

Lab 2 – Module γ_1

Bonding Effects on Electron Energy Levels

XPS Study of Core Electron Binding Energy Shifts in Polymers

OBJECTIVES

- ✓ Review electronic structure concepts
- ✓ Learn principles of x-ray photoelectron spectroscopy
- ✓ Investigate electron binding energies of various synthetic polymers

SUMMARY OF TASKS

- 1) Calculate the predicted area ratios of C 1s electrons in PVDF, PS, and Nylon
- 2) Measure XPS low and high resolution spectra for all polymers
- 3) Identify, Calibrate XPS C 1s peaks, and compare peak areas with values expected from chemical structure
- 4) Determine scaling relationship of 1s electron energies and atomic number
- 5) Interpret valence band spectrum for PE

BACKGROUND

Electronic Shells and Atomic Orbitals

As we have learned in 3.012, electrons orbiting the nucleus of an atom take on discrete energy values, specified by solutions to the Schrödinger equation. For the hydrogen atom,¹

$$E_n = -\frac{\mu e^4}{2(4\pi\epsilon_0\hbar n)^2} = \frac{-13.60eV}{n^2} \text{ where } n = 1, 2, 3\dots \quad (1)$$

where μ is the reduced mass, e is the electron charge, ϵ_0 is the free space permittivity, and the integer n is the principal quantum number, which specifies the electronic shell. From this expression we see that $n=1$ is the lowest energy state. For a hydrogen-like atom with a single electron and a nucleus having Z protons, we will learn in 3.012 that the energy eigenvalues are modified to¹:

$$E_n = -\frac{\mu Z^2 e^4}{2(4\pi\epsilon_0\hbar n)^2} = \frac{-13.60Z^2 eV}{n^2} \quad (2)$$

As one might expect, raising the nuclear charge causes the electron to be bound more tightly, lowering the energy (i.e., the energy becomes more negative). The wavefunction solutions of the Schrödinger equation quantify the probability distribution of the electron as a function of its distance from the nucleus.

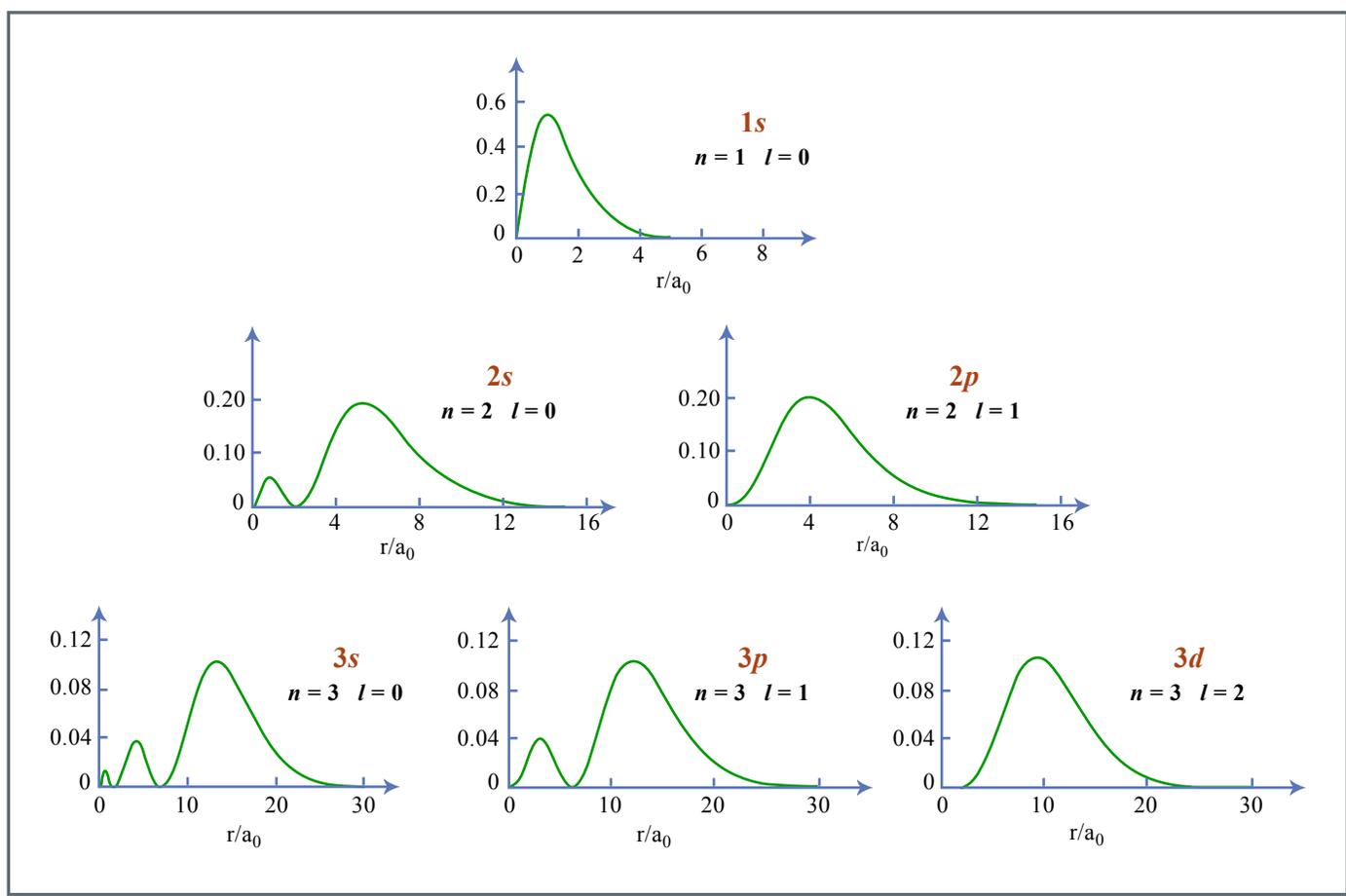


Fig. 1. Radial electron density distribution for atomic orbitals in hydrogen-like atom.

Figure by MIT OCW.

Note that the electron density is concentrated further from the nucleus for higher electronic shells.

For atoms with more than one electron, the Schrödinger equation can be solved only by approximation. In multi-electron atoms, electrons fill atomic orbitals of successive electronic shells. Electronic states are specified by the quantum numbers n , l , m , and m_s (principal, angular momentum, magnetic and spin), which have the allowed values:

$$n = 0, 1, 2, 3, \dots$$

$$l = 0, 1, 2, \dots, n-1$$

$$m = 0, \pm 1, \pm 2, \dots, \pm l$$

$$m_s = \pm 1/2$$

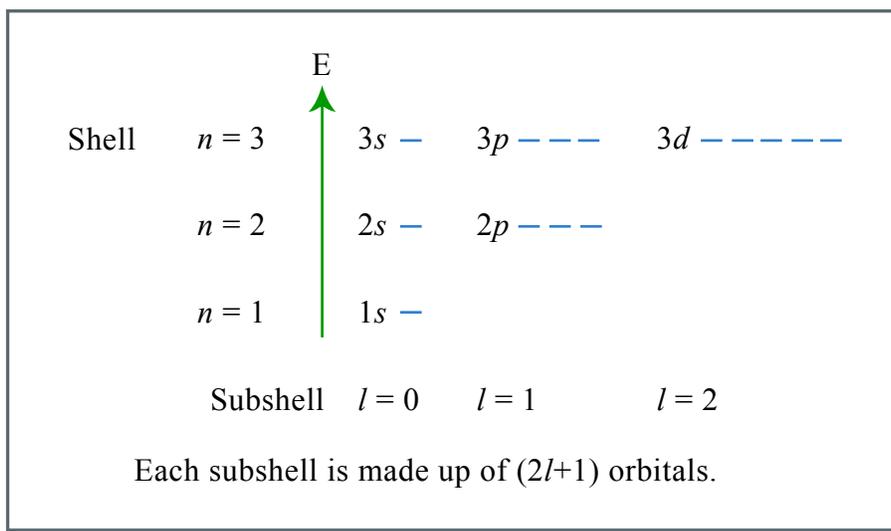


Fig. 2. Schematic of electronic shells, subshells and orbitals .

Figure by MIT OCW.

Addition of electrons to a hydrogen-like system of fixed nuclear charge will modify the binding energy of the residing electron—with the addition of electrons, the first electron becomes less tightly bound to the nucleus. The binding energy of electrons in multi-electron atoms can be approximately calculated by a method known as the Hartree-Fock method.¹

When atoms bond to make molecules, orbitals can *hybridize* in order to minimize overlap. The combination of s and p orbitals to create sp^3 and sp^2 hybrid orbitals occurs in carbon-based compounds such as the polymers we will investigate.

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Fig. 3 a) Combination of s and p orbitals to create sp^3 hybrid orbital. b) The ethane molecule incorporates a C-C sigma bond between sp^3 hybrid orbitals of the $n=2$ shell of carbon. (images from [2]).

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Fig. 4 a) Combination of s and p orbitals to create sp^2 hybrid orbital. b) The ethylene molecule has a C-C sigma bond between sp^2 hybrid orbitals of $n=2$ shell of C and a pi bond with the remaining 2p orbitals. (images from [2]).

Because the bonding of atoms changes the electron density distribution about the nucleus, bonding also affects the energies of electrons in lower electronic shells.

Photoelectron Spectroscopy

The direct measurement of electron binding energies in atoms and molecules can be accomplished using a technique known as photoelectron spectroscopy. Photoelectron spectroscopy is based on the photoelectric effect, discovered by J.J. Thompson in 1899 and explained by Einstein in 1905, who was later awarded the Nobel prize for his work. In X-ray Photoelectron Spectroscopy (XPS), also called Electron Spectroscopy for Chemical Analysis (ESCA), x-rays irradiated on a sample result in the ejection of secondary electrons (photoelectrons) from the sample near surface (0.5-10 nm) with characteristic energies. Analysis of the photoelectron energies can provide quantitative information about the elemental composition of the sample as well as its bonding environment.

An XPS instrument typically uses a monochromatic x-ray source with photon energy given by:

$$E = h\nu = \frac{hc}{\lambda} \quad (3)$$

To eject an electron from the surface of a material, a photon must have energy larger than the binding energy of the electron, E_B . The excess energy of the photon is transferred to the ejected electron as kinetic energy:

$$E_{kin} = h\nu - E_B \quad (4)$$

Because the binding energy of an electron is characteristic of the element, by measuring the value of the kinetic energy of photoelectrons, the binding energy can be calculated and the elements present in the material determined.

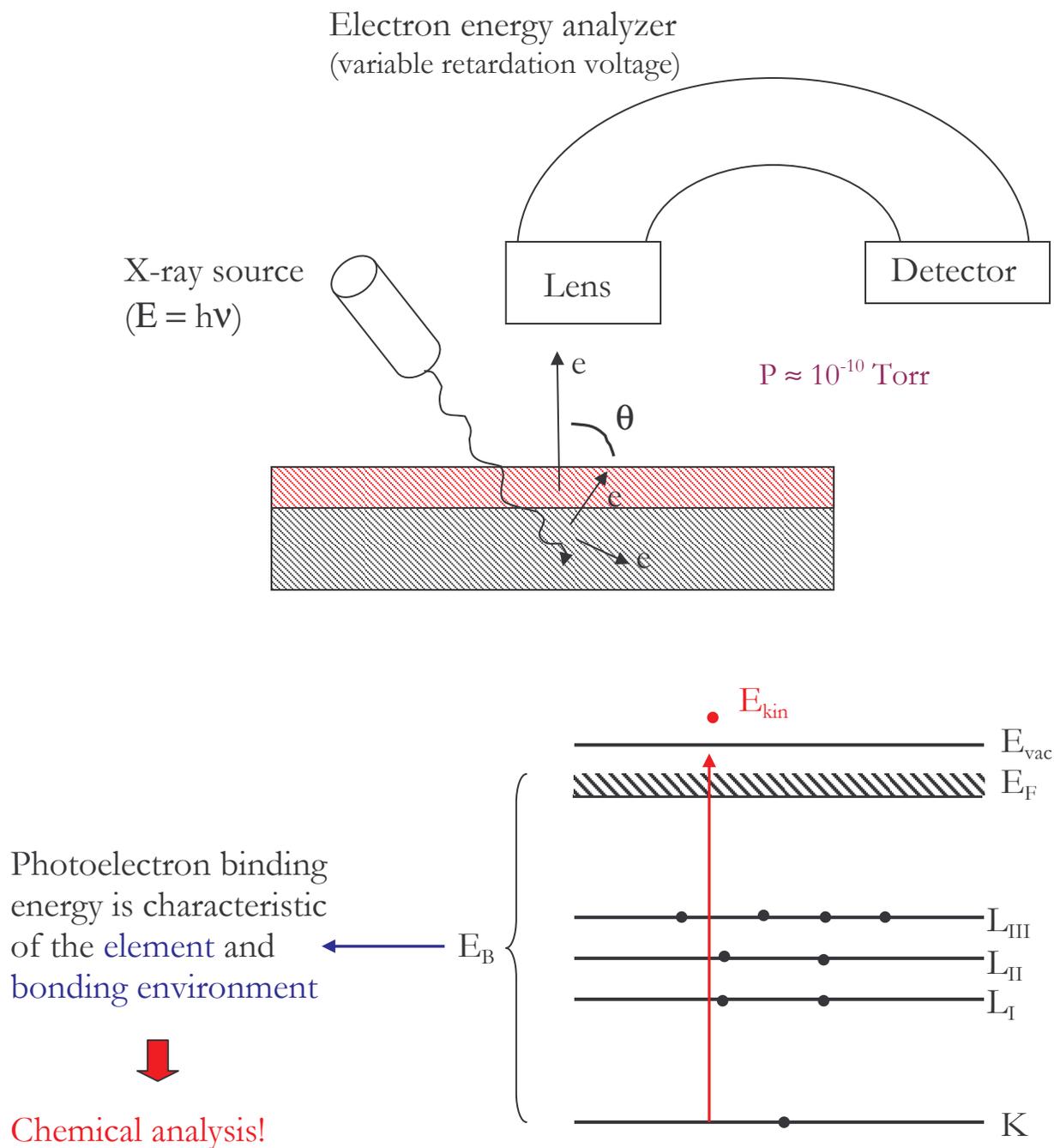


Fig. 5 Schematic of XPS experiment.

Note that XPS is intrinsically a surface-sensitive technique, because to identify the electron's binding energy, it must escape the sample surface without undergoing an inelastic collision that would cause it to lose kinetic energy. For the same reason, XPS is performed in a high vacuum environment. Electrons able to escape the surface are collected through a lens and passed through an energy analyzer to determine the spectral range of electron energies.

An XPS spectrum plots the number of electron counts vs. the electron binding energy calculated from (4). Core electron states are observed at high binding energies, along with Auger electrons.

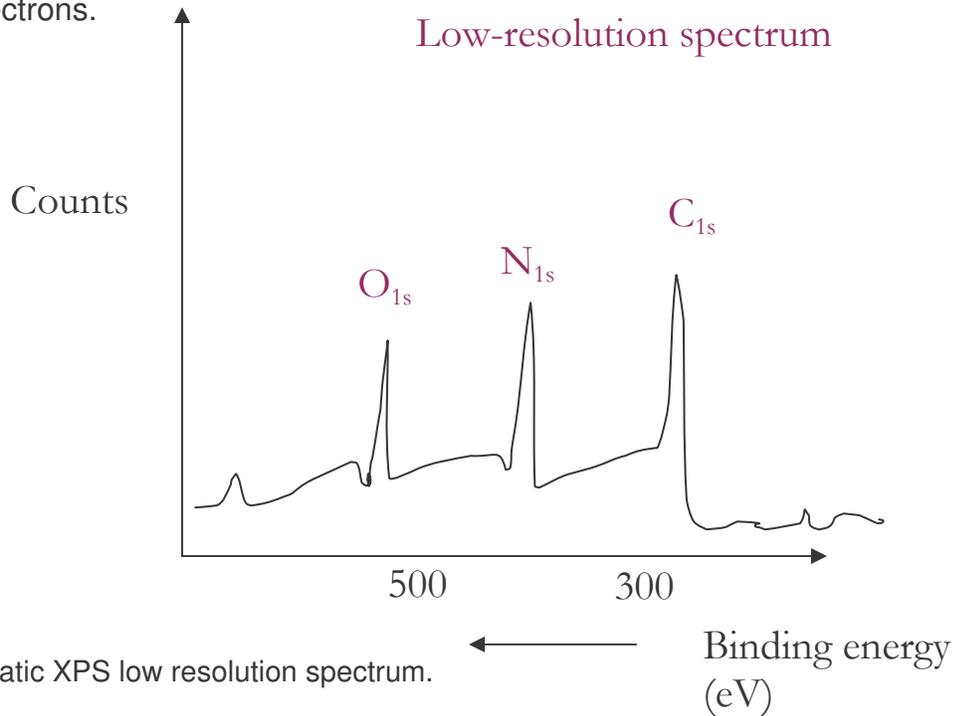


Fig. 6 Schematic XPS low resolution spectrum.

Auger electrons are created when electrons drop from a higher electronic shell to a lower one in order to fill the hole created by an ejected electron, and lower the energy of the atom. Excess energy from this process can result in the emission of a second electron from a higher energy shell, called an Auger electron, which also exhibits as characteristic kinetic energy, related to the energy levels of the three electrons.

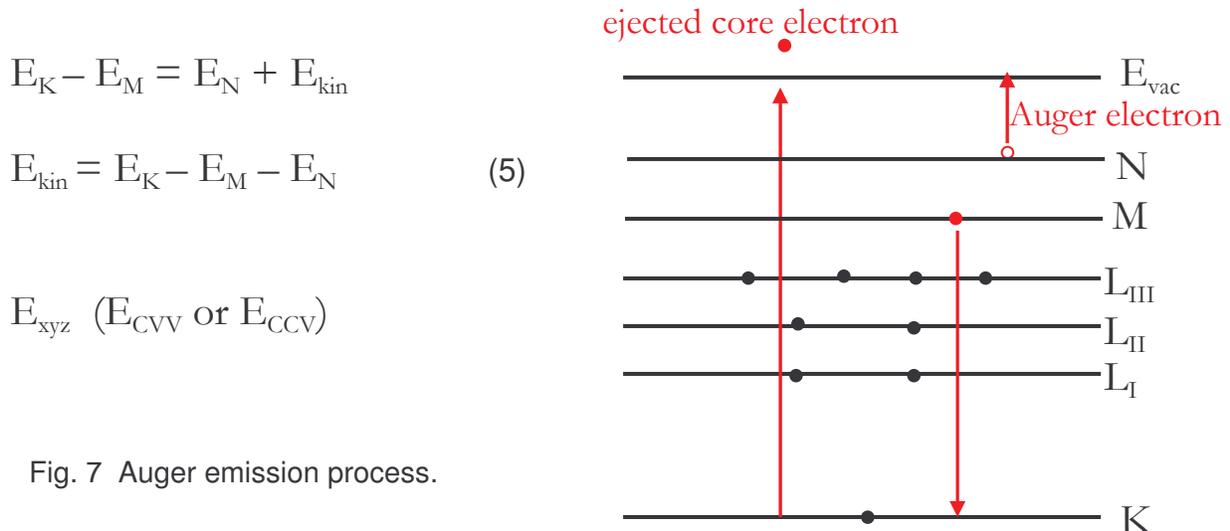


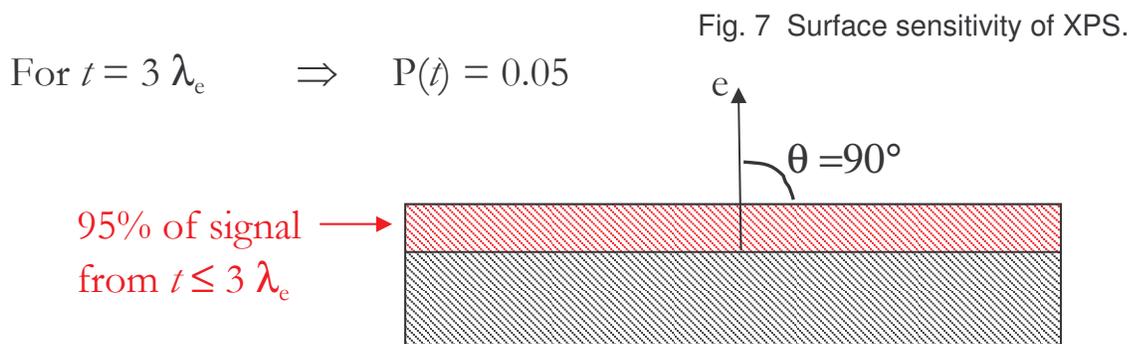
Fig. 7 Auger emission process.

Quantification of XPS Spectra

The probability of a photoelectron escaping the sample without undergoing inelastic collision is inversely related to its depth t within the sample:

$$P(t) \sim \exp\left(\frac{-t}{\lambda_e}\right) \quad (6)$$

where λ_e (typically $\sim 5\text{-}30 \text{ \AA}$) is the electron inelastic mean-free path, which depends on the electron kinetic energy and the material. (Physically, $\lambda_e = \text{avg. distance traveled between inelastic collisions.}$) The XPS signal thus arises from the first $\sim 10 \text{ nm}$ of sample surface.



The area under the j th peak of element i is the integral of attenuated contributions from all sample depths z :

$$I_{ij} = C_{inst} T(E_{kin}) L_{ij} \sigma_{ij} \int n_i(z) \exp\left(\frac{-z}{\lambda_e \sin \theta}\right) dz \quad (7)$$

C_{inst} = instrument constant

$T(E_{kin})$ = analyzer transmission function

L_{ij} = angular asymmetry factor for orbital j of element i

σ_{ij} is the photoionization cross-section

$n_i(z)$ is the atomic concn. of i at a depth z (atoms/vol)

For a semi-infinite sample of homogeneous composition:

$$I_{ij} = -C_{inst} T(E_{kin}) L_{ij} \sigma_{ij} n_i \lambda_e \sin \theta \exp\left(\frac{-z}{\lambda_e \sin \theta}\right) \Bigg|_0^{\infty} = S_i n_i \quad (8)$$

where $S_i = C_{inst} T(E_{kin}) L_{ij} \sigma_{ij} \lambda_e \sin \theta$ (9)

and S_i is the sensitivity factor. Quantification of atomic fraction C_i (of j elements detected) can be obtained from:

$$C_i = \frac{I_i / S_i}{\sum_j I_j / S_j} \quad (10)$$

As noted above, bonding between atoms modifies the energies of electrons located in lower shells. By performing a high resolution XPS scan, one can determine the bonding configurations of atoms.

High-resolution spectrum PMMA

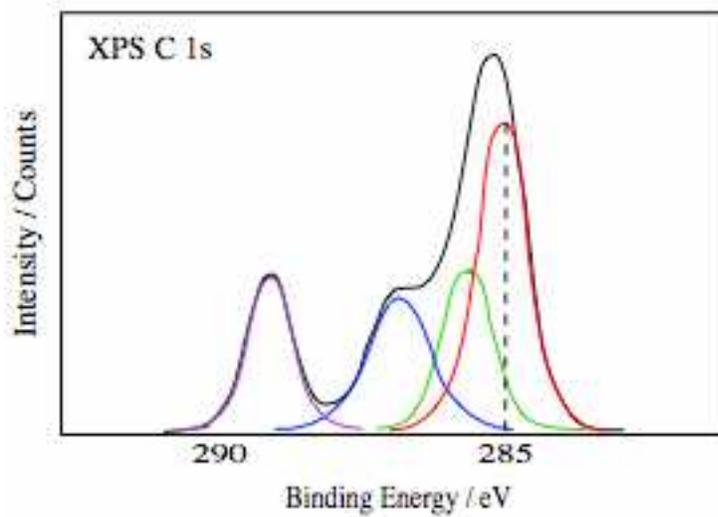


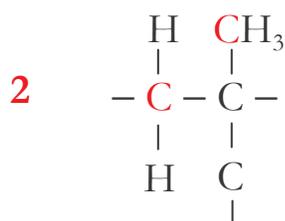
Fig. 8 Schematic XPS high resolution spectrum.

In PMMA, electronegative oxygen shifts the electron density away from the carbon nucleus of oxygen-bonded carbons, causing the core electrons of carbon to be held more tightly to the nucleus (the nuclear charge is less screened). This causes a slight shift to higher binding energies of oxygen-bonded carbons.

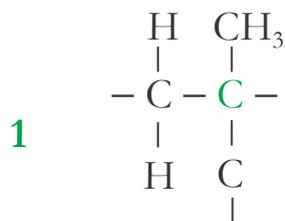
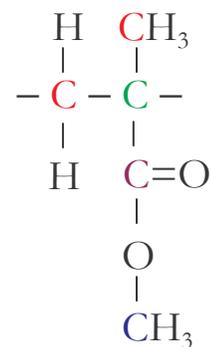
Taking the ratio of peak areas within a high resolution scan gives a ratio of photoelectrons ejected from atoms in a particular bonding configuration ($S_i = \text{constant}$).

5 carbons in total

Ex. PMMA



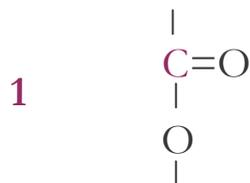
(a) Lowest E_B C_{1s}
 $E_B \approx 285.0 \text{ eV}$



(b) Second lowest E_B C_{1s}
 $E_B \approx 285.7 \text{ eV}$



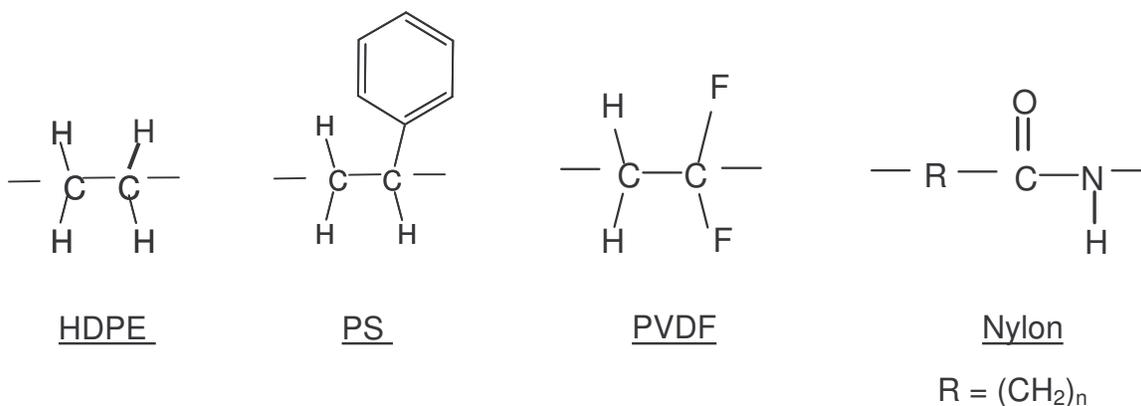
(c) Second highest E_B C_{1s}
 $E_B \approx 286.8 \text{ eV}$



(c) Highest E_B C_{1s}
 $E_B \approx 289.0 \text{ eV}$

Experimental

In our XPS experiments, we will study several polymers: PMMA, high density polyethylene (HDPE), polystyrene (PS), poly(vinylidene fluoride) or PVDF, and a polyamide (nylon).



Instrument: Kratos Axis Ultra

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