

# polymer papers

## Oxygen plasma induced degradation of the surface of poly(styrene), poly(bisphenol-A-carbonate) and poly(ethylene terephthalate) as observed by soft X-ray absorption spectroscopy (NEXAFS)

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Biaxially stretched poly(ethylene terephthalate) foils, poly(ethylene terephthalate) and poly(styrene) spin coated films as well as self-supporting poly(bisphenol-A-carbonate) films were analysed by surface sensitive near edge X-ray absorption fine structure spectroscopy (NEXAFS) before and after low pressure oxygen DC plasma treatments. The degradation effects of the treatment are discussed in a common way in terms of probable reaction pathways. The results are, when possible, cross-checked by XPS. NEXAFS analysis provides data on the phenyl ring, ester and carbonate group degradation in a straightforward manner. It can be shown that the phenyl rings in partially crystalline poly(ethylene terephthalate) are, in comparison, most effectively protected against plasma attack. In the case of poly(styrene), where the rings are located as side chains, they are most efficiently degraded © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: oxygen DC plasma treatment; plasma degradation; X-ray absorption spectroscopy (NEXAFS))

### INTRODUCTION

Recently, we published some X-ray absorption studies where the potential of this method in surface chemical analysis of polymers was successfully demonstrated. They were summarized in Ref. <sup>1</sup>. In detail, we have shown that one may differentiate between partially crystalline and amorphous states at the surface of poly(ethylene terephthalate)<sup>2</sup>. The chemical and conformational response of preferentially oriented polymer surfaces to oxygen plasma treatments was investigated with poly(propylene) and poly(ethylene terephthalate)<sup>3,4</sup>. Moreover, the chemical and structural effects of a chromium metallization on the surface chemistry of poly(ethylene terephthalate) and poly(bisphenol-A-carbonate) could be studied to some extent<sup>4,5</sup>.

In this communication the degradation phenomena, occurring at the surface of aromatic polymers, which are the result of oxygen DC plasma treatments are analysed, again using Near Edge X-ray Absorption Fine Structure (NEXAFS) spectroscopy<sup>6</sup>. As is known, plasma treatment is one approach to improve the surface properties of polymers with respect to adhesion of metals or polymers, etc.<sup>7</sup>. The whole matter is, of course, also of technological importance. Interesting questions are to what extent an oxygen plasma treatment degrades the polymer surface and how to analyse it. We found NEXAFS spectroscopy to be an instructive tool for monitoring effects due to plasma treatment.

Phenyl rings are often building units of technologically relevant polymers. Concerning the 'fate' of these phenyl rings in the course of an oxygen plasma treatment it is well known that, even when using the most advanced XPS instrumentation<sup>8</sup>, it is a very difficult task to extract the phenyl ring sub peak from the C 1s XP spectra in a reliable manner. Because in NEXAFS spectroscopy the C 1s →  $\pi^*$  phenyl ring resonance is one of the most prominent spectral features this special issue is exploited in this study to monitor the effects of plasma treatment. Once again, NEXAFS spectroscopy is proved to be a powerful extension to XPS in surface chemical analysis of polymers.

### EXPERIMENTAL

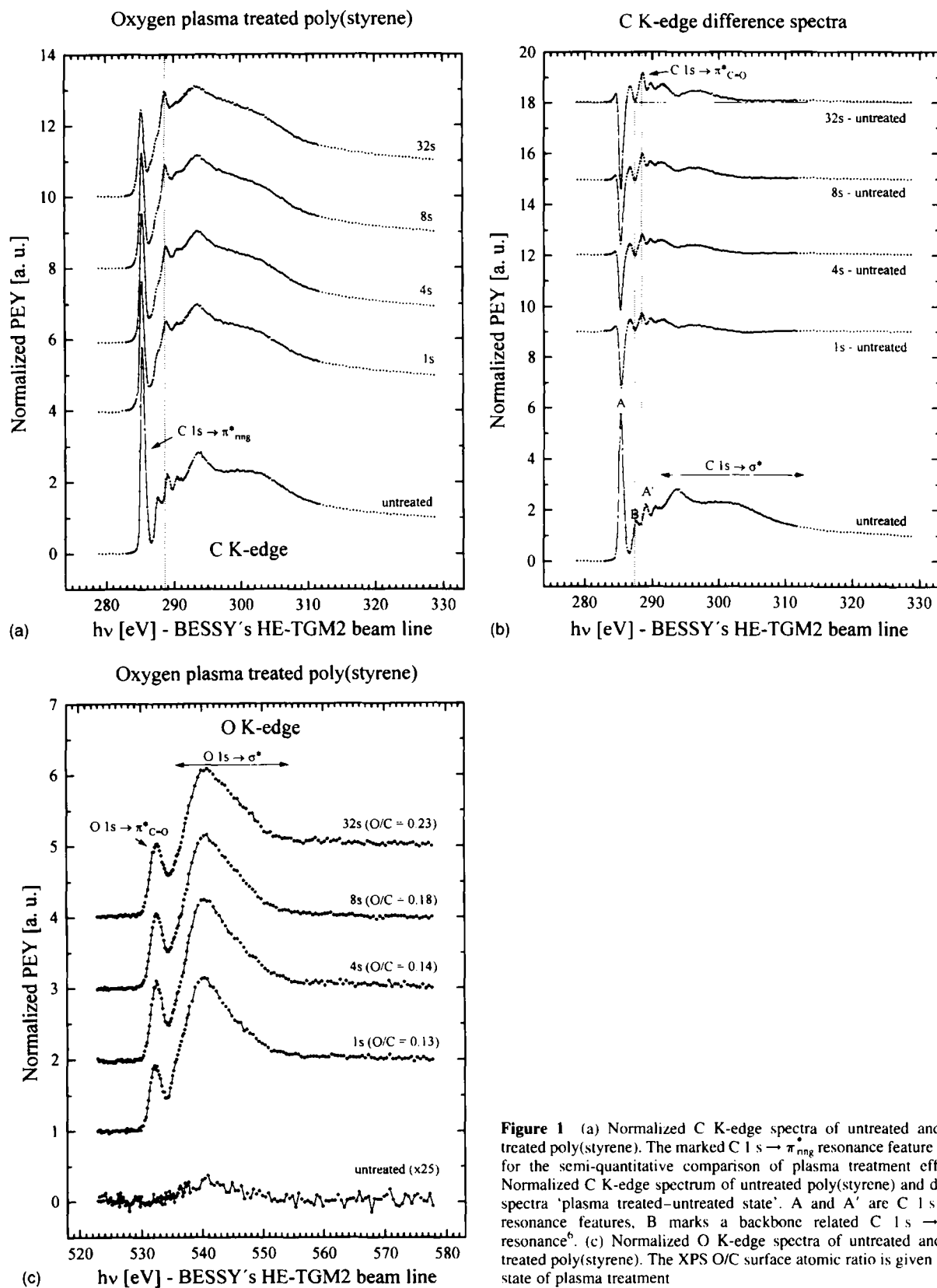
#### *Samples and plasma treatment*

Biaxially stretched 0.5  $\mu\text{m}$  poly(ethylene terephthalate) foils (Mylar<sup>®</sup>, Du Pont de Nemours) were used in this study. This polymer is characterized by an average molecular weight of 250 000 Da, crystallinity of 60–65% (density measurement) and stretching ratios  $\alpha_x$  and  $\alpha_y$  of 3.5.

Thin PET films were spin coated onto silicon wafers employing a 0.5 wt.% PET in hexafluoroisopropanol solution at 2000 rpm. The resulting film thickness was around 100 nm. No contributions of the substrate were detected in the respective XP spectra.

Poly(styrene) films were spin coated onto silicon wafers by solving 1 wt.% non-commercial, purely atactic poly(styrene) (BASF AG, Germany) in toluene. The resulting film thickness was again around 100 nm. The oxygen

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**Figure 1** (a) Normalized C K-edge spectra of untreated and plasma treated poly(styrene). The marked C 1s  $\rightarrow$   $\pi^*_{ring}$  resonance feature was used for the semi-quantitative comparison of plasma treatment effects. (b) Normalized C K-edge spectrum of untreated poly(styrene) and difference spectra 'plasma treated-untreated state'. A and A' are C 1s  $\rightarrow$   $\pi^*_{ring}$  resonance features, B marks a backbone related C 1s  $\rightarrow$  C—H<sup>+</sup> resonance<sup>6</sup>. (c) Normalized O K-edge spectra of untreated and plasma treated poly(styrene). The XPS O/C surface atomic ratio is given for every state of plasma treatment

content of the surface of these films was measured by XPS to be  $\approx 1.5$  at%. This small amount of oxygen was also proved by NEXAFS spectroscopy of the O K-edge region (cf. Figure 1c, bottom).

200 nm thick self-supporting poly(bisphenol-A-carbonate) films were prepared from a methylene dichloride solution of a commercially available polycarbonate sample (Macrolon 3200, Bayer AG, Germany) with the

help of a preparation procedure called 'spontaneous film formation'. This procedure was introduced and is practised by Hoffmann *et al.*, Technical University Berlin, Germany<sup>9</sup>. XPS analysis of the 'as received' sample revealed Si surface impurities at concentrations  $< 1$  at%.

Narrow XPS C 1s and O 1s scans obtained with all samples in the untreated state revealed spectra almost identical to the reference spectra published in Ref.<sup>8</sup>.

XPS and O<sub>2</sub> DC plasma treatments were carried out in a VG ESCALAB 200X electron spectrometer at BAM, Berlin. This instrument is equipped with a plasma reactor chamber separated by a gate valve. DC plasma treatments were carried out at 6 Pa of 99.999% grade oxygen. During the treatment, the sample was 25 mm away from the luminous plasma region ('after glow'). The plasma treated samples were exposed to laboratory atmosphere during the transfer into the NEXAFS apparatus located at BESSY, Berlin.

#### X-ray absorption spectroscopy

NEXAFS spectroscopy was carried out on the HE-TGM2 monochromator beam line (33.12) at the synchrotron light source BESSY (Berlin, Germany). Spectra were acquired at the C K-edge and the O K-edge in the partial electron yield mode (PEY) at a retarding voltage of -150 V. The monochromator resolution at the C 1s edge was better than 0.8 eV. Raw spectra were divided by the monochromator transmission function which was obtained with a freshly sputtered Au sample. Energy alignment of the energy scale was achieved by using the C 1s  $\rightarrow \pi^*$  resonance, measured with a pyrolytic graphite sample (Advanced Ceramic Corp., Cleveland, U.S.A.) which was fixed to the value of 285.4 eV<sup>10</sup>. Characteristic features in the flux monitor signals were used to align the energy scales of the spectra. However, the absolute energy calibration of the monochromators is known to be a severe, beam time consuming problem and is here, therefore, not better than about  $\pm 0.2$  eV. Reproducibility of the spectra was carefully checked by multiple scanning.

Spectra are shown with the pre-edge count rate subtracted and after normalization in units of the absorption edge jump<sup>6</sup>.

NEXAFS spectra were recorded at an angle of 55°, measured between the surface plane of the sample and the direction vector of the incident, linearly polarized light beam.

Principally, absorption spectra can be measured by monitoring the non-radiative decay (electron yield) of core holes, created in the sample by the photo absorption process itself<sup>6</sup>. Photoelectrons as well as C- and O-KLL series electrons contribute to this electron yield signal measured by a channeltron detector. Surface sensitivity is achieved by using the partial electron yield mode because low energy electrons, which may originate also from deeper layers, were suppressed by the pre-set threshold energy from entering the detector. The information depth, which is defined to be the depth from which 95% of the detected electrons originate<sup>11</sup>, is estimated to be  $\approx 30$  Å for the C K-edge signal and  $\approx 50$  Å for the O K-edge signals<sup>12</sup>. Here it was assumed that the respective Auger electrons dominate the measured partial electron yield signal<sup>6</sup>.

#### X-ray photoelectron spectroscopy

XP spectra were taken by an oil-free pumped VG Scientific ESCALAB 200X electron spectrometer (VG Scientific, East Grinstead, U.K.). Spectra were acquired at Mg-K <sub>$\alpha$</sub>  excitation (15 kV, 20 mA) in FRR mode (CRR 40) at a take-off angle of 20°. XP spectra analysis and quantification were performed by routines which are part of the SCIENTA ESCA-300 (SCIENTA AB, Uppsala, S) and VG's VGS 5250 data systems, respectively. For an estimation of the relative intensities (atomic ratios) we used Scofield's cross-sections<sup>13</sup>, inelastic electron mean

free path lengths  $\sim E_{\text{kin}}^{0.7}$  and a transmission  $\sim E_{\text{kin}}$ . The error of these data is estimated to be better than  $\pm 10\%$ .

## RESULTS AND DISCUSSION

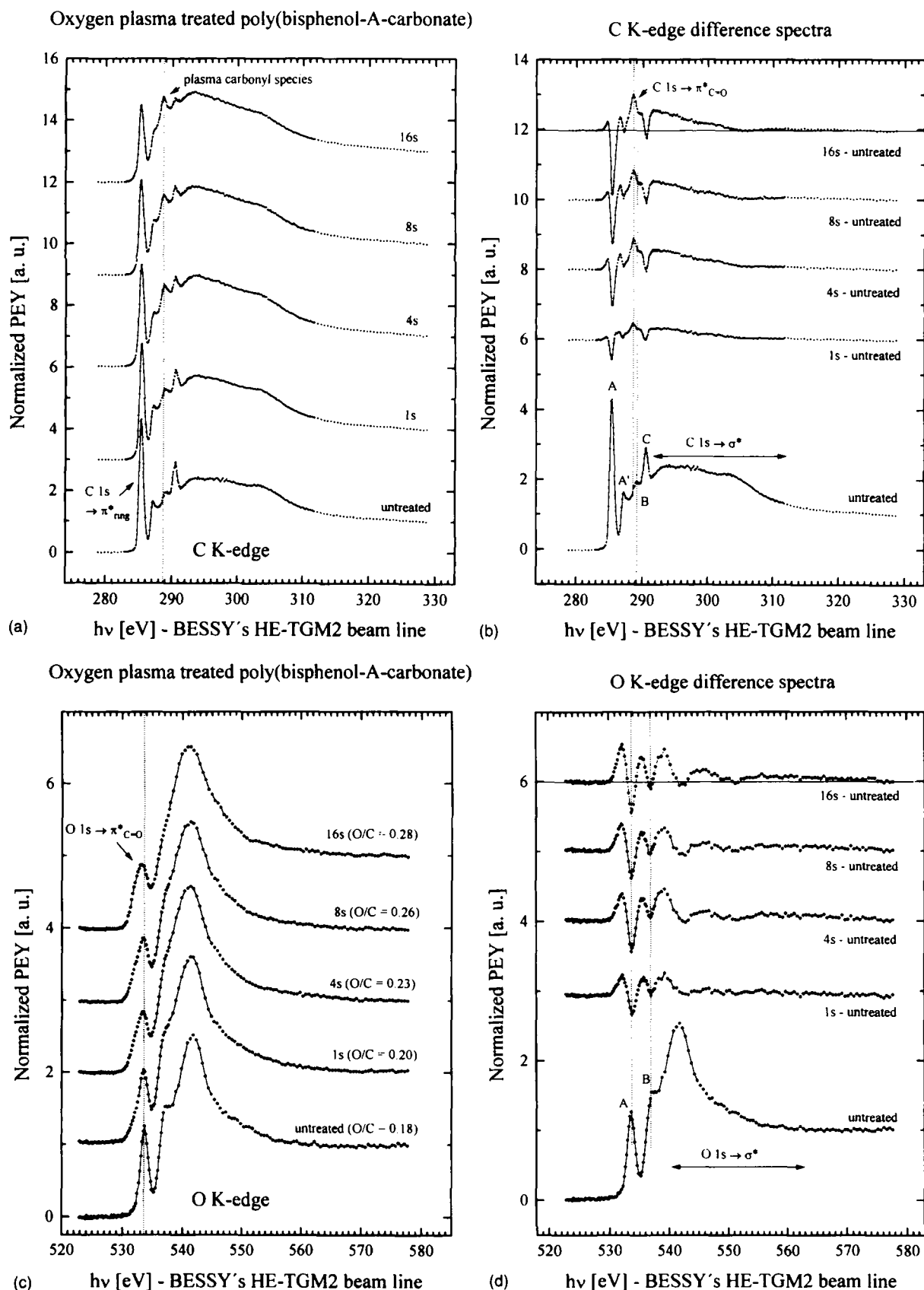
### Poly(styrene)

In *Figure 1a* the development of the poly(styrene) C K-edge spectrum is monitored *versus* increasing plasma treatment time. The most prominent effects are the broadening and decrease of the first sharp feature of the spectrum, the C 1s  $\rightarrow \pi_{\text{ring}}$  resonance, and the occurrence of a new feature at 288.5 eV due to a species formed by the plasma. In order to determine the effects more in detail, in *Figure 1b* difference spectra are evaluated and plotted together with an interpreted spectrum of the untreated polymer. Here it can be proved that a new feature, interpreted as a C 1s  $\rightarrow \pi_{\text{C-O}}$  resonance, was observed with increasing intensity *versus* increasing plasma treatment times. Consequently, also some alterations of the shape and an increase of intensity are observed in the  $\sigma^*$  region of the spectra. The respective O K-edge spectra, which exclusively represent species formed by the plasma, are given in *Figure 1c*. There are no strong effects on the shape of the normalized spectra when the treated states of the polymer surface are compared with each other. However, a small increase in the intensity of the O 1s  $\rightarrow \pi_{\text{C-O}}$  resonance intensity *versus* increasing plasma treatment time was observed. This is due to the formation of more higher oxidized carbon species. The O 1s  $\rightarrow \sigma^*$  resonance features comprise C—O and C=O bond contributions.

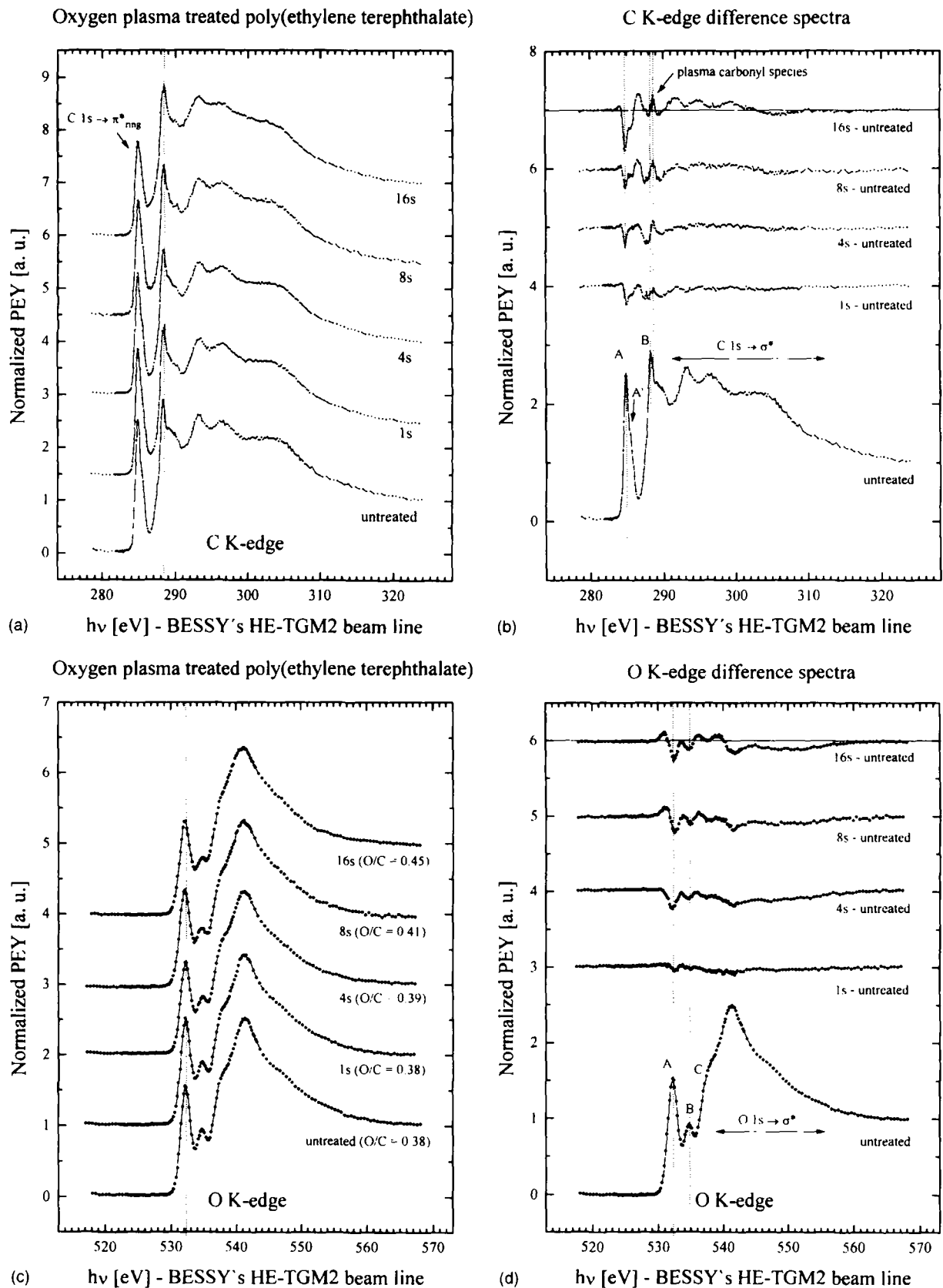
XPS surface analysis of all of the treated samples revealed a rather broad (FWHM  $\approx 2.7$  eV), symmetric and non-structured O 1s peak centered at 532.9 eV. This feature is broad enough to cover C—O and C=O related sub-peaks<sup>8</sup>. The C 1s spectrum was observed with significant C—O and C=O contributions for 1 and 4 s plasma treatment times and C—O, C=O and O—C=O contributions for 8 and 32 s oxygen DC plasma treatments (for the fitting strategy, see Ref. <sup>14</sup>). Going from 1 to 32 s plasma treatment the percentage of the total C 1s spectrum monotonously increases for C—O from 3 to 6%, for C=O from 1 to 3% whereas the  $\pi \rightarrow \pi^*$  shake-up feature intensity decreases from 5 to 1%. Considering O—C=O we found an increase from 1 to 3% for the 8 and 32 s plasma treatment times, respectively. These XPS results cross-check the nearly unchanged shape of the normalized O K-edge spectra of plasma treated poly(styrene) and the decrease of the C 1s  $\rightarrow \pi_{\text{ring}}$  resonance intensity *versus* plasma treatment time.

### Poly(bisphenol-A-carbonate)

In *Figure 2a* the development of the poly(bisphenol-A-carbonate) C K-edge spectrum is monitored *versus* increasing plasma treatment time. The most prominent effects are the broadening and decrease of the first sharp feature of the spectrum, the C 1s  $\rightarrow \pi_{\text{ring}}$  resonance, a decrease of the carbonate related carbonyl  $\pi^*$  resonance at 290.5 eV and the formation of a new feature, evolving at 288.5 eV, which is taken as a finger-print of a plasma species. Details are given in *Figure 2b* where difference spectra are evaluated and plotted together with an interpreted spectrum of the untreated polymer<sup>15</sup>. Obviously, the intensities of both the shifted (A') and non-shifted (A) C 1s  $\rightarrow \pi_{\text{ring}}$  resonances are strongly diminished due to plasma attack also at a 1 s plasma pulse. Moreover, the



**Figure 2** (a) Normalized C K-edge spectra of untreated and plasma treated poly(bisphenol-A-carbonate). The marked C 1s  $\rightarrow \pi^*_{ring}$  resonance feature was used for the semi-quantitative comparison of plasma treatment effects. (b) Normalized C K-edge spectrum of untreated poly(bisphenol-A-carbonate) and difference spectra 'plasma treated-untreated state'. A and A' are C 1s  $\rightarrow \pi^*_{ring}$  related features, B probably marks the onset of the continuum and C the carbonate related C 1s  $\rightarrow \pi^*_{C=O}$  resonance<sup>15</sup>. (c) Normalized O K-edge spectra of untreated and plasma treated poly(bisphenol-A-carbonate). The XPS O/C surface atomic ratio is given for every state of plasma treatment. (d) Normalized O K-edge spectrum of untreated poly(bisphenol-A-carbonate) and difference spectra 'plasma treated-untreated state'. A is a O 1s  $\rightarrow \pi^*_{C=O}$  resonance related to the carbonate carbonyl bond and feature B probably marks an axial oxygen related resonance O 1s  $\rightarrow \sigma^*_{C-O}$  superposed by the onset of the continuum of the carbonyl oxygen species<sup>15</sup>.



**Figure 3** (a) Normalized C K-edge spectra of untreated and plasma treated poly(ethylene terephthalate) spin coated films. The marked  $C 1s \rightarrow \pi_{ring}^*$  resonance feature was used for the semi-quantitative comparison of plasma treatment effects. (b) Normalized C K-edge spectrum of the untreated treated poly(ethylene terephthalate) spin coated film and difference spectra 'plasma treated-untreated state'. A and A' are  $C 1s \rightarrow \pi_{ring}$  related features and B the ester related  $C 1s \rightarrow \pi_{C-O}^*$  resonance<sup>15</sup>. (c) Normalized O K-edge spectra of untreated and plasma treated poly(ethylene terephthalate) spin coated films. The XPS O/C surface atomic ratio is given for every state of plasma treatment. (d) Normalized O K-edge spectrum of untreated treated poly(ethylene terephthalate) spin coated film and difference spectra 'plasma treated-untreated state'. A is an  $O 1s \rightarrow \pi_{C-O}^*$  resonance related to the ester carbonyl bond, feature B probably marks the chain oxygen related resonance  $O 1s \rightarrow \sigma_{C-O}^*$  and C the onset of the continuum of the carbonyl oxygen species<sup>15</sup>.

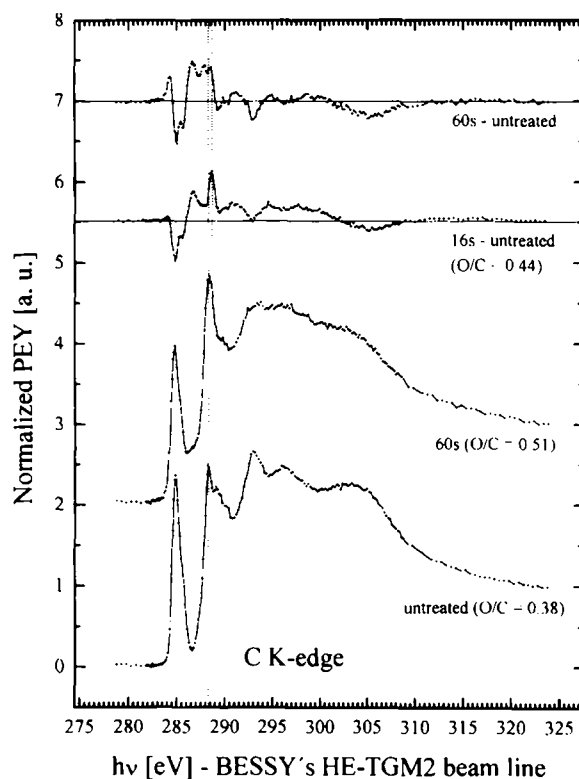
carbonate related  $C 1s \rightarrow \pi_{C=O}^*$  carbonyl resonance in the spectrum of the untreated polymer, which is shifted to 290.5 eV due to the presence of two electronegative chain oxygen atoms<sup>15</sup>, is also decreased in intensity. This effect becomes significant beginning with 1 s plasma treatment time (40% decrease) and reaches  $\approx 85\%$  at 16 s treatment time. The carbonyl resonance at 288.5 eV, related to species formed by the plasma attack, occurs already at 1 s treatment time at the same energy as in the poly(styrene) case. The respective O K-edge spectra are given in Figure 2c. Here we find strong effects on the shape of the spectra when the treatment time is successively increased. Additionally, a shift of about 0.6 eV of the  $O 1s \rightarrow \pi_{C-O}^*$  resonance feature towards lower energy has to be stated. Once again, difference spectra are used to make the effects clear (cf. Figure 2d). Without any doubt, the carbonate related resonances are destroyed due to oxygen plasma treatment, beginning with short plasma pulses and providing a strong effect at 16 s treatment time. The broad  $O 1s \rightarrow \sigma^*$  resonance feature comprising C—O and C=O bond contributions is also affected (intensity increases around 539 and 545 eV). The whole shape of the O K-edge spectrum after prolonged plasma treatment resembles this one measured with the plasma treated poly(styrene).

XPS analysis of the untreated poly(bisphenol-A-carbonate) sample revealed two oxygen species (C—O sub peak at 533.9 eV, FWHM = 1.9 eV, C=O sub peak at 532.2 eV, FWHM = 1.6 eV). Beginning with 4 s plasma treatment the O 1s spectrum turns more and more to that non-structured,  $\approx 3$  eV broad peak, centered at  $\approx 533$  eV, which was also observed with the plasma treated poly(styrene) samples. The C 1s spectrum was observed with a decreasing carbonate related sub-peak (at 290.8 eV binding energy) intensity which decreases from 6% of the total C 1s intensity, measured with the untreated sample, down to 3%. On the other hand, the C—O sub peak (at 286.3 eV binding energy) intensity increases from 12% (untreated state) to 16% (16 s plasma treatment). Beginning with 4 s plasma treatment time significant C=O and O—C=O contributions were observed with total area percentages  $\leq 4$ . These XPS results successfully cross-check the plasma degradation of the carbonate unit of the polymer and the plasma induced formation of new carbonyl species.

#### Poly(ethylene terephthalate)

In Figure 3a the C K-edge spectra of poly(ethylene terephthalate) spin coating films is monitored versus increasing plasma treatment time. The most prominent effects are the broadening and decrease of the  $C 1s \rightarrow \pi_{ring}^*$  resonances (cf. also Figure 3b) and the alterations around 288.2 eV where the ester related  $C 1s \rightarrow \pi_{C=O}^*$  resonance is found for the untreated poly(ethylene terephthalate). Here the formation of a new feature, evolving at 288.5 eV, can be concluded from the respective difference spectra given in Figure 3b. This feature contributes, beginning with 4 s plasma treatment time, to the spectra and is taken again as a finger-print of a plasma species. An interpreted spectrum of the untreated polymer<sup>15</sup> is included in Figure 3b. Obviously, also the  $C 1s \rightarrow \sigma^*$  region is affected by the plasma modification of the polymer. The respective O K-edge spectra are given in Figure 3c. Here we find only small effects on the shape of the spectra when the treatment time is successively increased. Additionally, a very small shift of about 0.2 eV

#### Oxygen plasma treated poly(ethylene terephthalate) foil



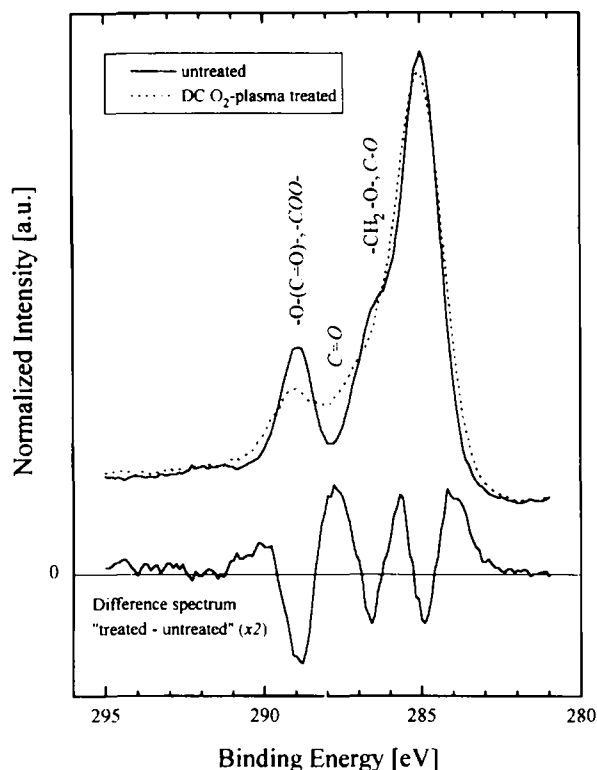
**Figure 4** Typical normalized XP C 1s spectra of an untreated and a drastically oxygen plasma treated, biaxially stretched poly(ethylene terephthalate) foil. The energetic positions of the coexisting structure groups formed by plasma treatment are marked by italics. Obviously, carbonyl species are formed whereas ester species are destroyed in the course of the reaction

of the  $O 1s \rightarrow \pi_{C-O}^*$  resonance feature towards lower energy has to be stated. Difference spectra may provide more details (cf. Figure 3d). It can be seen that the ester related resonances are diminished due to oxygen plasma treatment. However, the effect, becoming significant at a 4 s plasma treatment, is not very strong even at 16 s treatment time. The broad  $O 1s \rightarrow \sigma^*$  resonance feature is also slightly affected (intensity decreases above 541 eV).

XPS analysis of the untreated poly(ethylene terephthalate) spin coating film revealed the characteristic twin peak oxygen spectrum (C—O sub peak at 533.4 eV, FWHM = 1.8 eV, C=O sub peak at 532.0 eV, FWHM = 1.6 eV, cf. also Ref. 8). Beginning with 4 s plasma treatment this twin peak shape disappeared and the O 1s spectrum turned to a non-structured,  $\approx 3.3$  eV broad peak, centered around 532.8 eV. Similar effects were observed also with the other plasma treated polymers analyzed in this study. The C 1s spectrum was observed with a decreasing ester related sub-peak intensity (a typical result is given in Figure 4). On the other hand, a C=O sub-peak occurs between the ester and —C—O— sub-peaks, beginning with 4 s plasma treatment time with around 3% of the total C 1s intensity. For the 16 s plasma treatment this contribution increases to  $\approx 8\%$ . These XPS results may support the plasma degradation of the ester unit of the polymer and, once again, the plasma induced formation of new carbonyl species.

Figure 5 presents selected graphs from our study of the response of a biaxially stretched, partially crystalline poly(ethylene terephthalate) foil to oxygen DC plasma

## Oxygen plasma treated poly(ethylene terephthalate) foil



**Figure 5** Normalized C K-edge spectra of untreated and plasma treated, partially crystalline poly(ethylene terephthalate) foils. Spectra were acquired at  $55^\circ$  measured between the surface plane of the sample and the direction vector of the incident light beam. Examples of difference spectra 'plasma treated-untreated state' are inserted. The XPS O/C surface atomic ratio is given for every state of plasma treatment

treatment. As to be expected, there is no principal difference to the results obtained with the spin coated poly(ethylene terephthalate) samples. The main difference is that the C  $1s \rightarrow \pi_{\text{ring}}^*$  resonance intensities are less diminished when the spectra of equal treatment times are compared to each other. Even after an unusually long treatment (60 s) the decrease of the C  $1s \rightarrow \pi_{\text{ring}}^*$  resonance intensities do not reach the level observed with amorphous poly(ethylene terephthalate) due to 16 s treatment. Inspection of the '60 s-untreated' difference spectrum (cf. Figure 5) additionally reveals another new feature (at 287.8 eV) which was exclusively observed at long treatment times.

#### Comparison of results

To compare the effect of oxygen DC plasma induced benzene ring degradation for the investigated samples we summarized the results in an array presented in Figure 6. Integrated intensities of the NEXAFS C  $1s \rightarrow \pi_{\text{ring}}^*$  features (which are marked in Figures 1a-3a) were used to derive a measure for the aromatic ring degradation. Additionally, the respective XPS O/C atomic ratios are given. In detail, we found, within the scatter of data, very similar results for the ring degradation when the spin coated poly(ethylene terephthalate) film and the poly(bisphenol-A-carbonate) sample are considered (continuous degradation down to  $\approx 70\%$  after 16 s plasma treatment). The degradation is much stronger for poly(styrene) where a drop down to  $\approx 70\%$  is already observed at a short plasma pulse. Than the degradation levels off with increasing

treatment times. Considering the partially crystalline poly(ethylene terephthalate) foil, a drop down to  $\approx 90\%$  at a short plasma pulse can be stated. At 16 s treatment time a further degradation pulse down to  $\approx 85\%$  was obtained, a level which is significantly above this one obtained with the amorphous poly(ethylene terephthalate) film. Prolongation of the treatment time to 60 s gives only small additional enhancement in the degradation of the aromatic rings.

The main result is that the rings in partially crystalline poly(ethylene terephthalate) are most effectively protected against plasma attack. On the other side, in the case of poly(styrene), where the rings are located as side chains, they are most efficiently degraded. Finally, we observed the interesting fact, that, for all samples analysed, the FWHM of the C  $1s \rightarrow \pi_{\text{ring}}^*$  resonance is already increased after rather short plasma pulses from  $\approx 0.8$  eV to  $\approx 0.9$  eV, reaching numbers around 1.0 eV after extensive plasma treatment. Similar effects are usually observed for C  $1s$  and O  $1s$  XP peaks measured with polymers after oxygen plasma treatment.

Considering the formation of plasma species on the surface of the investigated aromatic polymers we found a common feature, the formation of a C  $1s \rightarrow \pi_{\text{C-O}}^*$  resonance at 288.5 eV. One interpretation could be that a plasma induced ring-opening reaction leads to carbonyl formation accompanied by a consecutive loss of aromatic character of the polymer surface. It is interesting, that Richard *et al.*<sup>16</sup> also found just the same feature in their NEXAFS spectra of oxygen plasma treated poly(phenylquinoxaline). The reaction pathway referred to above was supported by their XPS results, too. The first step of this scenario, i.e. the destruction of the aromatic ring, was also found by TOF-SIMS with oxygen plasma treated poly(styrene)<sup>17,18</sup>. Here the loss of aromaticity was correlated to a disappearance or intensity decrease of the fragments  $C_7H_7^+$  (tropylium ion) and  $C_6H_5^+$ . In an extended XPS study Gerenser also reported a decrease of the aromaticity, i.e. breaking of phenyl or phenylene rings, at the surface of oxygen plasma treated poly(styrene) and poly(ethylene terephthalate), respectively<sup>19</sup>. This conclusion was drawn from a respective decrease of the XPS carbon C  $1s \pi \rightarrow \pi^*$  shakeup peaks. Destruction of aromatic rings in poly(ethylene terephthalate) by plasma treatment was also reported in Ref.<sup>20</sup>. Here the authors discuss the formation of polyene and crosslinking via plasma formed hexatriene-diradicals. Carbonyl formation at the surface of oxygen plasma treated polyenes is, amongst other oxidation processes, well known. On the other hand, also the ester groups of the terephthalic unit can be destroyed by the oxygen plasma resulting in CO and CO<sub>2</sub> and benzoic acid ester radicals. These radicals, existing in the plasma surroundings, can be the starting point for a huge number of subsequent reactions which may result also in carbonyl group formation<sup>20</sup>. In addition to the particle induced effects, also plasma radiation induced photodegradation may play a role. For instance, in the case of poly(bisphenol-A-carbonate) a photo-Fries rearrangement of building units resulting in simple carbonyl species between ortho-hydroxy phenyl groups<sup>21</sup> has to be taken into account.

#### CONCLUSIONS

The following conclusions can be drawn from our NEXAFS spectroscopy study of oxygen plasma treated poly(styrene), poly(bisphenol-A-carbonate) and

$\pi^*$  resonance intensity, normalized to the untreated state, for DC  $O_2$  plasma treated PS, PET and PC

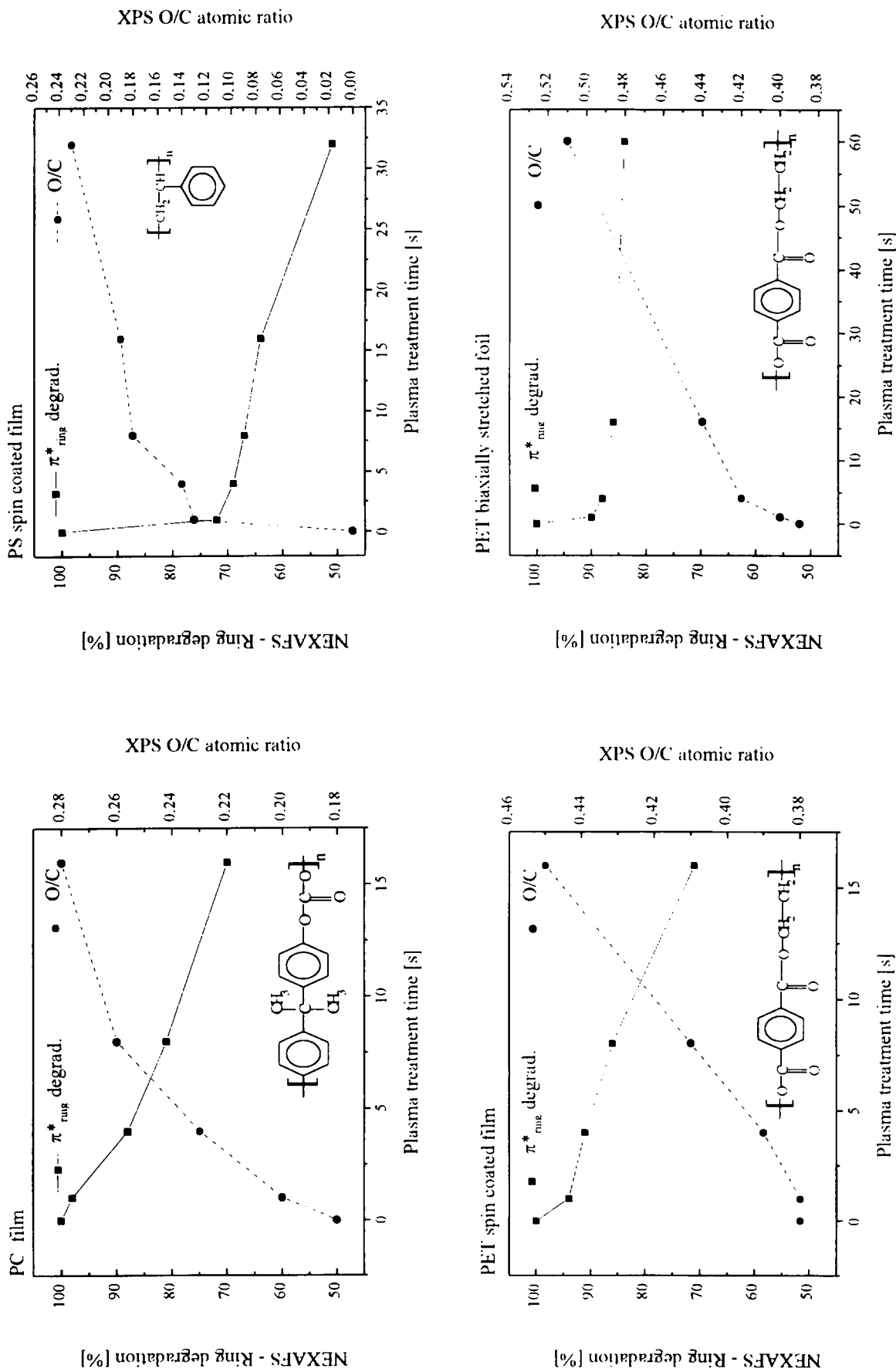


Figure 6 The decrease of aromaticity of poly(styrene), poly(bisphenol-A-carbonate) and poly(ethylene terephthalate) samples in the course of oxygen DC plasma treatments, monitored by the integrated area ratio  $I_{\text{plasma treated}}/I_{\text{untreated}}(\text{C } 1s \rightarrow \pi^*_{\text{ring}}) \times 100$ . To enable direct comparison, the 'NEXAFS-Ring degradation' scales are the same for all plots. Additionally, the respective XPS O/C atomic ratios are included



poly(ethylene terephthalate):

- Poly(styrene), where the phenyl rings are located as side chains, undergoes the strongest decrease of its aromaticity, even at short plasma pulses. Oxygen plasma species characterized by a  $C\ 1s \rightarrow \pi_{C=O}^*$  resonance at 288.5 eV and a characteristic O K-edge spectrum are formed. The variety of oxygen functionalized plasma species at the exposed surface seems to be independent of treatment time.
- Poly(bisphenol-A-carbonate), with its phenylene rings as a part of the polymer backbone, is characterized by a moderate loss of aromaticity. The carbonate group, caused by its labile nature, is efficiently destroyed by the plasma. The oxygen functionalized plasma species seem to be very similar to those observed with poly(styrene).
- Spin coated poly(ethylene terephthalate) films are also characterized by a moderate loss of aromaticity. The ester group is, in comparison, stable against the oxygen plasma attack. Also for this polymer a  $C\ 1s \rightarrow \pi_{C-O}^*$  resonance at 288.5 eV was observed to be a finger-print of oxygen functionalized plasma species.
- Biaxially stretched, partially crystalline poly(ethylene terephthalate), as is to be expected, is the sample which is rather resistant to plasma degradation when the aromaticity is the selected parameter.

#### ACKNOWLEDGEMENTS

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#### REFERENCES

1. Unger, W. E. S., Lippitz, A., Wöll, C. and Heckmann, W., *Fresenius J. Anal. Chem.*, 1997, **358**, 89.
2. Lippitz, A., Friedrich, J. F., Unger, W. E. S., Schertel, S. and Wöll, Ch., *Polymer*, 1996, **37**, 3151.
3. Gross, Th., Lippitz, A., Unger, W. E. S., Friedrich, J. F. and Wöll, Ch., *Polymer*, 1995, **35**, 5590.
4. Lippitz, A., Koprinarov, I., Friedrich, J. F., Unger, W. E. S., Weiss, K. and Wöll, Ch., *Polymer*, 1996, **37**, 3157.
5. Koprinarov, I., Lippitz, A., Friedrich, J. F., Unger, W. E. S. and Wöll, Ch., *Polymer*, 1997, **38**, 3005.
6. Stöhr, J., *NEXAFS Spectroscopy*. Springer Verlag, Heidelberg, 1992.
7. Friedrich, J. F., Unger, W., Lippitz, A., Gross, Th., Rohrer, P., Saur, W., Erdmann, J. and Gorsler, H.-V., *J. Adhesion Sci. Technol.*, 1995, **9**, 575.
8. Beamsom, G. and Briggs, D., *High Resolution XPS of Organic Polymers*. Wiley, Chichester, 1992.
9. Hoffmann, A., Becker, K.-F., Pigur, B. and Hinrichsen, G., Abstracts, Berliner Polymeren-Tage, Potsdam, Germany, 5.-7.10.1994, Vol. 5, 1994, p. 173.
10. Batson, P. E., *Phys. Rev. B*, 1993, **48**, 2608.
11. Standard Terminology Relating to Surface Analysis, ASTM E 673-91c. *Annual Book of ASTM Standards*, Vol. 03.06. ASTM, Philadelphia, 1993, p. 525.
12. Seah, M. P. and Dench, W. A., *Surf. Interface Anal.*, 1979, **1**, 2.
13. Scofield, J. H., *J. Electron. Spectrosc. Relat. Phenom.*, 1976, **8**, 129.
14. Unger, W. E. S., Lippitz, A. and Friedrich, J. F., *Materialprüfung*, 1995, **37**, 233.
15. Pettersson, L. G. M., Ågren, H., Schürmann, B. L., Lippitz, A. and Unger, W. E. S., *Int. J. Quantum Chemistry*, 1997, **63**, 749.
16. Richard, G., Cros, A., Mathy, Y., Tourillon, G., Laffon, C. and Parent, Y., *Journal de Physique IV*, 1993, **3**, 789.
17. Petrat, F. M., Wolany, D., Schwede, B. C., Wiedmann, L. and Benninghoven, A., *Surf. Interface Anal.*, 1994, **21**, 402.
18. Lianos, L., Parrat, D., Hoc, Tran Quoc and Duc, Tran Minh, *J. Vac. Sci. Technol. A*, 1994, **12**, 2491.
19. Gerenser, L. J., *J. Adhesion Sci. Technol.*, 1993, **7**, 1019.
20. Friedrich, J., Loeschke, I., Frommelt, H., Reiner, H.-D., Zimmermann, H. and Lutgen, P., *Polymer Degradation and Stability*, 1991, **31**, 97.
21. Rabek, J. F., *Polymer Photodegradation*. Chapman and Hall, London, 1995, p. 44.