

## Photodegradation of fluorocarbon polymer thin films by inner shell excitation

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### Introduction

Poly (tetrafluoroethylene) (PTFE,  $(-CF_2-)_n$ ) and poly (vinylidene fluoride) (PVDF,  $(-CF_2CH_2-)_n$ ) may be one of the most suitable materials for making microparts for bioscience and medical application due to the chemical inertness and the thermal stability. Recently, it was possible to manufacture PTFE to generate microstructures using synchrotron radiation [1,2]. To achieve more efficient ablation and higher aspect ratio, one needs to clarify the photodegradation mechanism of PTFE and PVDF. The analysis of desorption ion by inner shell excitation is one of useful methods for clarification of the relationship between the photodegradation mechanism and the electronic configuration of excited states. Inner shell excitation is highly localized on specific atoms in molecules. The difference in core electron binding energies is large to allow selective excitation of different atoms or even the same atom in inequivalent chemical environment in the molecule state created in the polymer film by inner shell excitation.

### Experimental

Thin films of PTFE and PVDF with thickness of 250Å were prepared by vacuum evaporation on Cu plates. PTFE films were rubbed at room temperature. Experiments were performed at the beamline BL13C at the Photon Factory of the High Energy Accelerator Research Organization. PIY spectra were measured using a time-of-flight (TOF) mass spectrometer. NEXAFS spectra were obtained by the total electron yield method. At the measurements of PIY and NEXAFS spectra, the incidence angle of photon was about 55° from the surface normal

### Results and Discussion

Figure 1 shows ion TOF spectra of PTFE and PVDF thin films obtained at  $h\nu=723\text{eV}$ . For the PTFE thin film, peaks corresponding to  $F^+$ ,  $CF^+$  and  $CF_3^+$  were observed, while for the PVDF thin film,  $H^+$  and  $F^+$  peaks were mainly observed. These indicate that for PTFE the polymer chain (C-C bonds) as well as C-F bonds are broken by irradiation of photons above fluorine K-edge, while for PVDF the bond scission occurs mainly at the C-F and C-H bonds

Figure 2 shows NEXAFS and PIY spectra of  $F^+$ ,  $CF^+$  and  $CF_3^+$  for PTFE thin film near fluorine K-edge. It is noted that the intensity of  $F^+$  ion increases strongly at  $h\nu=689\text{eV}$  corresponding to the transition from  $F1s$  to

$\sigma^*(C-F)$ , although the intensities of  $CF^+$  and  $CF_3^+$  ions do not. It indicates that the bond scission of PTFE by inner shell excitation depends on the electronic configuration of the excited states.

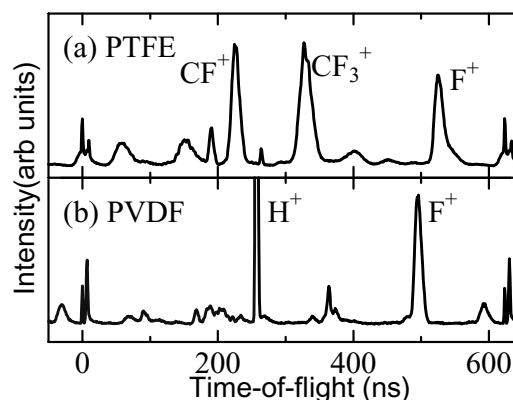


Figure 1 Ion TOF mass spectra of PTFE (a) and PVDF (b) obtained at  $h\nu=723\text{eV}$ .

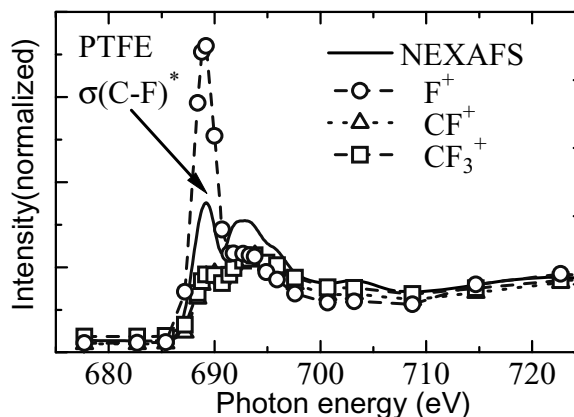


Figure 2 NEXAFS and PIY spectra of  $F^+$ ,  $CF^+$  and  $CF_3^+$  for PTFE thin film near fluorine K-edge. Intensities of PIY spectra are normalized at  $h\nu=715\text{eV}$ .

### References

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