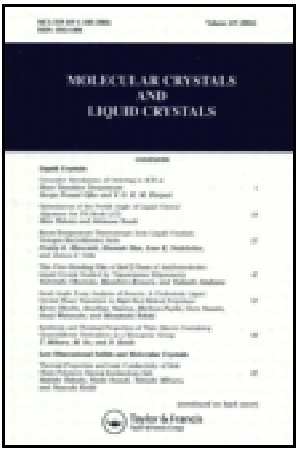

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

New Results on Metal-Polymer Interfaces

P. Dannetun [a] , M. Lögdlund [a] , W. R. Salaneck [a] , C. Fredriksson [a] , S. Stafström [a] , A. B. Holmes [b] , A. Brown [b] , S. Graham [b] , R. H. Friend [b] & O. Lhost [a]

[a] Department of Physics, IFM Linköping University, S-581 83, Linköping, Sweden

[b] Cavendish Laboratory, University of Cambridge Cambridge, CB3 OHE, England

Version of record first published: 24 Sep 2006.

To cite this article: P. Dannetun , M. Lögdlund , W. R. Salaneck , C. Fredriksson , S. Stafström , A. B. Holmes , A. Brown , S. Graham , R. H. Friend & O. Lhost (1993): New Results on Metal-Polymer Interfaces, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 228:1, 43-48

To link to this article: http://dx.doi.org/10.1080/10587259308032141

Mol. Cryst. Liq. Cryst. 1993, Vol. 228, pp. 43-48
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Printed in the United States of America

NEW RESULTS ON METAL-POLYMER INTERFACES

P. DANNETUN, M. LÖGDLUND, W. R. SALANECK,
C. FREDRIKSSON, and S. STAFSTRÖM
Department of Physics, IFM
Linköping University
S-581 83 Linköping, Sweden, and

A. B. HOLMES, A. BROWN, S. GRAHAM, R. H. FRIEND and O. LHOST
Cavendish Laboratory, University of Cambridge
Cambridge CB3 OHE, England.

Abstract: New results on studies of the early stages of formation of the aluminum-poly(*p*-phenylenevinylene) interface are presented.

INTRODUCTION

The strong interest which exists today in metal contacts on conjugated polymers goes beyond simple measurements of electrical conductivity on "conducting polymers". Because of recent developments in polymeric field effect transistors (FET's)[1], light emitting diodes (LED's)[2], information about the metal-polymer interface is increasingly relevant to assessing both the science done with these devices as tools, as well as eventual applications performance[3]. These developments are partial indication that organic polymer materials in general are finding an ever increasing number of applications as *electronic materials*[4,5] .

At EROPS-6, we reported upon our work on model molecules of conjugated polymers to study the chemical and electrical structural details of the early stages of metal-polymer interface formation, studied by X-ray and ultraviolet photoelectron spectroscopy (XPS and UPS). We contrasted the behaviour of Na and Al vapour-deposited on a diphenylpolyene, namely α, ω-diphenyltetradecaheptaene, denoted DP7. The chemical structure is drawn in Fig. 1. The polyene part of the DP7 molecule is esentially o short chain of *trans*-polyacetylene[6-8]. In addition, we discussed new data on the early stages of interface formation of aluminum on poly(*p*-phenylenevinylene), or PPV. Because of space limitations here in the proceedings, we present only some of our Al/PPV spectra, and discuss a preliminary interpretation.

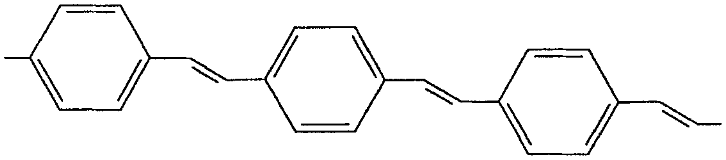

Figure 1: The chemical structure of poly(*p*-phenylenevinylene) is illustrated.

EXPERIMENTAL METHOD

The spectroscopy which has been found to be most appropriate in studying the (surface) electronic and chemical structure of organic materials is photoelectron spectroscopy, UPS and XPS. XPS stands for X-ray photoelectron spectroscopy (called ESCA[9] by chemists), and employs soft X-ray excitation to excite electrons in atoms of the molecular (or other) system under study, and then involves the analysis of the kinetic energy distribution of the photo-emitted electrons. If ultraviolet photons are used, the technique is called UPS. XPS provides information of core-level electrons in the solid, while UPS provides a measure of the valence electronic structure. Both XPS and UPS are surface sensitive.

Simultaneous with the photoionization of an atom by removing a core-electron from an atom in a molecule in XPS, the remaining electrons in the molecule may be excited, some across the forbidden electron energy gap, leading to weak satellite structure on the high binding energy side of a given core level spectral peak. These socalled shake-up, or simply s.u., peaks corresponds to real many-body, almost optical-like, excitations in the molecular ion[10,]. They represent a measure of the *electronic localization* of the π-system under investigation[11]. The application of UPS and XPS to studies of metal-(conjugated polymer) interfaces has been reviewed recently[3].

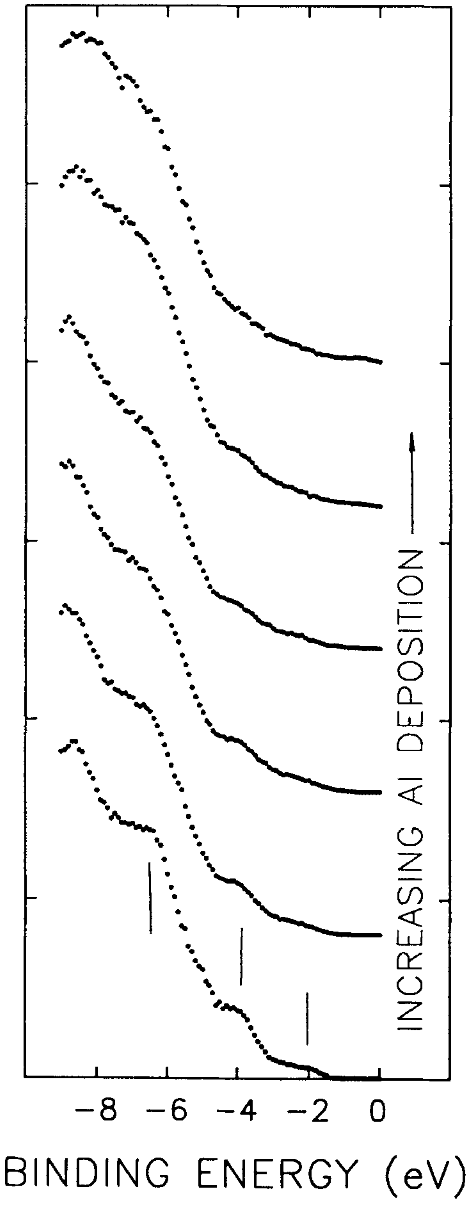

Figure 2: The low binding energy portion of He I spectra of clean PPV (bottom, Ref. 12) and with increasing monolayers of Al on PPV are shown.

RESULTS AND DISCUSSION

In Fig. 2 are shown several He I (21.2 eV photons) UPS spectra of the lowest binding energy region of the valence band of PPV during the early stages of interface formation with Al. The Fermi energy, as determined from the spectrometer, is at 0 eV in the figure. The peaks at approximately -2, -4 and -6½ eV, marked by small lines, correspond to major structure in the π-system of clean PPV[12]. The valence band edge is seen near -1½ eV, corresponding reasonably well with the optically determined electronic band gap in PPV[13]. Clearly, the π-structure, especially that at the band edge, is strongly affected, essentially destroyed, by the physical deposition of aluminum. The interpretation of the effects seen in the UPS spectra shown in Fig. 2 are confirmed by the XPS C(1s) core spectra, in particular, by the s.u. satellite features.

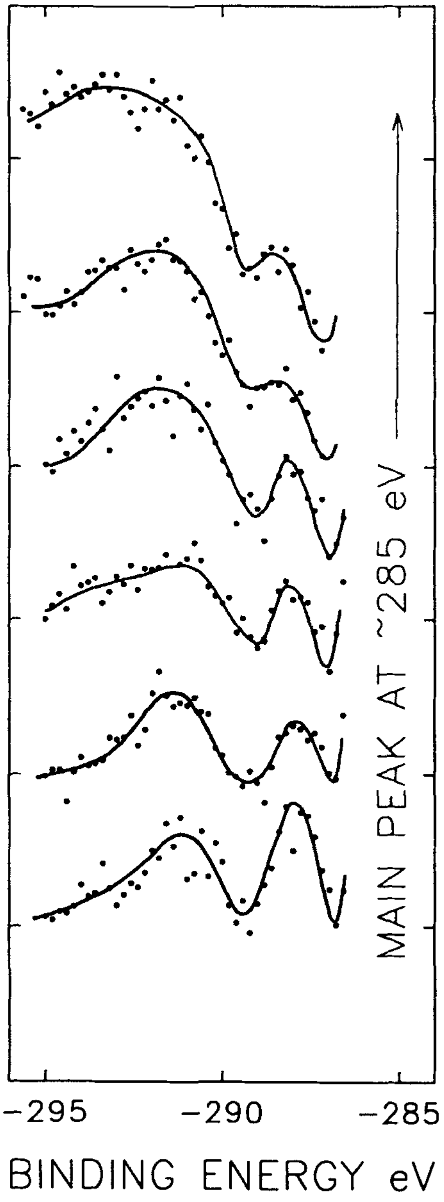

Figure 3: The shake-up portion of the C(1s) spectra of PPV (lower curve) as aluminum is vapour deposited, approximatley in monolayer steps (successive curves above), is shown.

In Fig. 3 is shown the shake-up satellite portion of the C(1s) spectra for PPV as Al is vapour deposited essentially at a monolayer at a time. The data are somewhat noisy because the shake-up features are intrinsically weak. The C(1s) main line (peak) has been omitted for clarity. There is a small shift in the position of the maximum of the main peak in each, due to small work function changes during deposition of aluminum. These small shifts, which are hardly visible on the energy scale shown, have not been removed from the data in Fig. 3.

As aluminum is deposited, approximately in monolayer steps, it is seen in the succesive upper curves in Fig. 3, that the -288 eV peak is affected (decreases in intensity). The region for $-E \geq 289$ eV exhibits an increasing background intensity, due to electrons from the C(1s) level in the atoms of PPV which are inelastically scattered in the aluminum overlayer. A variety of finger prints with in the full C(1s) spectra, however, indicate that the lower energy peak actually does decrease in intensity, and is not merely covered up by the inelastic electron background. In parallel with the results on α, ω-diphenyl-tetradecaheptaene[6,7], the "low energy" shake-up peak (closest to the main peak), near -288 eV in Fig. 3 (bottom), corresponds approximately to electrons removed from the vinyl-group portion of clean PPV.

While the "higher energy" shake-up peak, near -291 eV, corresponds to electrons removed primarily from the benzene ring portion of PPV.

In our previous work on the vapour deposition of aluminum on α, ω-diphenyltetradecaheptaene[6,7], we found that the XPS shake-up spectra are more distinctly divided between a polyene-derived "lower energy" peak and a phenyl-group-derived "higher energy" peak, in the same approximate binding energy regions as the two peaks discussed for the case of PPV above. In the case of DP7, the π-system is clearly affected by the vapour deposition of aluminum, and the lower energy shake-up peak completely disappears after a few monolayers coverage. The UPS spectra of DP7 are very clearly affected when aluminum is vapour-deposited on to the surface, in that the two lowest binding energy peaks, corresponding to two distinct π-states on the polyene chain, also completely disappear. Thus, even though the indications in the UPS and XPS spectra of the early stages of formation of the Al/PPV interface are less distinct than in the case of Al/DP7, the final chemical and electronic structural changes appear to be similar. Quantum chemical calculations of the interaction of aluminum with PPV are under way, and will be reported elsewhere[14].

SUMMARY

An example of the type of information which can be obtained on polymer-metal interfaces using photoelectron spectroscopy has been illustrated with the results of a study of the interaction of aluminum with poly(*p*-phenylenevinylene). The example serves to illustrate that chemical interactions at the surfaces of conjugated materials may lead to electronic structural changes, which in turn may affect the charge injection characteristics at the interface between certain metals and certain conjugated polymers.

ACKNOWLEDGEMENTS

Part of this work was carried out with support from the EEC SCIENCE program, under contract number 0661. The authors in Linköping are greatful for general support from the Swedish National Board for Industrial and Technical Development (NUTEK), the Swedish Natural Sciences Research Council (NFR) and the Neste Corporation, Finland.

The authors are particularly greatful for discussions with, and other help from, Professor J. -L. Brédas.

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