peaks at m/z 93, 117, 133, 149 and 211;

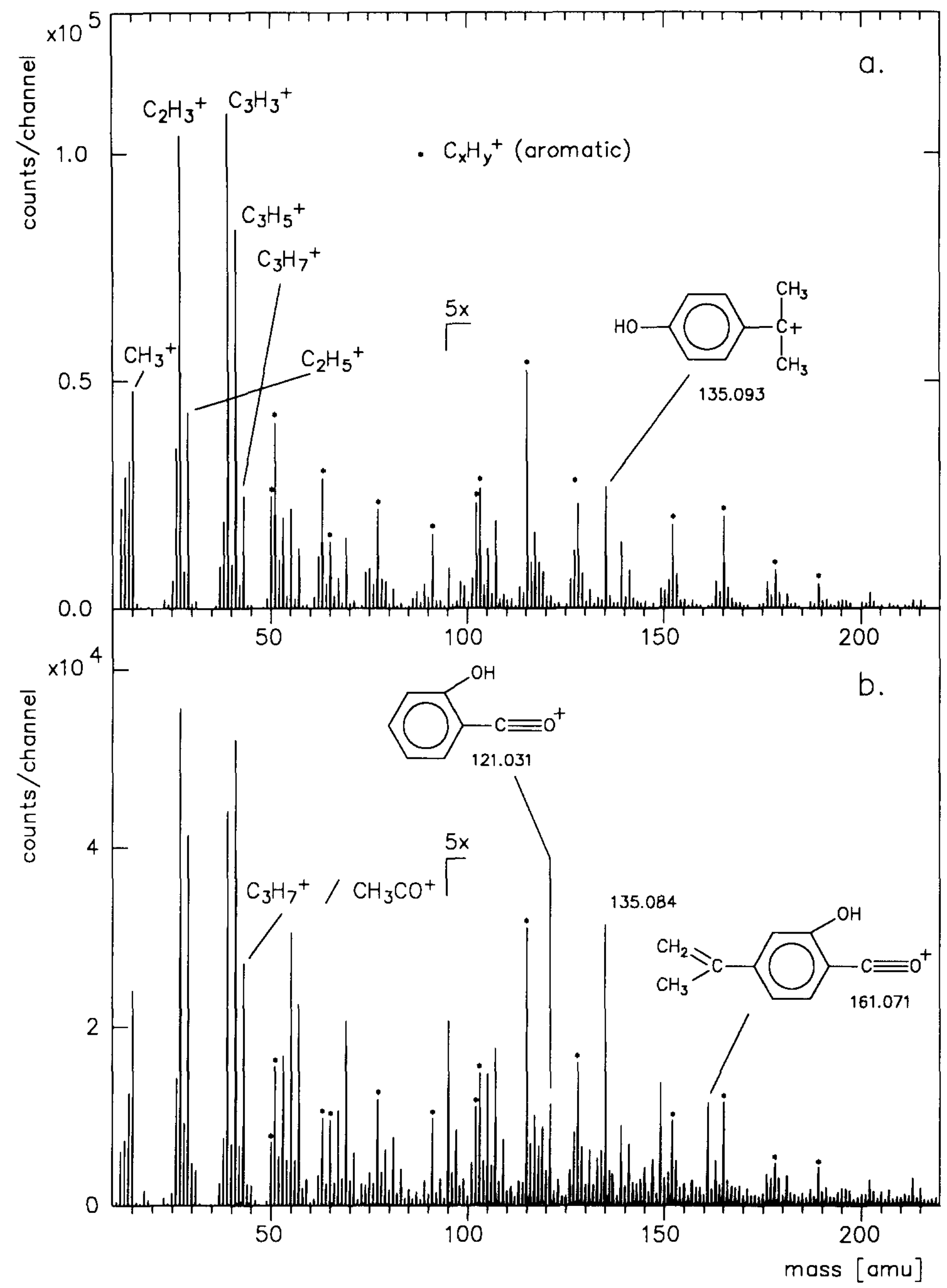


Figure 1 Positive static-SIMS spectra of a thick layer of PC-A on a silicon wafer (a) before and (b) after 20 min u.v. irradiation in Ar

(c) an intensity decrease of the peaks at *m/z* 149 and 211 (characteristic for the PC-A end-group and repeating unit, respectively) relative to the other PC-A peaks in the negative spectra.

After prolonged irradiation (>60 min) the spectra of PC-A show that almost all characteristic peaks have disappeared without the generation of new peaks. Rinsing the irradiated surfaces with ethanol gives an increase in intensity of the characteristic PC-A peaks and the spectra resemble more those of the non-irradiated surface.

Similar changes are observed for PC-B. However, in the positive spectra the peak at *m/z* 135 for PC-A is observed at *m/z* 197: one of the methyl groups is exchanged by a phenyl group. In the negative spectra the peak at *m/z* 135 for PC-A is observed both at *m/z* 135 and 197, in agreement with a structure in which only one methyl group is present.

The observations in the static-SIMS spectra point to three, possibly related, reactions during the photolysis of the polycarbonates. The first reaction is oxidation of the polymer due to the formation of CH_3CO^+ (*m/z* 43) and $CH_3CO–C_6H_4–O^-$ (*m/z* 135) ions. A reaction scheme for the formation of these ions is given in *Scheme 2*.

A second reaction, probably as a result of oxidation and the Photo-Fries pathway, is chain scission with the formation of polycarbonate molecules with bisphenol-A end-groups ($–O–C_6H_4–C(CH_3)_2–C_6H_4–OH$ in the case of PC-A) due to observation of *m/z* 135 cations and *m/z* 227 anions and a decrease of peaks from original end-groups. Similar observations are made for oxygen plasma treatment of PC-A[16] and corona-discharge

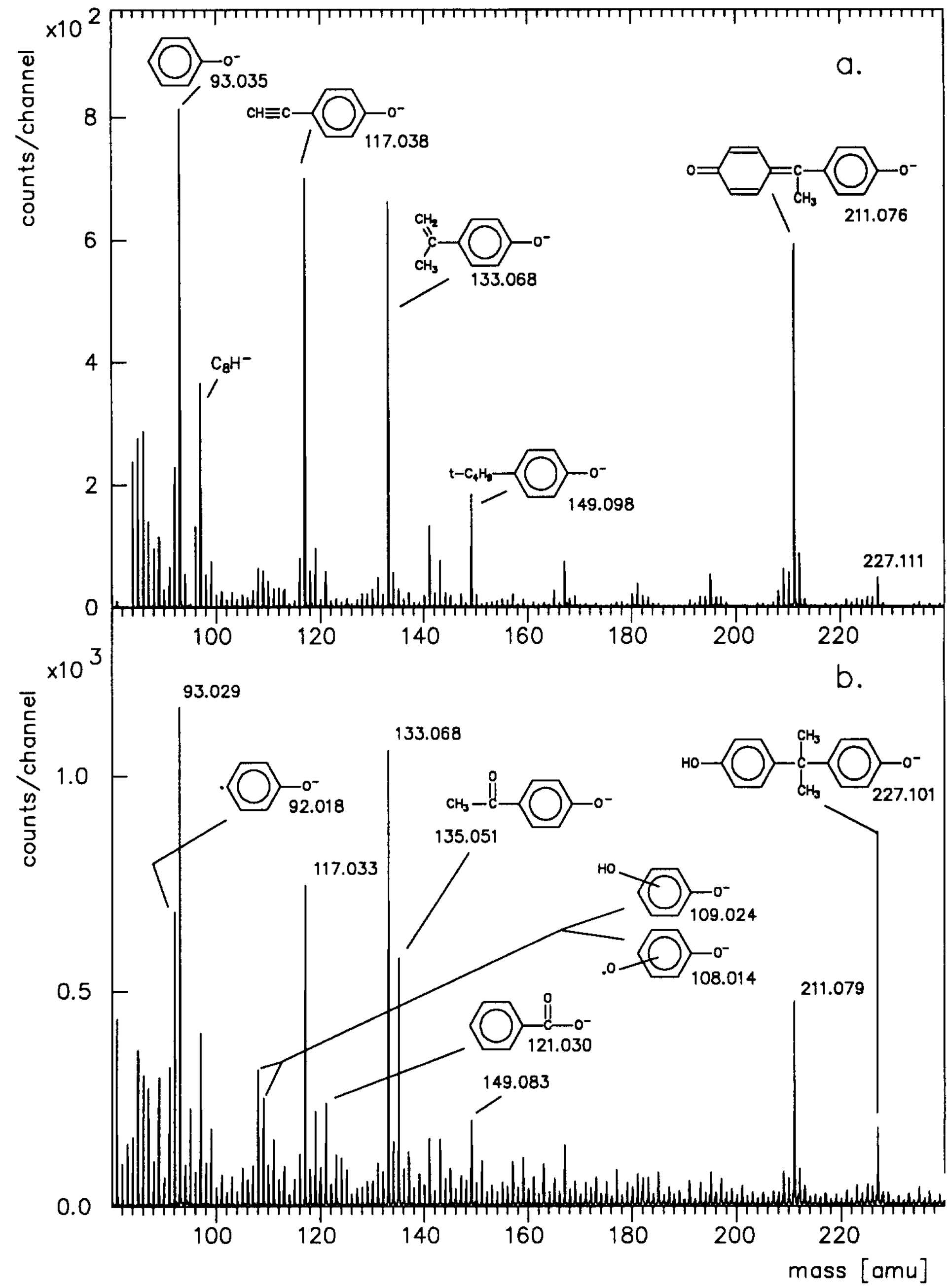


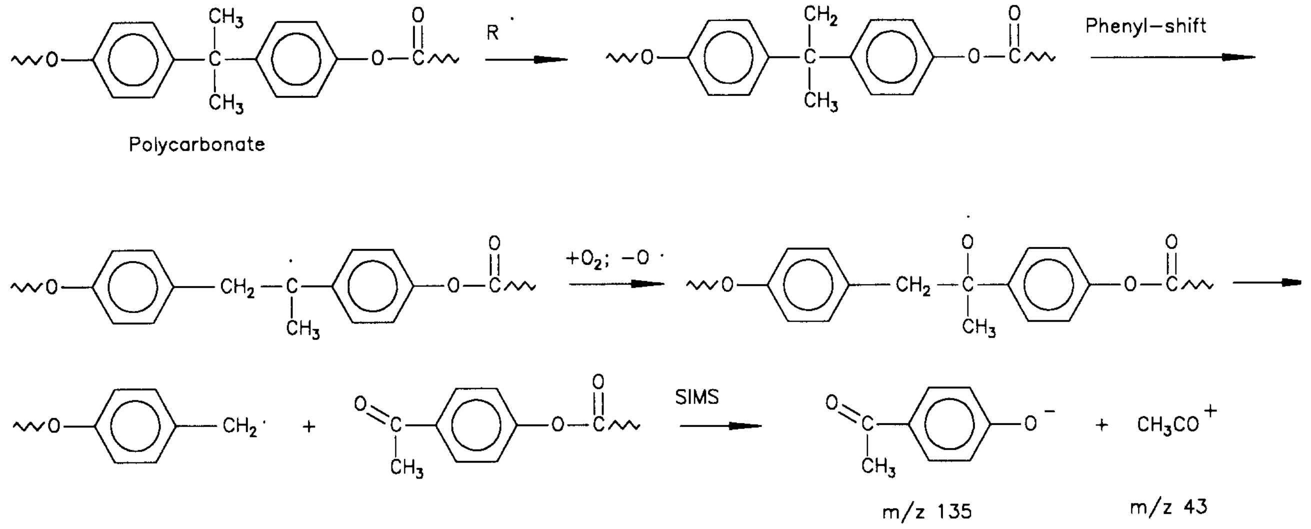
Figure 2 Negative static-SIMS spectra of a thick layer of PC-A on a silicon wafer (a) before and (b) after 20 min u.v. irradiation in Ar

treatment of PC-A. By oxygen plasma treatment the ions CH_3CO^+ (*m/z* 43), the cations (*m/z* 135) and the bisphenol-A anion (*m/z* 227) are also formed. Corona-discharge treatment was carried out in this study for comparison with the u.v. treatment. After 10 and 60 min corona-discharge treatment and rinsing with ethanol the intensities of the *m/z* 43 and 135 peaks in the positive spectrum and of the *m/z* 92, 108, 109, 121, 135 and 227 peaks in the negative spectrum increase relative to the intensity of the characteristic polycarbonate peaks. Especially in the spectra of surfaces without ethanol rinse, the intensity of background signals increases considerably. Some of the modified structures have been washed away by the ethanol rinse.

The static-SIMS spectra from the u.v. irradiated surfaces differ from those of the oxygen plasma and corona-discharge treated PC-A surfaces by the presence of peaks due to the cations at *m/z* 121 and 161. These ions can easily be formed from Photo-Fries reaction products (see *Scheme 1*). The occurrence of this third reaction path via the Photo-Fries rearrangement is in agreement with results from other studies[6–9].

Finally the anions of low intensity, with *m/z* 92, 108 and 109, could originate from mono- or dihydroxybiphenyl, hydroxydiphenylether groups formed by CO and CO_2 loss during photo-oxidation and/or chain scission[6,7].

The results show that oxygen is involved during the reactions although the irradiations were performed in Ar atmosphere. Small amounts of oxygen could be left in the polymer. The quartz irradiation vessels were flushed with Ar of purity 99.998% for at least 1 min. In addition, the reaction with oxygen could have occurred after the



Scheme 2 Formation of oxidized PC-A fragments and their static-SIMS ions

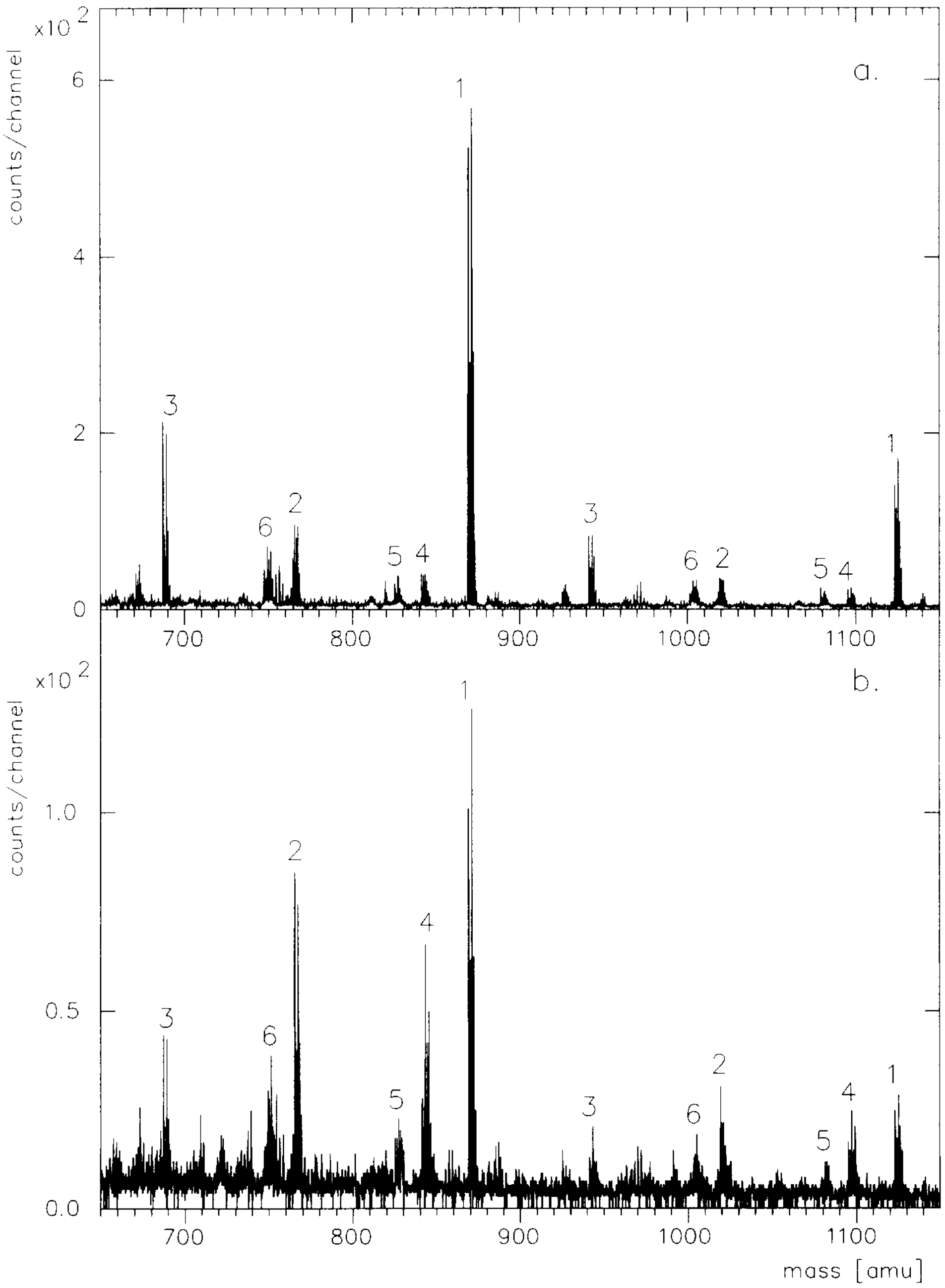
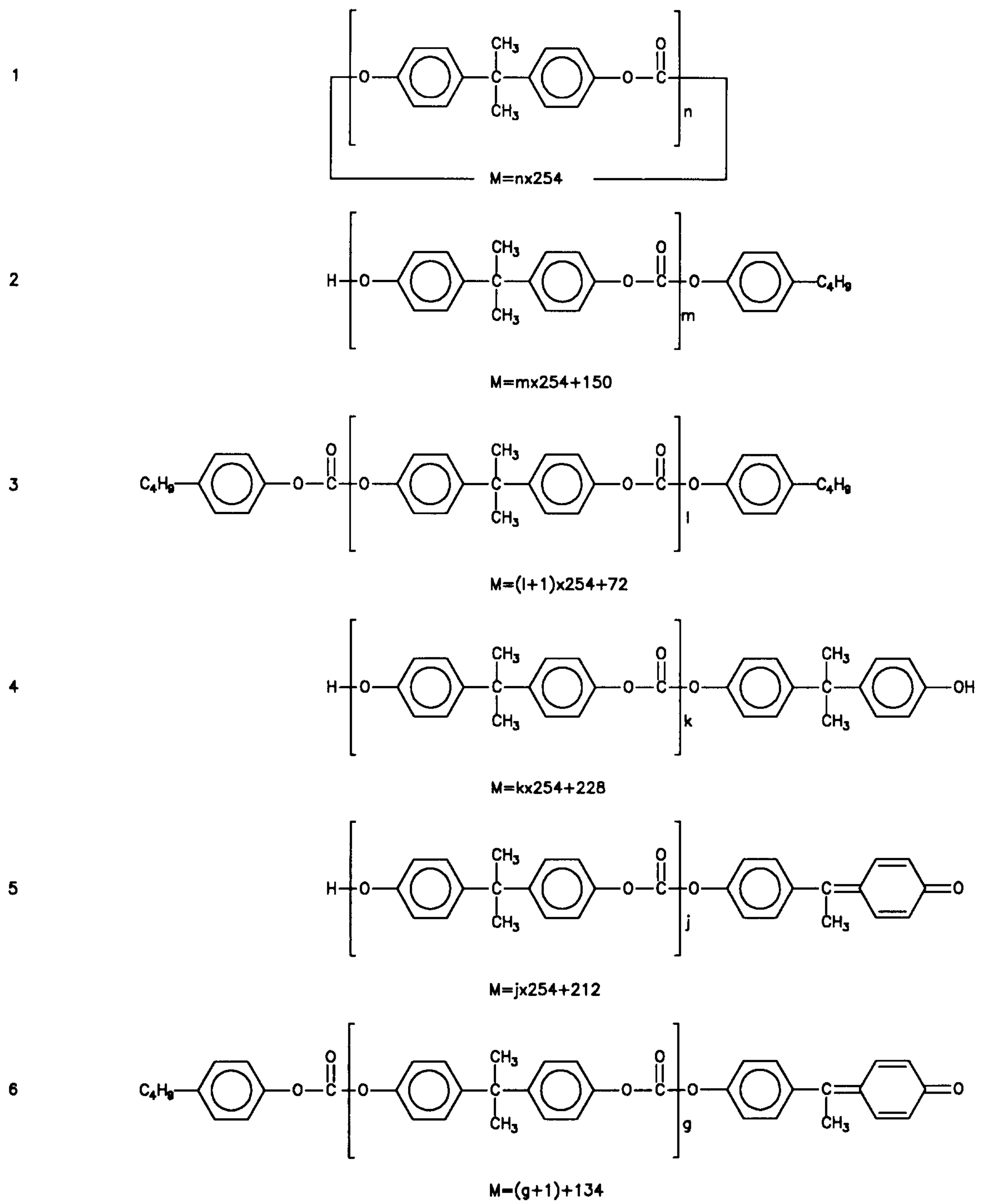


Figure 3 Positive static-SIMS spectra of a thin layer of PC-A on an Ag substrate (a) before and (b) after 10 min u.v. irradiation in Ar atmosphere. The mass range is 650–1150 amu. The peaks are mainly due to neutral PC-A species clustered to Ag^+



Scheme 3 Structures of oligomers detected as Ag^+ cationized species in *Figure 3*

irradiation, when the samples are brought in air to the mass spectrometer. Irradiation in air gives a higher intensity of peaks due to the cations at m/z 43, 135 and 213 and the anion with m/z 135 and a faster decrease of characteristic PC-A peaks.

As shown above by the u.v. treatment, hydroxyl groups are introduced on the polymer surface. These groups can be used for further chemical modification reactions. The formation of these hydroxyl groups is also apparent from the lowering of the contact angle[22] of a drop of water on the polymer surface. This angle changes from 75° for the untreated PC-A surface to 49° for the PC-A surface after 15 min u.v. irradiation in Ar atmosphere, and to 63° after u.v. irradiation and ethanol rinse. Shortly after the modification of the polycarbonate surfaces by u.v. light, these surfaces were subjected to chemical identification reactions with $(CH_3)_3SiCl$ and $(CF_3CO)_2O$, characteristic for hydroxyl groups:

$$\sim OH + (CH_3)_3SiCl \rightarrow \sim O\text{–}Si(CH_3)_3 + HCl$$

$$\sim OH + CF_3CO_2COCF_3 \rightarrow \sim OCOCF_3 + CF_3CO_2H$$

Without u.v. irradiation the polycarbonates hardly react with $(CH_3)_3SiCl$ and $CF_3CO_2COCF_3$. However, after u.v. irradiation intense peaks are observed in the spectra due to $(CH_3)_3Si^+$ and $(CH_3)_3SiO^-$ after the reaction with $(CH_3)_3SiCl$ and CF_3^- and $CF_3CO_2^-$ after the reaction with $CF_3CO_2COCF_3$.

Thin PC-A layers on Ag substrates

For the detection of changes in the polymer end-groups, thin layers of PC-A on Ag substrate were subjected to u.v. irradiation. Ag^+ cationized neutral polymer fragments, which contain information about the complete polymer structure, are obtained from such surfaces by the SIMS process[20]. In *Figure 3* the positive static-SIMS spectra of a thin layer of PC-A on Ag before and after 10 min u.v. irradiation in Ar atmosphere are shown for the mass range 650–1150 amu. The peaks in the spectra are due to the Ag^+ cationized neutral polymer fragments given in *Scheme 3*.

Neutral fragments contain the original polymer end-group ($-O-C_6H_4-C_4H_9$) or new end-groups ($-O-C_6H_4-C(CH_3)_2-C_6H_4-OH$ and $-O-C_6H_4-C(CH_3)=C_6H_4=O$), generated by the primary ion bombardment during the SIMS analysis. The origin of the cyclic neutral 1, which has its highest intensity for *n* is 3, is not clear[20]. After the u.v. irradiation the peaks due to neutral molecules with the bisphenol-A end-groups increase in intensity relative to the other peaks. Again, this can be explained by the formation of bisphenol-A end-groups generated by chain scission of PC-A upon u.v. irradiation and is in agreement with the results from the thick polycarbonate samples. However, no evidence could be found for neutral polycarbonate molecules changed by the Photo-Fries rearrangement in the spectra of the Ag samples.

In conclusion, the formation of OH groups on the polycarbonate surface, probably by main chain scission and the Photo-Fries pathway upon u.v. irradiation, is confirmed by the static-SIMS results and the identification reactions. These OH groups may be used for improving adhesion of a metal layer on the polycarbonate surface.

REFERENCES

1 Mittal, K. L. 'Physicochemical Aspects of Polymer Surfaces', Plenum Press, New York, 1983

2 Briggs, D. in 'Surface Analysis and Pretreatment of Plastics' (Ed. D. M. Brewis), Applied Science, London, 1982, p. 199

3 Lazare, S., Hoh, P. D., Baker, J. M. and Srinivasan, R. *J. Am. Chem. Soc.* 1984, **106**, 4288

4 Breuer, J., Metev, S., Sepold, G., Hennemann, O.-D., Kollek, H. and Krüger, G. *Appl. Surf. Sci.* 1990, **46**, 336

5 Adams, M. R. and Garton, A. *Polym. Mater. Sci. Eng.* 1991, **65**, 253

6 Rivaton, A., Sallet, D. and Lemaire, J. *Polym. Degrad. Stab.* 1986, **14**, 1

7 Factor, A., Ligon, W. V. and May, R. J. *Macromolecules* 1987, **20**, 2461

8 Belluš, D., Hrdlovic, P. and Maňásek, Z. *J. Polym. Sci. B* 1966, **4**, 1

9 Humphrey, J. S. Jr, Shultz, A. R. and Jaquiss, B. D. *Macromolecules* 1973, **6**, 305

10 van der Wel, H., Lub, J., van Velzen, P. N. T. and Benninghoven, A. *Mikrochim. Acta* 1990, **1990** (II), 3

11 van der Wel, H., van Velzen, P. N. T., Jürgens, U. and Benninghoven, A. in 'Analysis of Microelectronic Materials and Devices', (Eds M. Grasserbauer and H. W. Werner), Wiley, Chichester, 1991, p. 461

12 Briggs, D. *Polymer* 1984, **25**, 1379

13 Briggs, D. *Surf. Interf. Anal.* 1986, **9**, 391

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

15 Vickerman, J. C. in 'Spectroscopy of Surfaces' (Eds R. J. H. Clark and R. E. Hester), Advances in Spectroscopy Vol. 16, Wiley, Chichester, 1988, p. 155

16 Lub, J., van Vroonhoven, F. C. B. M., van Leyen, D. and Benninghoven, A. *Polymer* 1988, **29**, 998

17 Lub, J., van Velzen, P. N. T., van Leyen, D., Hagenhoff, B. and Benninghoven, A. *Surf. Interf. Anal.* 1988, **12**, 53

18 Niehuis, E., van Velzen, P. N. T., Lub, J., Heller, T. and Benninghoven, A. *Surf. Interf. Anal.* 1989, **14**, 135

19 Niehuis, E., Heller, T., Feld, H. and Benninghoven, A. *J. Vac. Sci. Technol.* 1987, **A5**, 1243

20 Lub, J. and Werumeus Buning, G. H. *Polymer* 1990, **31**, 1009

21 Lub, J. and van der Wel, H. in 'Secondary Ion Mass Spectrometry SIMS VIII' (Eds A. Benninghoven, K. T. F. Janssen, J. Tümpner and H. W. Werner), Wiley, Chichester, 1992, p. 803

22 Ponjeé, J. J., Marriot, V. B., Michielsen, M. C. B. A., Touwslager, F. J., van Velzen, P. N. T. and van der Wel, H. *J. Vac. Sci. Technol.* 1990, **B8**, 463