# Pt AND Pd CONTAINING ORGANOMETALLIC POLYMER FILMS AT METAL INTERFACES: REAL SYSTEMS STUDIED BY REFLEXAFS

X-ray Absorption Spectroscopy (XAS) experiments were performed at ESRF storage ring at the GILDA CRG beam-line. The monochromator was equipped with Si(311) crystals and was run in dynamical focusing mode. Armonic rejection was achieved by using a pair of Pd coated mirrors with a cutoff energy of 21 KeV. In order to obtain information only on the surface part of the specimen data were collected with the probe beam in total reflection mode. Prior to each measurement the reflectivity of the sample was collected at an angle $\phi$ about 0.6 times lower than the critical angle for total external reflection $\phi_c$ measured at 11700eV. For the Cr substrate $\phi$ resulted to be 0.13 deg whereas for the Au substrate it was 0.21 deg. XAS data in the so-called *extended* region were extracted with the AUTOBK code [1] by linear fitting of the pre-edge region and subtraction of the atomic background fitted with a cubic spline. Theoretical XAS signals were generated with the FeFF810 [2] program starting from the same cluster used for XANES analysis and that will be described hereafter.

XANES data collected at the Pt-$L_{III}$ edge were analysed using a 15 atoms cluster (5.5 Å); the minimal polynomial for the cluster chosen to interpolate the spectrum was: p1+p2+p3+ p1^2+p2^2+p3^2+p1*p2+p2*p3+p2*p3^2+p2^2*p3+p1^2*p2+p1*p2^2; the last four terms influence on the spectrum is little, but not negligible. The influence of the exchange potential on the peaks position is very strong for Pt-DEBP; Hedin-Lunqvist exchange potential was used for the fitting.

## A) XANES Pt-$L_{III}$ edge

XANES Pt-$L_{III}$ edge (11564 eV) spectra have been taken on Pt-DEBP polymer pellet; the data analysis permitted to deduce the atomic distances Pt-C, Pt-P and C-C. In order to calculate the atomic distances from the metal centre, a cluster with fifteen atoms has been used as a model; the structure of tributylphosphine ligands (PBu$_3$) were extracted from a literature model [3]; the structural parameters obtained for the pellet sample showed bond distances Pt-P, Pt-C and C-C of 2.34 Å, 1.99 Å and 1.29 Å respectively, fully consistent with the proposed molecular structure, i.e. a square planar arrangement of the phosphine and acetylene groups in *trans* configuration around the Pt centre; the proposed molecular structure of Pt-DEBP polymer is shown as inset of Fig.1.

The sensitivity of the XANES spectra to the angular distortions and the bond distances has been tested.

## B) XAS Pt-$L_{III}$ edge

The XAS data in the *extended* region, extracted as explained before, are shown in Fig.1 whereas the Fourier Transforms are shown in Fig.2. Contribution to the total XAS signal from the C1, P and C2 atoms were considered by including the single, double and triple scattering paths for the photoelectron. For describing the single scattering involving the Pt atom and the C1, P and C2, i.e. Pt-C1, Pt-P and Pt-C2 respectively, we used the bond length and Debye-Waller factors $R_1$, $\sigma_1$, $R_2$, $\sigma_2$, $R_3$, $\sigma_3$; each path has a two-fold degeneration reflecting the presence of two P and two acetylene groups around Pt. The double scattering Pt-C2-C1 has been described by the parameters $R_3$, $\sigma_3$ and with a fourfold degeneration. To describe the triple scattering Pt-C1-C2-C1 the parameters $R_3$, $\sigma_3$ with twofold degeneration were chosen. The global amplitude factor $S_0^2$ and the edge position $\Delta E_0$ were also refined for each data set; due to a limited number of free

parameters in the data relative to the film $S_0^2$ and Debye-Waller factors were fixed to the best-fit values found for the bulk form. Fits of the data were carried out in R space after Fourier Transform of the $k^3$ weighted EXAFS data in the range k=3.5-13.5 Å$^{-1}$ for the pellet and k=3.5-8.0 Å$^{-1}$ for the thin films. The R range for the fits was R=1.4-3 Å. Fits were made by using the FEFFIT code [4] and the results are collected in table 1.

The data analysis results reported in Tab.1 bring to the conclusion that atomic distances and geometrical arrangement of phosphines and acetylenes around the transition metal in Pt-DEBP macromolecules are not influenced by the substrate, being all the parameters almost identical for the films deposited onto Au and Cr and for the pellet sample. Moreover, if the C≡C distance determined for the pellet sample is attributed to a triple imperturbed bond, the similarity between the C≡C distances obtained for the pellet and for the film sample deposited onto Au/Si (111) and Cr/Si(111) is an indication for the absence of either partial or full opening of triple bonds, i.e. of the absence of any interaction between the acetylene groups and the substrate surface that would be responsible of a partial opening of the triple bonds and subsequential elongation of the C≡C distance.



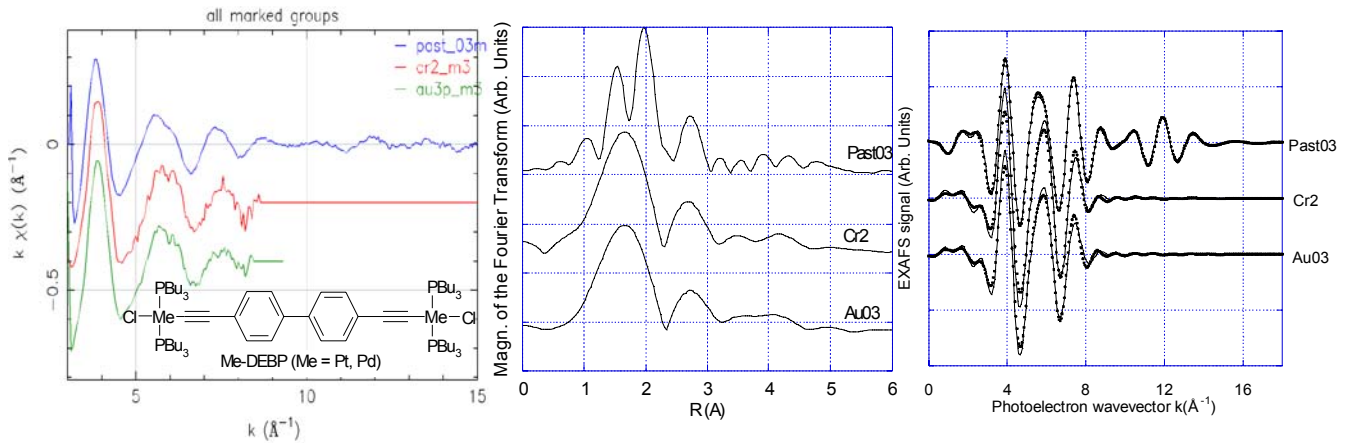Fig.1: XAS data in the *extended* region      Fig.2: Fourier Transforms of the XAS data

| Sample | $R_1$ Å | $\sigma_1$ *$10^{-4}$ Å$^2$ | $R_2$ Å | $\sigma_2$ *$10^{-4}$ Å$^2$ | $R_3$ Å | $\sigma_3$ *$10^{-4}$ Å$^2$ |
|---|---|---|---|---|---|---|
| Past03 | 1.98(1) | 17(5) | 2.30(1) | 38(4) | 3.21(1) | 52(7) |
| cr2 | 1.94(3) | 17 | 2.28(3) | 38 | 3.19(4) | 52 |
| au3p | 1.94(4) | 17 | 2.26(4) | 38 | 3.18(4) | 52 |

*Tab.I: Results of the quantitative data fits. The Debye-Waller factors were fitted in the Past03 smple and then kept fixed for the others. Errors are calculated by a $\chi^2$ analysis at a 68% confidence level.*

**References:**
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