NOTES

Ultraviolet Photoelectron Spectroscopy of Fluoro-Substituted Polyethylenes

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A study was made of the observation of the electronic structures of a series of mono-substituted polyethylenes[1] by ultraviolet photoelectron spectroscopy (UPS). In this note are presented photoemission data on multi-substituted polyethylenes: polyvinylidenefluoride (PVdF), polytrifluoroethylene (PTrFE), and polytetrafluoroethylene (PTFE). Fluoro-containing polyethylenes, known as typical functional polymers, have been widely used in the electronic industry as good insulator materials and for other purposes. To our knowledge, however, there has been no report to date on the threshold ionization potentials of fluoro-containing polyethylenes except for polyvinylfluoride (PVF).[1] This work was carried out to obtain these basic data. Fluorine has the highest electronegativity of the all elements, and substitution of a hydrogen by a fluorine atom affects the electronic structure significantly. Fluoro-substituted polyethylenes are thus appropriate systems for evaluating the influence of substituent groups. Theoretical calculations and studies by X-ray photoelectron spectroscopy (XPS) on these polymers have been published,[2-4] but UPS provides the most accurate values of thresholds. Results from previous studies have been used for assigning the spectral features of the UPS spectra of fluoro-substituted polyethylenes.

EXPERIMENTAL

Powder samples of PVdF and PTFE were supplied from General Science Corporation. Fine granules of PTrFE were provided by Daikin Kogyo Co., Ltd. PTFE tapes were made available by Chuko Kasei Kogyo Co., Ltd. The samples were used without further purification. Films of PVdF and PTrFE were prepared by casting from solutions. Solutions of about 1 wt% were prepared using special grade N,N-dimethylacetamide (Wako Pure Chemical Ind. Ltd.). After the samples were completely dissolved, each solution was left standing overnight and used for coating. The casting process has been described in detail elsewhere.[1] For preparation of PTFE the films, two methods were used. In the first one, the sample powder was allowed to evaporate *in situ* in a UPS chamber by heating at 500°C. At this temperature, PTFE decomposed into its constituent monomers which polymerized again[5] at the surface of the copper substrate. In the second method, a thin tape of about 9 μm in thickness was biaxialy stretched by hand to a transparent thin ($\sim 10^3$ Å) film. The two films prepared by these methods gave identical spectra except that the peak associated with the lowest-kinetic-energy was higher in the film prepared by the second

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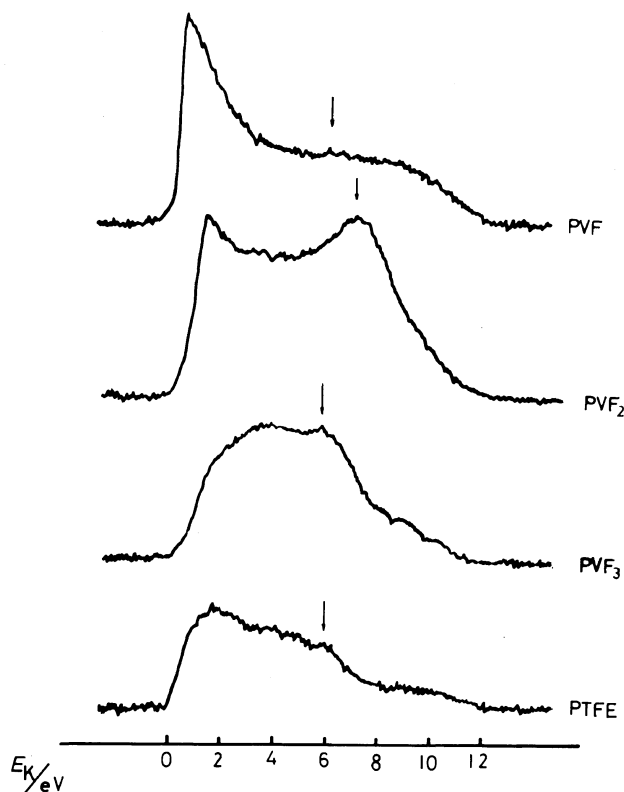
Figure 1. Photoelectron spectra of PVF, PVdF, PTrFE, and PTFE on a kinetic energy scale. The light source was He I (21.2 eV). The arrows indicate the F_{2p} lone pair orbitals.

Table I. Threshold ionization potentials of fluorosubstituted polyethylenes in eV units

Compound	PE	PVF	PVdF	PTrFE	PTFE
Obsd	8.5[a]	9.2[b]	9.2	9.2	9.0
Calcd (extended Hückel)	12.05	11.88	11.72	11.55	11.37

[a] Reference 7. [b] Reference 1. [c] Reference 2.

method. Exposure of the sample prepared by the first method to air did not affect the spectra. This insensitivity ruled out the possibility of surface-contamination in the second method.

A retarding potential-type photoelectron spectrometer described in a previous paper[6] was used. As light sources, He I (21.2 eV), Ne I (16.8 eV), and Ar I (11.7 eV) rare gas resonance lines were used. The use of low intensity light prevented the sample from charging, but made it difficult to obtain really good S/N ratios. The measured ionization potentials were reproducible within a standard deviation of ± 0.2 eV.

RESULTS AND DISCUSSION

The He I photoelectron spectra of PVdF, PTrFE, and PTFE are shown in Figure 1 along with the spectrum of PVF[1] for comparison. The threshold ionization potentials I_s^{th} of PVF, PVdF, PTrFE, and PTFE were calculated by the equation $I_s^{th} = hv - E_k^{max}$ and are listed in Table I, where hv and E_k^{max} are the photon energy and the maximum kinetic energy of photoelectrons, respectively.
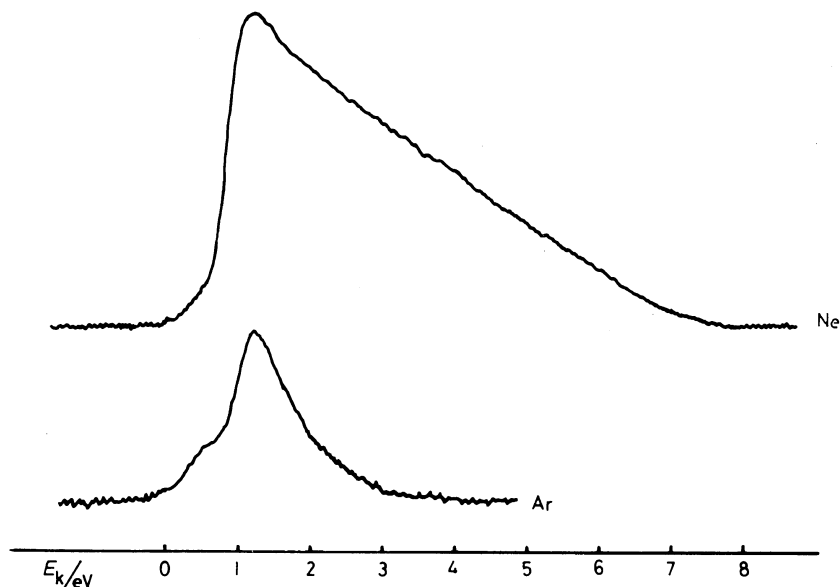
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Figure 2. Photoelectron spectra of PVF_2 on a kinetic energy scale. The light sources were Ne I (16.8 eV, upper) and Ar I (11.7 eV, lower).

Table I also shows the experimental value of polyethylene (PE)[7] and orbital energies of the highest occupied orbitals calculated by the extended Hückel (EH) band method for an isolated chain.

Both the theoretical calculation and XPS measurements[2-4] indicate that the highest occupied orbitals for PVF, PVdF, and PTrFE are of the σ_{CH} character. On the other hand, the highest occupied orbital for PTFE, where no C–H bond exists, consists of F_{2p} orbitals forming a band by the F$\cdots$F interaction on the same carbon atom (F$\cdots$F band).[2] A significant change in I_s^{th} may be expected to occur by the successive introduction of electronegative fluorine, which would even induce such a change in the character of the highest occupied orbital. However, the observed I_s^{th} of the four polymers were the same within experimental error. Theoretical band calculations for isolated chains also gave similar threshold ionization potentials. A calculation for PTFE indicated the F$\cdots$F band to be broader than those for PVdF and PTrFE. This broadening lowers the threshold ionization potential to a value comparable to those of the σ_{CH} bands.

Table I also shows that the ionization potentials of four fluoro-substituted polyethylenes are higher than those of unsubstituted PE (8.5 eV)[7] and other vinyl polymers (7.5 to 8.8 eV).[1] This is consistent

with the high electronegativity of fluorine, but the theoretical calculation (EH) for an isolated chain gave an opposite result. Since the difference in the state of aggregation between isolated chain and solid does not lead to such a discrepancy,[1] we may conclude that the EH calculation is inadequate for predicting the effect of fluorine substitution on ionization thresholds. The lesser reliability of the EH method has already been pointed out previously by other authors[4] for the uppermost part of occupied states of fluorine-containing polymers.

A comparison of the XPS and theoretical results makes it possible to locate the F_{2p} lone pair orbitals in the photoelectron spectra in Figure 1, as indicated by the arrows (the peak in PVF, though weak, was reproducible). In PTFE, the right-hand side of the spectrum with the higher kinetic energy may possibly be associated with the F$\cdots$F band.

Finally, we note some charactristic features of the low kinetic energy part of the spectra. In the Ar I and Ne I spectra of PVdF shown in Figure 2, there are two fixed kinetic energies (1.1 eV and 0.5 eV). The former appears in the He I spectra, and similar large secondary electron bands are usually present for other organic solids. On the other hand, the origin of the latter at $E_k \sim 0.5$ eV is not clear. The Ar I and Ne I spectra of PTrFE have similar

features. Such weak spectral features in the lowest-kinetic-energy region are characteristic of fluoropolymers and cannot be observed in other organic.

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