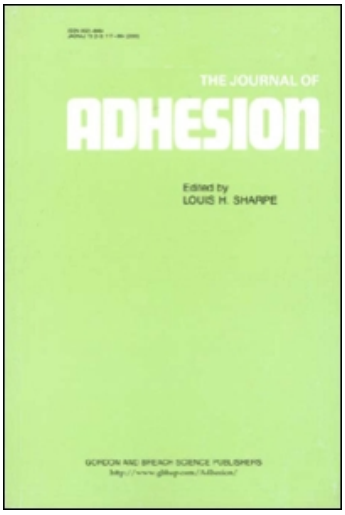

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X-ray Photoelectron Spectra of Poly(2-vinylpyridine) and its Adduct with Boron Trifluoride

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NOTE

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The sources of interactions at an interface and in solution have been subjects which have occupied both experimentalists and theorists for some time. Several types of interactions, e.g. donor-acceptor,[1-6] have been suggested to explain deviations in adhesion and solution data from that predicted from London dispersion forces. The experimentalist has employed both infrared spectroscopy and calorimetry to measure donor-acceptor interactions. It is the purpose of this note to show that X-ray photoelectron spectroscopy (XPS) can be used also to detect donor-acceptor interactions in polymeric systems.

The classification of small molecule compounds by Drago and collaborators[4,5] was used to select a strongly interacting donor-acceptor pair, viz. poly(2-vinylpyridine) and boron trifluoride, respectively. A 1:1 mixed solvent of acetonitrile and 1,2-dimethoxyethane was used to dissolve poly(2-vinylpyridine) and serve as an "inert" reaction medium. Films were prepared from these solutions by (1) casting on solvent cleaned (trichloroethylene) silicon disks and (2) removing solvent with a stream of nitrogen.

X-ray photoelectron spectra were obtained with a dispersion compensated monochromatized spectrometer using Al(Kα) radiation (Hewlett–Packard Model 5950A). Since the locus of any interaction would involve the pyridine nitrogen, the C(1s) electrons were chosen as an internal standard with a binding energy assumed to be 285.0 eV. This binding energy was used to correct for any shifts in spectra due to differences in the charging characteristics of

the insulating layers. Figure 1 and Table I show that the donor-acceptor interaction of poly(2-vinylpyridine) with boron trifluoride resulted in an increase of 2.5 eV (~57 kcal) in the N(1s) binding energy. This is consistent with the electrophilic nature of the boron trifluoride. Although the O(1s) peaks were used with the C(1s) peaks to calculate an average shift, the source of oxygen was not established.

Using solvent blanks, no evidence could be found by electron spectroscopy for solvent reacting with boron trifluoride.

Figure 2 shows the F(1s) and B(1s) portions of the spectrum for the donor-acceptor reaction product. Since neither of these binding energies appear in

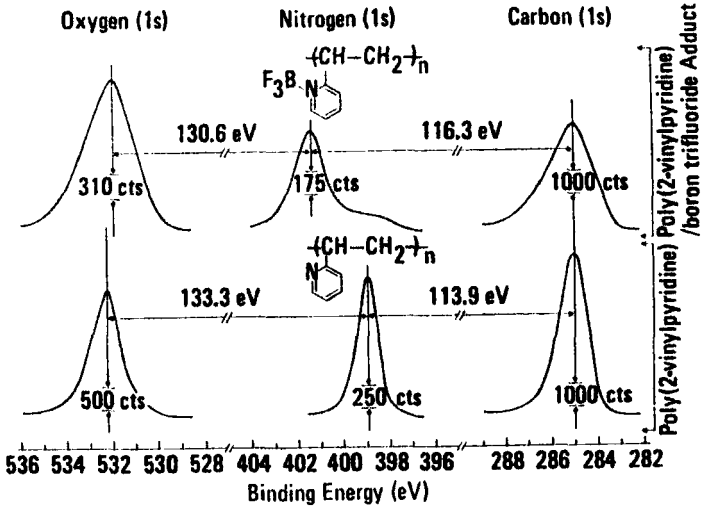

FIGURE 1 X-ray photoelectron spectra of poly(2-vinylpyridine) and its reaction product with boron trifluoride.

TABLE I

Binding energies for poly(2-vinylpyridine) and its reaction product with boron trifluoride

	Binding energies (eV)†						
	B(1s)	C(1s)	N(1s)	O(1s)	F(1s)	[N(1s)–C(1s)]	[O(1s)–N(1s)]
Poly(2-vinylpyridine)	—	285.0	398.9	532.2	—	113.9	133.3
Poly(2-vinylpyridine)/ BF_3 adduct	193.4	285.0	401.3	531.9	685.6	116.3	130.6
			average shift of N(1s) peak = 2.5 eV				

† All binding energies referenced to C(1s), which was assumed to be 285.0 eV.

the spectrum for the poly(2-vinylpyridine) film, further evidence is provided that boron trifluoride chemically reacts with, and is incorporated into the polymer molecule.

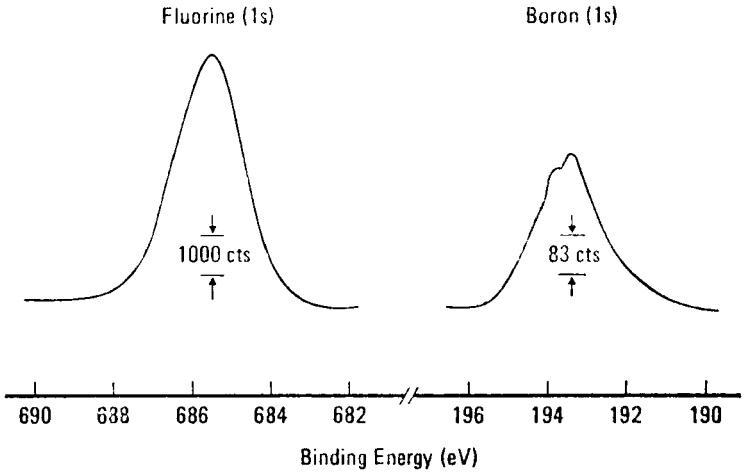

FIGURE 2 Boron (1s) and fluorine (1s) X-ray photoelectron spectra of the reaction product of poly(2-vinylpyridine) with boron trifluoride.

Since the escape distance of the various photoelectrons is the order of 2–5 nm, work is in progress to (1) relate the chemical shifts in X-ray photoelectron spectra with Drago's enthalpies of adduct formation, and (2) determine the potential of this technique as a direct measure of donor-acceptor interactions at an interphase.

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