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Surface analysis of metallized poly(bisphenol A carbonate) films by X-ray absorption spectroscopy (NEXAFS)

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The surface region of thin self-supporting poly(bisphenol A carbonate) films were analysed by X-ray absorption spectroscopy (NEXAFS) before and after metallization with chromium. C- and O-*K*-edge spectra were interpreted by comparison to spectra obtained with poly(hexanediolcarbonate) and bisbenzene chromium multilayer. A reaction of condensing Cr atoms with aromatic rings and carbonate units of the poly(bisphenol A carbonate) substrate was observed. The response of the polymer surface to the deposited chromium is discussed. Copyright © 1996 Elsevier Science Ltd.

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Introduction

Recently we reported X-ray absorption (NEXAFS) results obtained with oxygen plasma treated poly(propylene) foils[1] and conformationally different poly(ethylene terephthalate) samples[2]. We found that NEXAFS spectroscopy may reveal information on the molecular conformation and the chemistry at modified polymer surfaces. These X-ray absorption experiments may complete the information provided by e.s.c.a., nowadays the most important direct method in surface chemical analysis of polymeric materials. In this communication we report results of a NEXAFS spectroscopy study in the field of plastics metallization where special emphasis was given to the problem of the response of the polymer's surface. Here the application of e.s.c.a. is subjected to some subtle problems. The unambiguous identification of metal surface species, for instance the often discussed Me–O–C species requires a *fully verified* stabilization or compensation of surface charge. This is, in fact, a severe problem when monochromated X-rays are used in the experiments. We found that Near Edge X-ray Absorption Fine Structure (NEXAFS) spectroscopy carried out with virgin and metal covered polymers may substantially contribute to the discussion of reaction pathways and surface states. NEXAFS spectroscopy can be a surface analytical method providing molecular specific information because the excitation of electrons into unoccupied molecular orbitals via dipole transition from core levels are probed[3].

Samples and experimental

200 nm thick self-supporting poly(bisphenol A carbonate) films were prepared from a methylen 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 practiced by Hoffmann *et al.*, Technical University Berlin, Germany[4]. Surface charging was small with these films thus allowing for *partial electron yield* NEXAFS spectroscopy. Before NEXAFS spectroscopic analysis the films were analysed by X.p.s. to verify sufficient purity for a surface study. We found only Si surface impurities at concentrations ≤1 at%. Narrow X.p.s. C 1 s and O 1 s scans obtained with the untreated films resulted in spectra almost identical to the poly(bisphenol A carbonate) reference spectra published in ref. 5. Additionally, a polycarbonate, nominally free of phenyl rings, was analysed. Here we used a linear poly(hexanediolcarbonate), $\text{-}[\text{COO--(CH}_2)_6\text{--O}]_n\text{-}$ (Desmophen 2020, Bayer AG, Germany) which was smeared onto a silicon wafer as a thin film. This sample was also checked for purity by X.p.s. and MALDI-TOF-MS. It contains small amounts of aromatic and –OH terminating groups. Moreover, a NEXAFS spectrum of a multilayer of a chromium bis(arene) complex condensed and frozen onto an Au(1 1 1) single crystal surface is presented (for details see ref. 6). This spectrum was obtained with the same apparatus on the same beamline under equal conditions as the polycarbonate spectra reported in this communication.

Partial electron yield (PEY) X-ray absorption experiments were carried out on the HE-TGM 2 synchrotron beam line at BESSY I at a resolution better than 0.8 eV at the C 1s edge. The monochromator transmission function was obtained with a freshly sputtered Au sample. The energy scale was calibrated with the help of the C 1s → π^* resonance peak measured with a pyrolytic graphite sample (Advanced Ceramics Corp., Cleveland, OH, USA) which was fixed at 285.4 eV[7]. Characteristic features in the flux monitor signals were used to align the

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energy scales of all spectra relative to this value. Reproducibility of the spectra was carefully checked and verified by multiple scanning, typically four times. No indication for beam damage effects was found. Normalized spectra were scaled in units of the C- or O-*K*-absorption edge jump[3].

One mode of NEXAFS analysis, which is surface sensitive like X.p.s., is the *partial electron yield* (PEY) mode. In this case only electrons with energies higher than a pre-set threshold energy (150 eV for our experiments) may enter the channeltron detector. The information depth[8] of this NEXAFS mode, which is defined to be the depth, from which 95% of the detected electrons were generated, is estimated to be ≈30 Å for the C *K*-edge signal and ≈50 Å for the O *K*- as well as the Cr *L*-edge signals[9]. Here it was assumed that the measured signals predominantly originate from either C and O *KLL* or Cr *L* series Auger transitions including subsequent inelastic scattering events[3]. Low energy electron contributions to the signals were discriminated by the retarding potential. The pressure within the analysis chamber was 4×10^{-10} mbar during acquisition of NEXAFS spectra.

To look for crystallinity effects (cf. ref. 2) the polar angle of incidence of the linearly polarized synchrotron light was varied between 90° (electric field vector **E** lies *in the surface plane*) and 20° (**E** nearly parallel *to the surface normal*). No angle dependence was found at all with the PC films investigated suggesting statistical orientation of molecular structure units.

Cr evaporation was carried out *in-situ* within a preparation chamber (base pressure 1×10^{-9} mbar, 1×10^{-8} mbar during Cr evaporation) using a home-made evaporation system. The heater was fully heat shielded with tantalum. Cr was sublimed onto the substrate from 99.997% purity Cr through an aperture of the shielding. The aperture was located 7 cm away from the sample surface. An evaporation rate of ≈1 Å min^{-1} was estimated using a quartz micro balance.

Results

Figures 1a and *b* present C *K*-edge and O *K*-edge NEXAFS spectra obtained in the surface sensitive, angle resolved PEY mode with the polycarbonate film before Cr evaporation. Since there was no angle dependence, all 20°, 55° and 90° spectra of one selected set were added together thus giving improved statistics. In a first approach some of the spectral features marked with capitals will be interpreted in terms of the building block model for large molecules proposed by Stöhr[3] and by comparison to the spectra of a poly(hexanediolcarbonate) sample.

Considering the C *K*-edge spectra of the polycarbonate film (*Figure 1a*) we found a dominating sharp C 1s → π^*_{ring} resonance (A) at 285.4 eV. The intense feature D at 290.5 eV is most probably a C 1s → $\pi^*_{\text{C=O}}$ resonance. This interpretation is supported by several facts. The spectrum of isolated carbonate[3] reveals this resonance at a similar energy. The spectrum of poly(hexanediolcarbonate) is consistently dominated by this $\pi^*_{\text{C=O}}$ resonance (cf. *Figure 1a*). Last, but not least, there is a strong effect on this resonance when Cr is condensed onto the polycarbonate film. The less intense feature B at 287.2 eV can be tentatively attributed to a further, small C 1s → π^*_{ring} resonance (relying on benzene results[3]). The other small feature C at 289.3 eV, observed with *both* polycarbonate samples, is attributed to a C1s → C–H* resonance. The broad features between 292 and 305 eV are σ^* resonance contributions attributed to phenyl ring, –C–C–, C=O and C–O bonds.

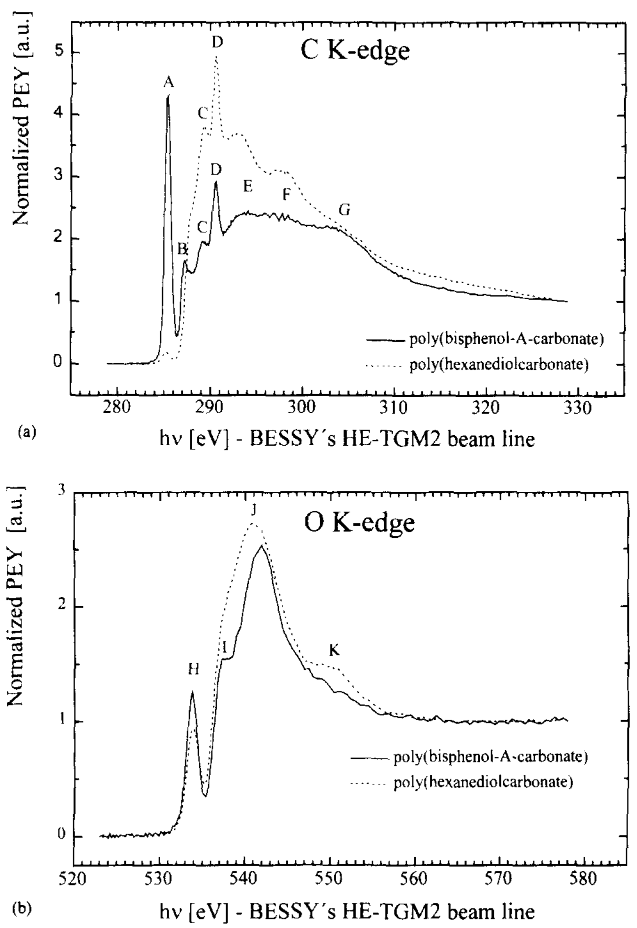

Figure 1 X-ray absorption partial electron yield (PEY) C (a) and O *K*-edge (b) spectra of a 200 nm thick self-containing poly(bisphenol A carbonate) film (Macrolon 3200, Bayer AG) and a poly(hexanediolcarbonate) sample (Desmophen 2020, Bayer AG). Proposals for an interpretation of spectral features marked by capitals are given in the text

The O *K*-edge spectra of both polycarbonate samples (*Figure 1b*) are also very similar to those reported in ref. 3 for an isolated carbonate species. An intense O 1s → $\pi^*_{\text{C=O}}$ resonance (H) was obtained at 533.7 eV. The pronounced edge I at a ≈4 eV higher photon energy could be a second O 1s → $\pi^*_{\text{C=O}}$ resonance contribution which occurs in certain cases due to a splitting of the carbonyl π^* system arising from bond–bond interactions[3]. Here an interaction with the phenyl ring system in poly(bisphenol A carbonate) could be the reason. This problem will be analysed by a quantum chemistry approach in the future. The second intense feature at 542.0 eV (J) observed with both samples is an O 1s → $\sigma^*_{\text{C–O}}$ resonance. Feature K is also assumed to be a σ^* contribution. The differences between both O *K*-edge spectra should be due to additional $\sigma^*_{\text{C–OH}}$ contributions originating from terminal –OH groups verified for the linear poly(hexanediolcarbonate). We found all the spectral features reported here to be fully reproducible with a series of samples.

Figure 2 presents C-*K*-edge spectra of poly(bisphenol A carbonate) after metallization with Cr. Obviously, there are strong effects. Unfortunately there is a spectral overlap with the second order Cr *L*-edge spectrum. We measured the effect carefully with a pure Cr sample. In that way the second order contribution characteristic of the used HE-TGM2 monochromator configuration was evaluated to be 6% of the first order Cr *L*-edge signal. With these reference data we were able to estimate the respective second order Cr contributions to the C-*K*-edge spectra. They are included in *Figure 2*. *Figure 3a* presents the C-*K*-edge spectra of metallized poly(bisphenol A carbonate) which were corrected for the second order Cr contributions. As the main result, we found that the π^*_{ring} resonance A and the carbonate related $\pi^*_{C=O}$ resonance D are substantially diminished in intensity. The effect increases with the dose of Cr atoms. For the 1 min Cr deposition an intensity decrease of ≈20% occurs, while for 4 min deposition one of ≈60% has to be stated for the π^*_{ring} resonance A. On the other hand we observed intensity gains on the low-energy side of feature A, in the valley between A and B, on the low energy side of feature C and in the region of the σ^* contribution. The effects of metallization at the O *K*-edge spectrum are illustrated by *Figure 3b*. A broadening and shifting to lower energies of feature H, characteristic of the carbonate's O 1s $\rightarrow \pi^*_{C=O}$ resonance in the case of untreated polycarbonate, is unequivocally observed. The valley between features H and I is filled and I itself is no longer observed after 4 min Cr deposition. The σ^* resonance region of the spectrum is also affected. Increasing Cr coverage is accompanied by a broadening of the σ^* features. Considering the O *K*-edge spectrum we remember the lowered surface sensitivity of the method in this energy range in comparison to the case of C *K*-edge spectroscopy. *Figure 3b* includes *L*-edge spectra of the condensed chromium. Here we refer to the significantly smaller absorption cross section for O 1s core hole formation when it is compared to the Cr 2p photoionization value.

Discussion and conclusions

Relying on the NEXAFS data we conclude that there must be an interaction between the Cr atoms condensing at the surface of the polycarbonate and the π electron system of the aromatic ring already at the early stages of metallization. This is clearly evidenced by the development of the C *K*-edge spectra. The result was confirmed by dedicated X.p.s. experiments. Here we found a decrease of the intensities of the aromatic ring $\pi \rightarrow \pi^*$ shake up structures and the carbonate related peak in the C 1s spectra vs. increasing Cr coverages. However, in X.p.s. one has to evaluate a rather low intensity $\pi \rightarrow \pi^*$ shake up feature in the C 1s spectrum, which is additionally superimposed by the more intense carbonate peak. For the discussion of possible species formed by the Cr–aromatic ring interaction, we recall results published by Francis and Timms[10] several years ago. The authors investigated the interaction of Cr vapours with low volatility, aromatic rings containing polymers and polymer solutions. They found the formation of stable bis(arene) complexes where the co-ordination of the Cr atom to two phenyl groups can be either intra- or intermolecular. Sometimes it was only possible to form 'half sandwich' complexes caused by steric problems in the later stages of metal addition. It should be possible to adopt this reaction pathway to the case of condensation of Cr atoms onto a poly(bisphenyl A carbonate) surface. Reaction of Cr atoms with aromatic rings available at

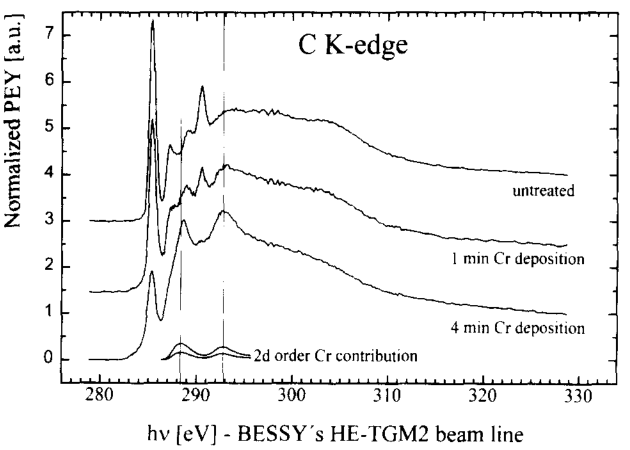

Figure 2 X-ray absorption partial electron yield C *K*-edge X-ray absorption spectra of a 200 nm thick self-containing poly(bisphenol A carbonate) film after 1 min and 4 min Cr evaporation at a rate of ≈1 Å min^{-1}. The second order Cr *L*-edge contributions at the bottom was included to show their peak positions on the energy scale. Both Cr spectra are properly scaled (in arbitrary units) to each other but are not related to the normalized C *K*-edge spectra

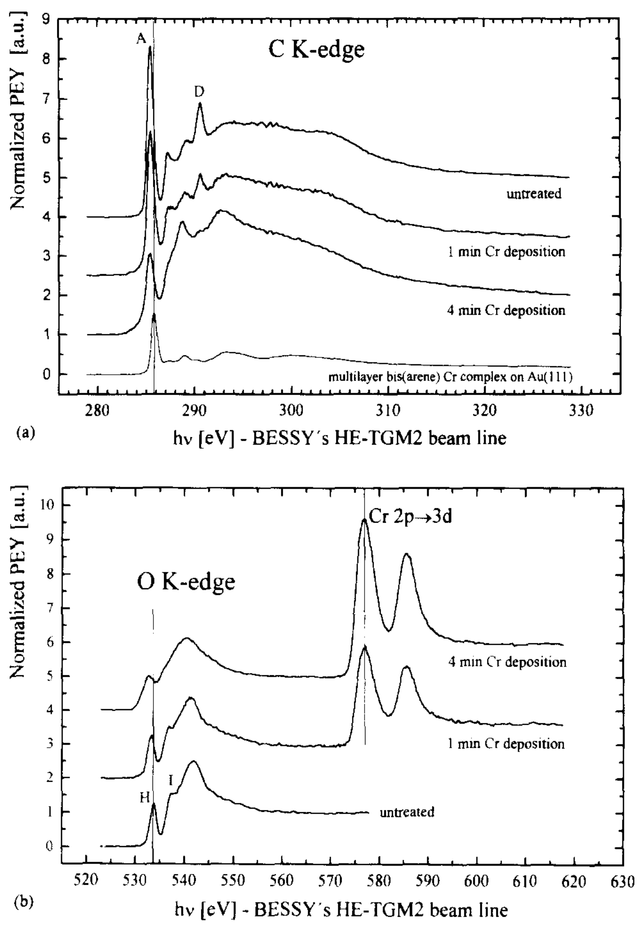

Figure 3 X-ray absorption partial electron yield (PEY) spectra (a) of the C *K*-edge and (b) of the O *K*-edge–Cr *L*-edge region of a 200 nm thick self-containing poly(bisphenol A carbonate) film 1 and 4 min evaporated with Cr. The C *K*-edge spectra are corrected for the second order Cr contribution. The C *K*-edge spectrum of a chromium bis(arene) complex multilayer condensed and frozen onto an Au(1 1 1) single crystal surface is given at the bottom (not scaled in intensity, from ref. 6)

the surface of the tangles of polycarbonate macromolecules could occur in a random pattern giving 'half-sandwich' and, with lower probability, bis(arene)-Cr complexes, also. One hint can be derived from the NEXAFS spectrum obtained with a bis(arene)-Cr complex multilayer which is included in *Figure 3a*. Its strong π^* resonance occurs at an energy of about 285.8 eV, just at the low energy side of the $\mathrm{C\ 1s} \rightarrow \pi^*_{\mathrm{ring}}$ resonance (A) of the polycarbonate. In another experiment, where Cr was evaporated onto the surface of a phenyl tricosanethiol monolayer on an Au substrate, Weiss *et al.*[6] also observed a strong decrease of the $\mathrm{C\ 1s} \rightarrow \pi^*_{\mathrm{ring}}$ resonance together with its shift from 285.2 to 285.8 eV. After Cr evaporation the shifted π^*_{ring} resonance was characterized by a small shoulder on the low-energy side. The authors concluded that most of the phenyl rings of the monolayer are in interaction with chromium atoms leading to Cr arene complex formation. In the given case of Cr evaporated on poly(bisphenol A carbonate) many phenyl rings in the investigated surface layer cannot be reached by Cr atoms. So one can only expect a certain effect on the high-energy side of $\mathrm{C\ 1s} \rightarrow \pi^*_{\mathrm{ring}}$ resonance. The filling of the valley between features A and B we observed with increasing Cr dose (cf. *Figure 3a*) is, in this picture, a result which is consistent with the assumption of the formation of Cr arene complexes, also.

Furthermore, we obtained another strong decrease of a feature in the C-*K*-edge spectra (D, cf. *Figure 3a*) with increasing Cr exposure, which is interpreted to be the $\mathrm{C\ 1s} \rightarrow \pi^*_{\mathrm{C=O}}$ resonance. The conclusion, supported by a diminished carbonate peak intensity in the X.p.s. C 1s spectrum, is that there is also an interaction of Cr with the carbonate unit of the polycarbonate. *Figure 3b* gives the respective O *K*-edge X-ray absorption spectra. The effect of Cr deposition on the O-*K*-edge spectrum should be interpreted to be the result of a superposition of the spectrum of the polycarbonate's $\mathrm{O1s} \rightarrow \pi^*$ and σ^* resonances and the respective contributions of –C–O–Cr complexes or Cr oxide species formed in the course of interaction. The finger-print NEXAFS spectrum of a Cr surface oxide was found to be very similar to the '4 min Cr evaporation' spectrum presented in *Figure 3b*.

In another X.p.s. study, where the thermally evaporated aluminium/poly(bisphenol A carbonate) interface was investigated[11], the authors reported the result that Al begins to interact with the C = O bond of the carbonate unit followed by reaction with its C–O bonds. In any case, the formation of an Al–O–C complex together with Al oxide and hydroxide are supposed to be the result of these interactions. At higher coverages another Al/polycarbonate interfacial reaction was found. An experimentally (X.p.s.) verified perturbation of the aromatic system together with the occurrence of a new low binding energy C 1s contribution were taken for a proof of a new Al–C bond with the polycarbonate's phenyl rings.

Our NEXAFS spectroscopy study supports the model of an interaction of the evaporated metal with both the aromatic rings and the carbonate units of poly(bisphenol A carbonate). The difference is that for the Cr/polycarbonate interface both anticipated reaction pathways, which are in competition, have to be taken into account already at low coverages. For the Al/polycarbonate interface the Al/–$(\mathrm{CO_3})$– interaction is, at low coverage, superior to the Al–phenyl ring interaction.

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