

High Resolution XPS Spectra of Polymers

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About this Compilation

Many polymers have closely similar core level XPS spectra: one of the basic ideas behind this brief compilation is to provide an indication of how previously unused or inaccessible features in XPS spectra such as valence band signals may be employed to distinguish materials.

Although the cross section of valence band orbitals is not high for Mg K α and Al K α excitation, AXIS 165 provides excellent collection efficiency for these low binding energy transitions, enabling their acquisition within a matter of seconds. Valence band “fingerprinting” for qualitative identification becomes routine and the use of characteristic individual valence peaks in quantitative determinations and mapping provides new possibilities. Far from being simply exotic objects of purely theoretical interest, valence band spectra from AXIS spectrometers have become a useful practical tool, e.g. as a sensitive indicator of surface cleanliness.

The approach in presentation mirrors the earlier publication¹ and is designed to emphasise the key differences (as well as the similarities) in the polymer spectra. Simple comparison by eye of the appropriate region should be sufficient to characterise an unknown spectrum qualitatively even if the spectrometer transmission function on which the wide scan is recorded is significantly different from that of AXIS 165. Despite the obvious theoretical difficulties involved in exhaustive valence band structure studies (see p. 10), the fingerprint nature of the valence energy levels clearly may be used to good analytical advantage. Comparison with appropriate model systems enables an unambiguous assignment of structure. This is particularly useful in the case of isomeric materials as shown on pages 18 and 19.

This collection of spectra is intended to supplement the earlier “AXIS HS” collection and other collections^{2,3}, rather than to supplant them. AXIS 165 represents a major improvement in both sensitivity and resolution beyond the AXIS HS used to collect data for the original compilation, and this is reflected both in the speed of acquisition and the fresh detail - some of it confirming previous theoretical speculation - available in both region and valence band scans. The curve fitting information remains, however, a representation of achievable capability with particular instrumentation, rather than a specification of performance, and should be interpreted appropriately.

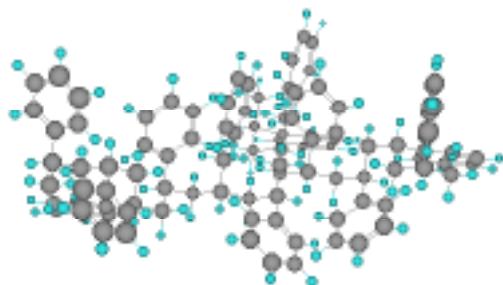
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1. Kratos Publication A496 (August 1992)
 2. “Surface Science Spectra” (ISSN: 1055-5269), American Institute of Physics (AIP), New York
 3. “High Resolution XPS of Organic Polymers” (ISBN 0 471 93592 1) G. Beamson and D. Briggs, Wiley, London (1992)

Hydrocarbon polymers

Polyethylene, polypropylene, and polystyrene.

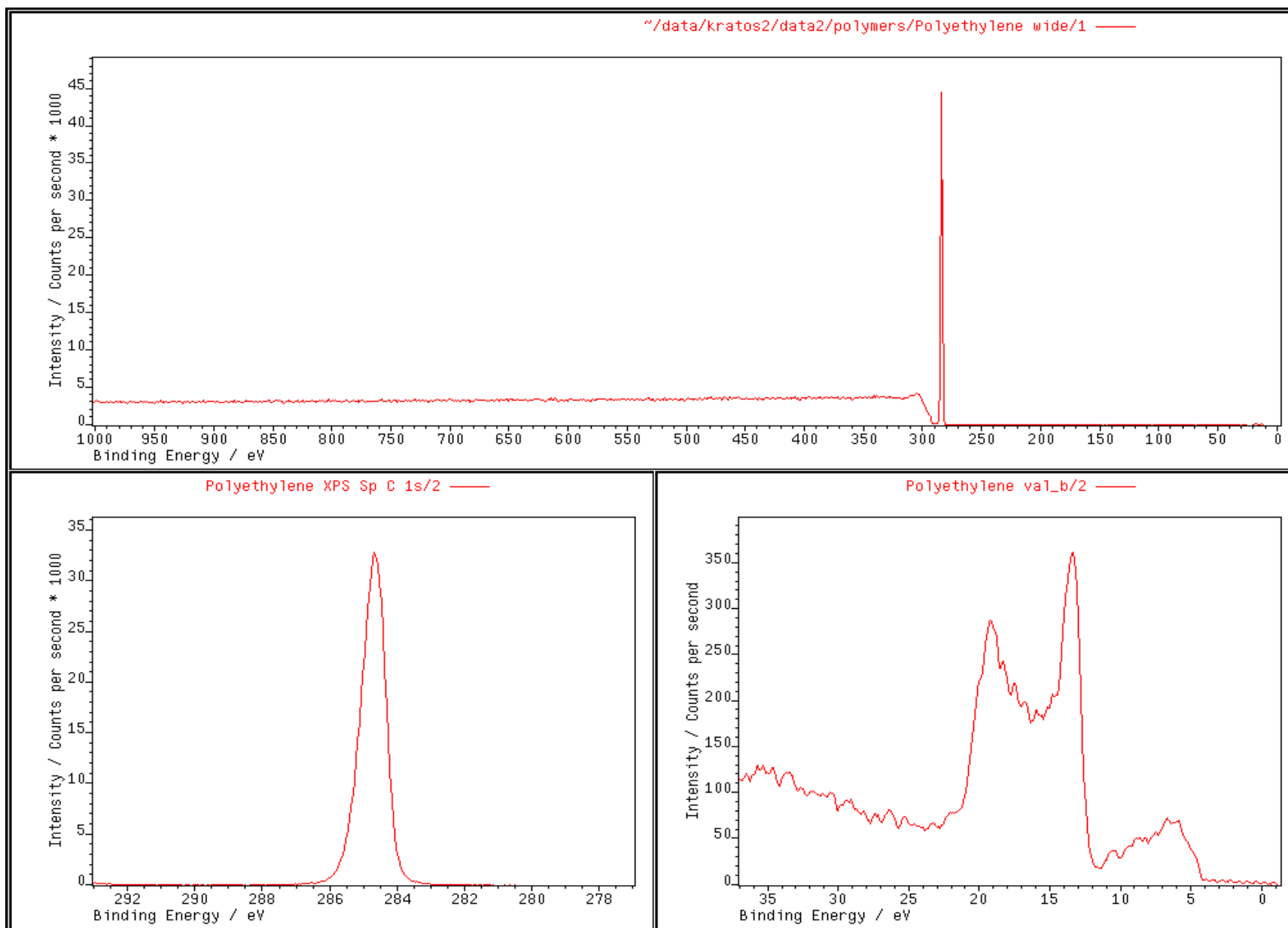
Note again the subtle differences in detail, despite the close similarity of the survey scans. The C 1s peak shapes are almost identical, but reveal slight differences in overlay as well as different charging shifts. The $\pi \rightarrow \pi^*$ shake up satellite characteristic of conjugated systems is clearly visible for polystyrene, with a hint of a second loss peak (better signal to noise) The remarkable resolution available in the valence bands shows clear and meaningful fine structure.

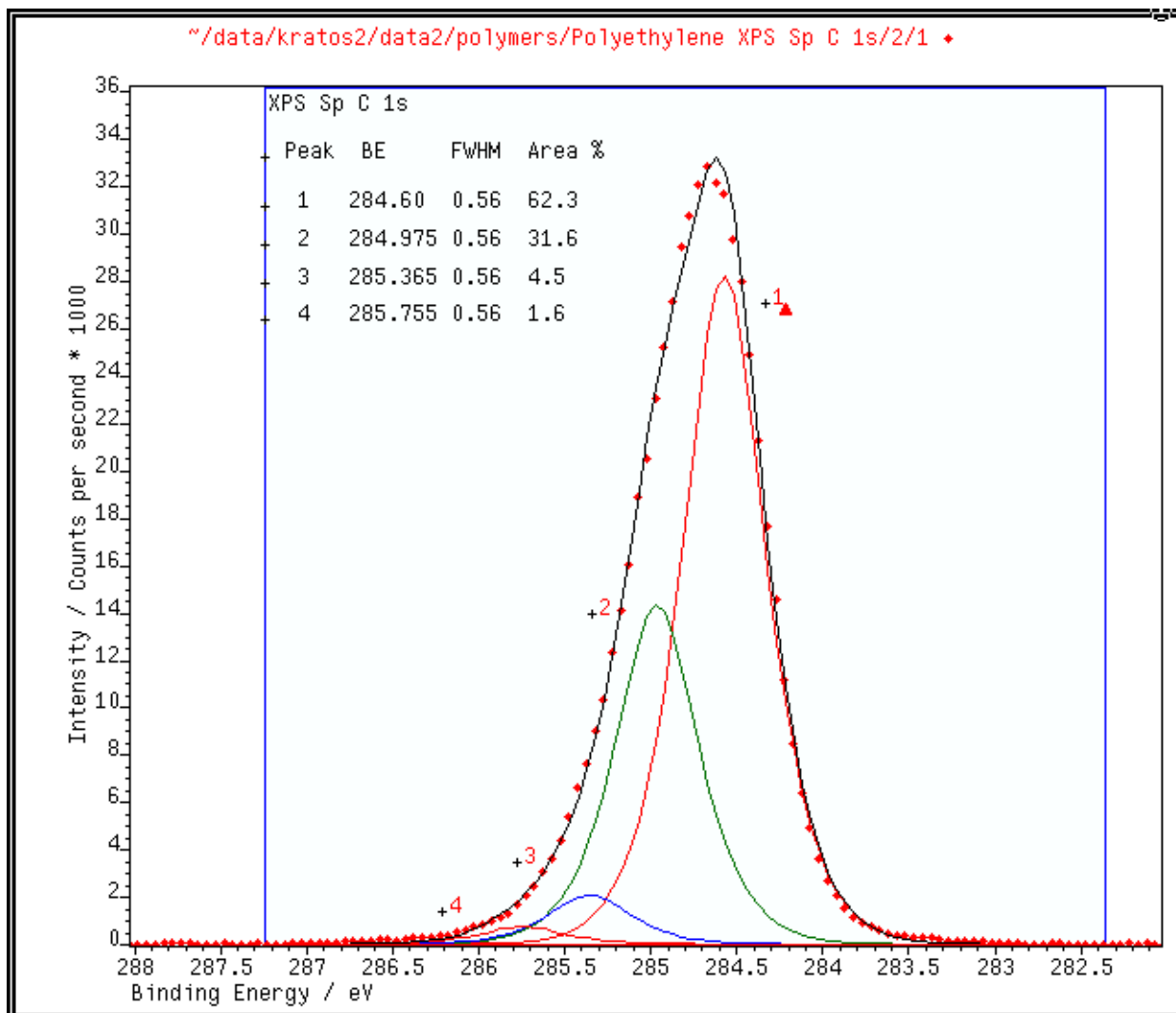
The asymmetric peak fit for polyethylene is after the method of Beamson *et al.*¹ mirroring their findings with respect to resolution of vibrational levels and again hinting at a “fifth” level. Component width here is significantly better than for the AXIS HS and Scienta fits (0.56eV vs 0.59 and 0.67eV respectively, constrained) and is achieved without “enhancement”. The differences in plot resolution reflect different “screen capture” conditions, the “low resolution” plots approximating to the normal size of a PC screen (640 x 480 pixels), and the “high resolution” according with Sun workstation practice (1005 x 790 pixels, about). Data were *collected* under the same conditions.

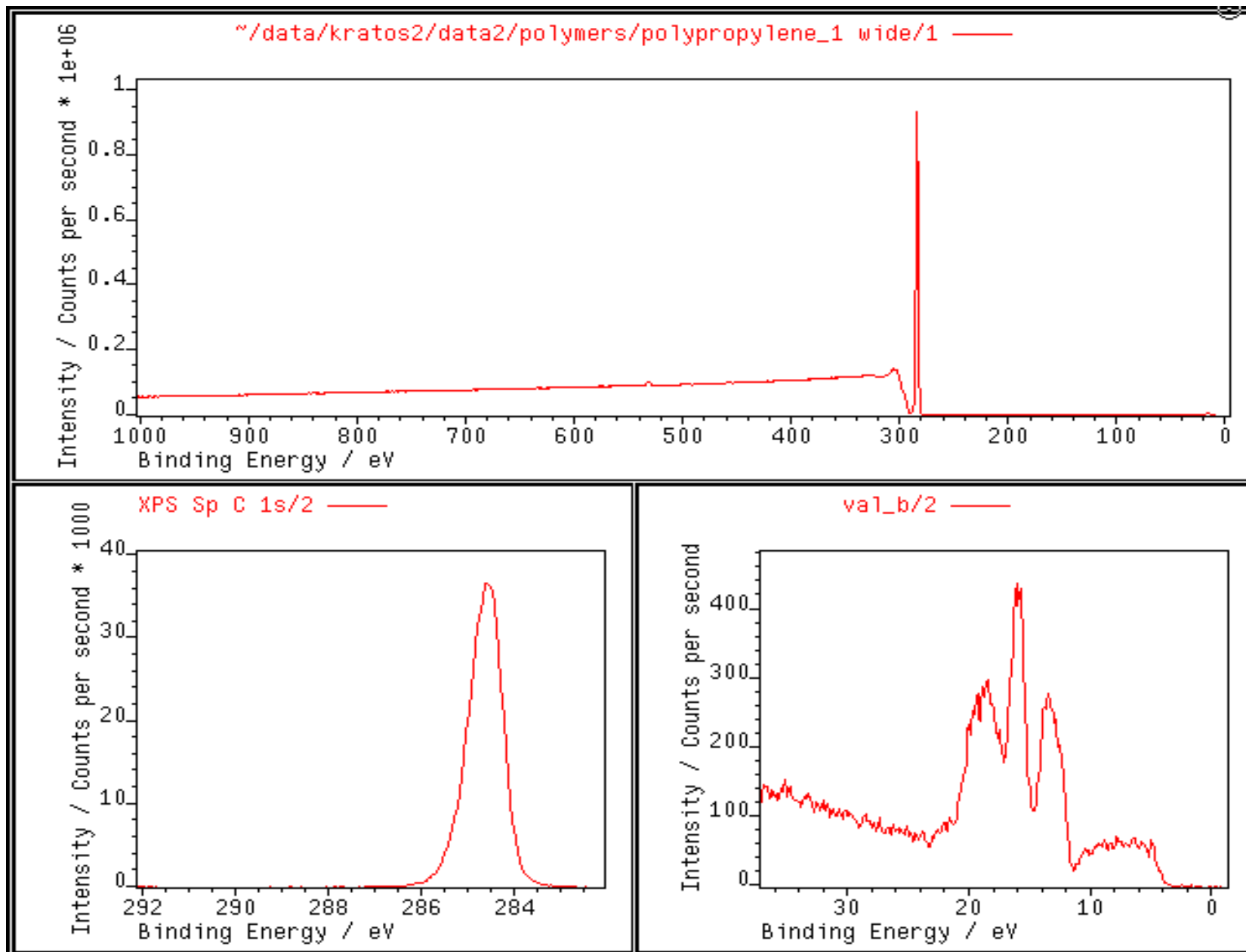


Polystyrene - a reminder that not all structures are as simple as their empirical formulae suggest, especially if large, rigid groups are present.

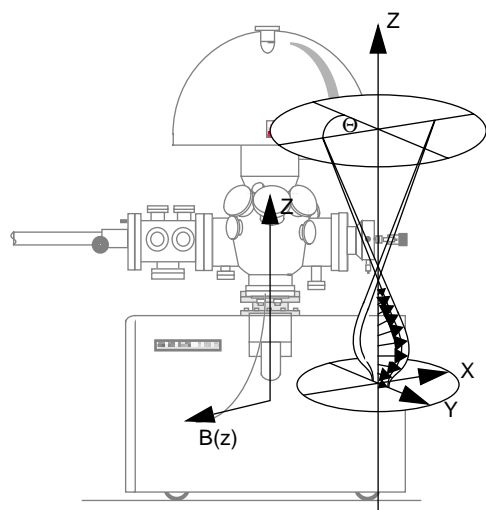
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1. G. Beamson, D.T. Clark, J. Kendrick, and D. Briggs, *J. Electr. Spectroscopy & Rel. Phenom*, 57 (1991), 79







AXIS 165 - The Instrument



AXIS 165 is a photoelectron spectrometer designed for multi-technique applications.

Imaging XPS comes as standard, evolving naturally from the AXIS system approach. More important, imaging is totally integrated with microanalysis procedures. Key design elements include an innovative magnetic immersion lens, developed from the device invented by Kratos and pioneered in AXIS HS, and a high efficiency lens-analyser combination. The large analyser size, as well as giving AXIS 165 its name, (the analyser has 165mm mean radius) enables use of more detectors at the output and provides a better optimisation for the zoom lens at its input. An incidental but equally important property of the large diameter analyser is a higher ultimate energy resolution, seen clearly in these polymer spectra. A unique dual mode transfer lens system gives an elegant balance between complexity and simplicity, four element electrostatic components exploiting improvements in optics and control over simpler three element approximations. Each component of the AXIS 165 system performs a unique task - the hemispherical analyser is concerned solely with high performance energy analysis. A single detector for both mapping and spectroscopy in all modes

removes the need for cross calibration and obviates gain drift. The input lens system provides electron transport from the sample to the analyser and precision apertures define exact spatial relationships for XPS analysis. XPS images are derived by scanning the focal point of the lens across the sample, which provides the unique advantage of multipoint XPS analysis without need for sample repositioning, just as in Auger point analysis. The input lens column also carries an integral coaxial charge neutraliser (another Kratos patent) which exploits the unique properties and geometry of the immersion lens to provide almost perfect charge compensation for analysis of polymers and other insulators and for work with rough surfaces such as powders.

For further information contact your local Kratos representative today!