Analysis of the Photodegradation at 157 nm of Photolithographic-Grade Teflon® AF Pellicles

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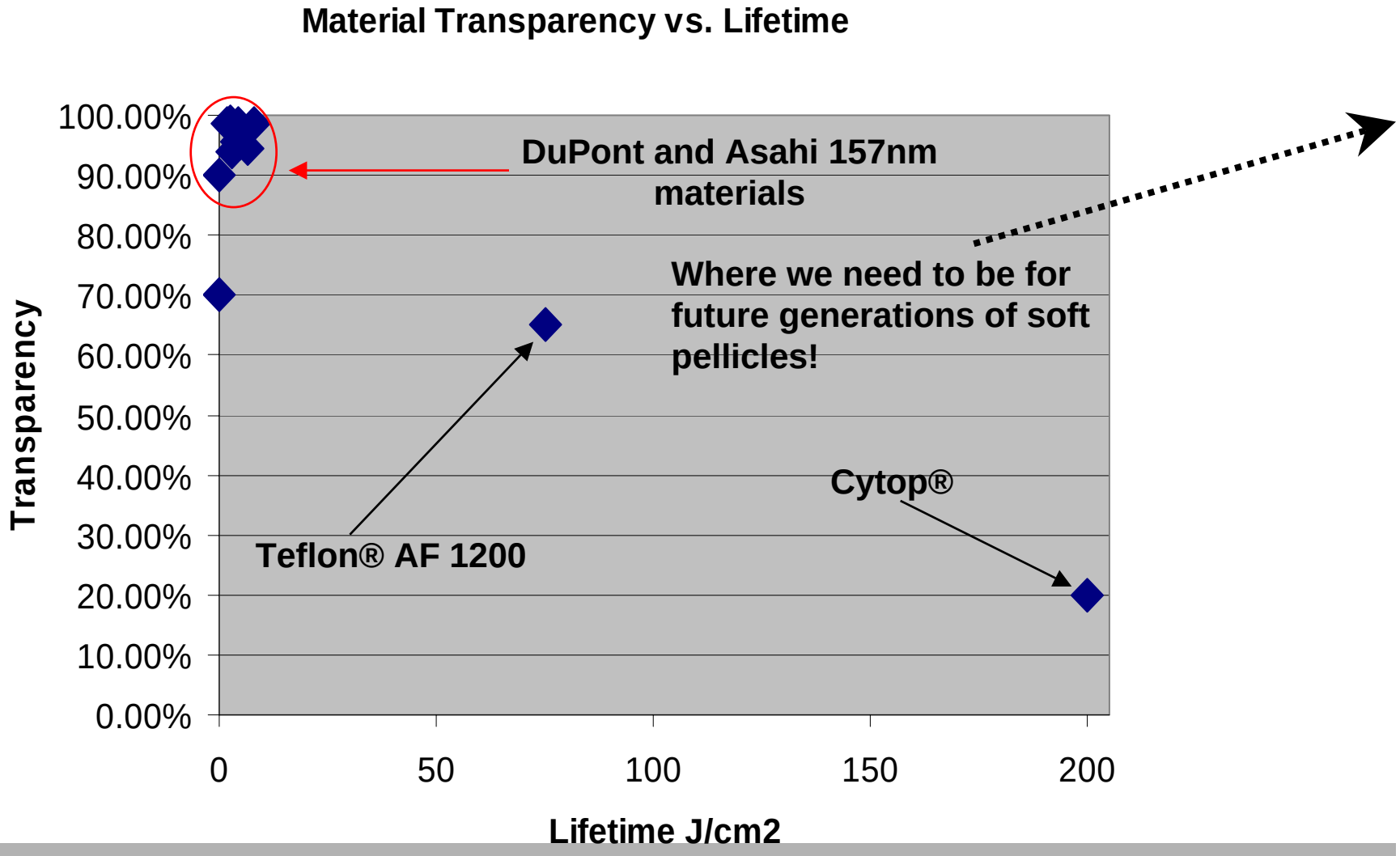
Pellicle Requirements for 157 nm

- The requirements for 157 nm soft pellicles were
  - materials with >95% transparency at 157nm
  - exposure lifetimes of 3 kJ/cm^2
  - <1% deviation in transparency during this period

Current Materials for Soft Pellicles

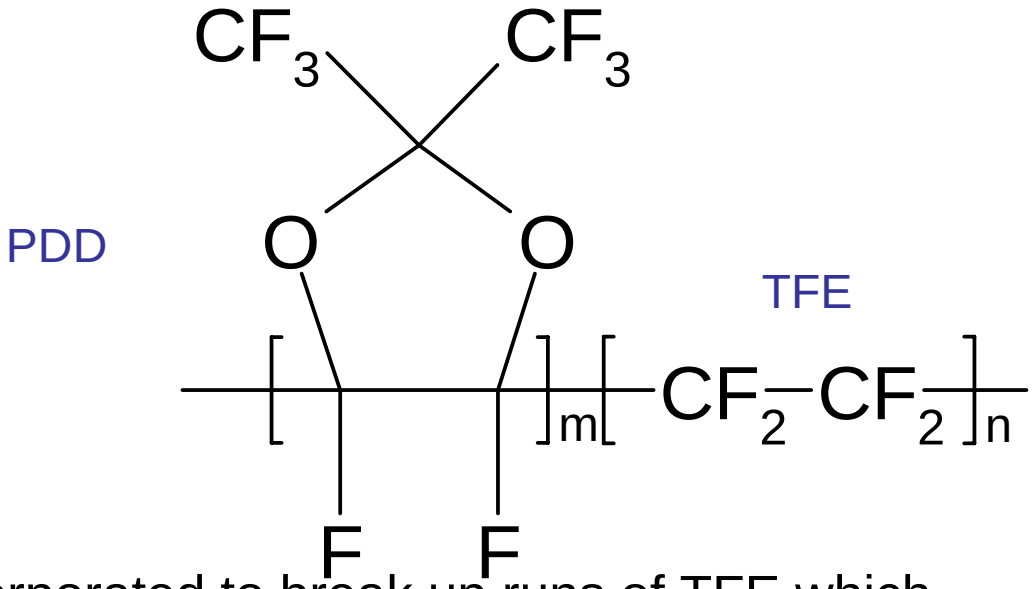


Aims of this Study

- To understand photodegradation mechanisms of Teflon® AF type copolymers so that polymers with improved lifetimes and transparency could be designed

Polymers Studied

- Teflon® AF 1200 (PDD:TFE, 48:52)
- Teflon® AF 1600 (PDD:TFE, 65:35)
- Teflon® AF 2400 (PDD:TFE, 89:11)

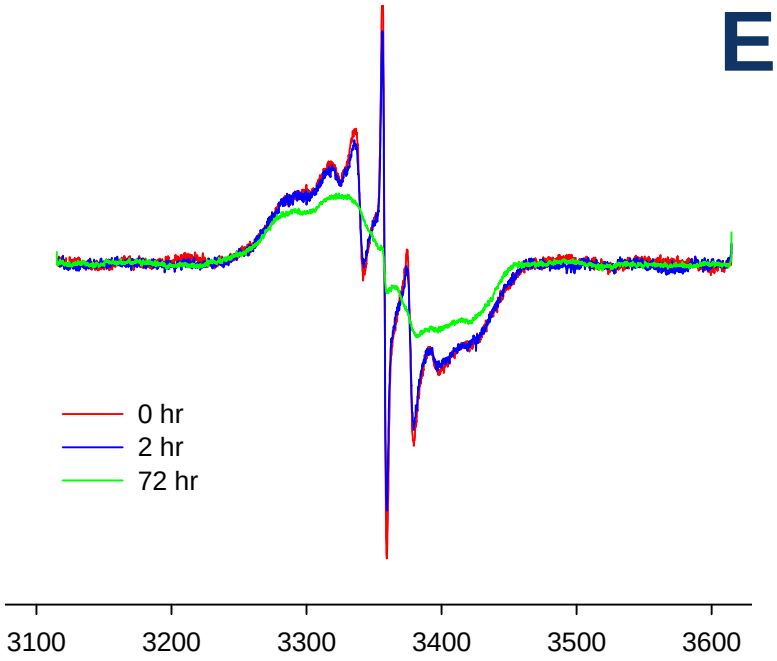


- PDD units incorporated to break up runs of TFE which results in increased transparency
- Generally polymers studied as thin films
  - Spin coated from Fluorinert solutions onto CaF_2

Instrumentation Used

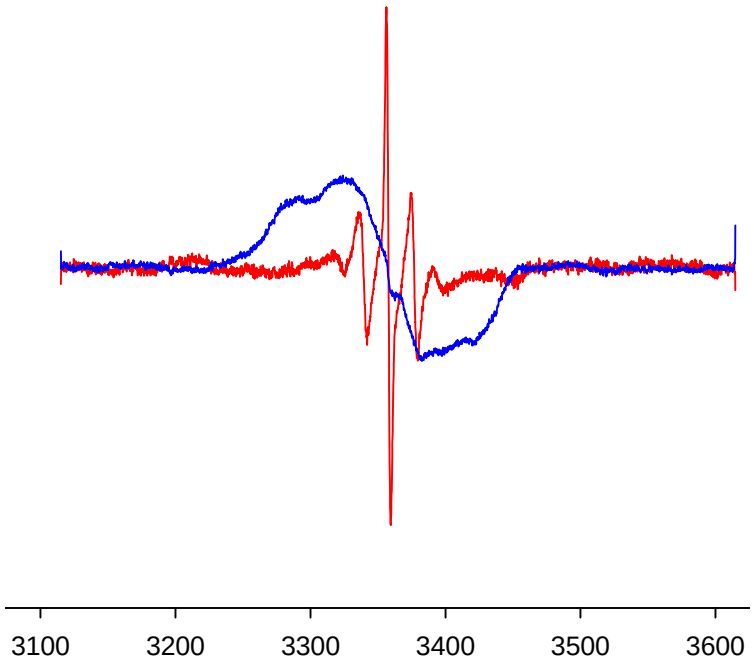
- Electron Spin Resonance (ESR)
  - Presence of radicals
- X-ray Photoelectron Spectroscopy (XPS)
  - Atomic ratio changes and changes in functionality
- Raman Microscopy
  - Effect of polymer sequence
- ^{19}F Nuclear Magnetic Resonance (NMR)
  - Changes in functionality
- FT-Infrared (FTIR)
  - Changes in functionality
- Mass Spectrometry (MS)
  - Low molecular weight fragments

ESR



TAF1600

immediately after 20 J irradiation (red),
2 hours after irradiation (blue)
72 hours after irradiation (green).

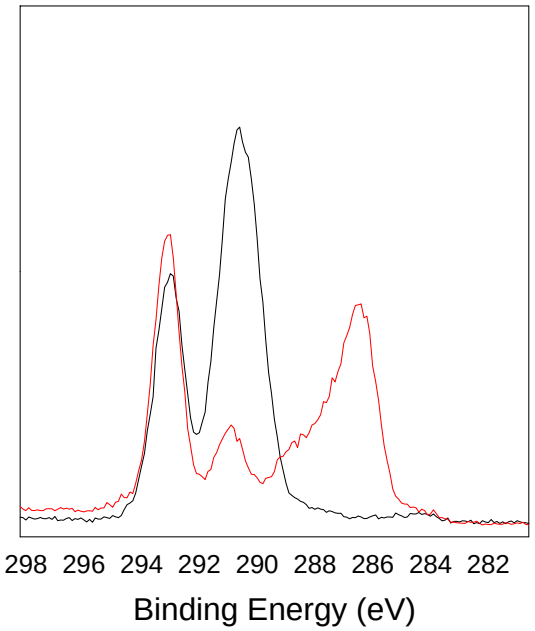


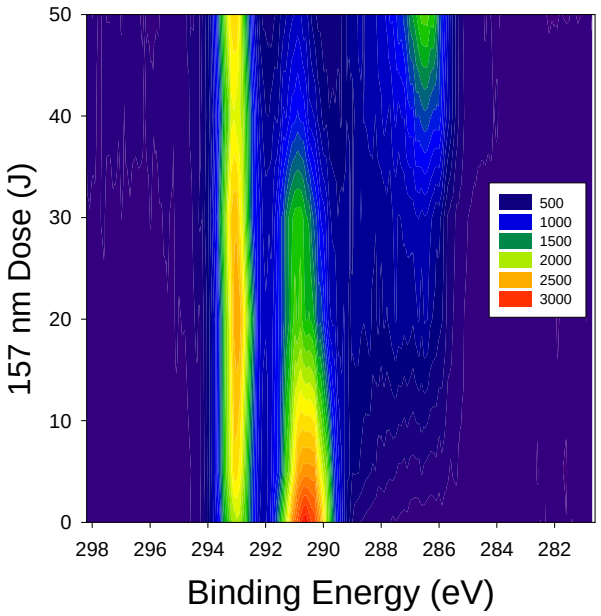
TAF1600

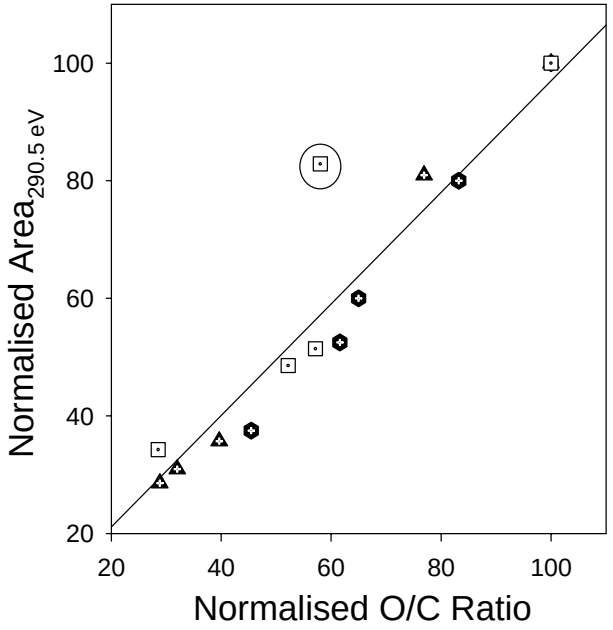
Long lived species (blue),
Short lived species (red)

- radicals are involved in process
- More than one species present
  - Short lived mobile (chain end?) radicals
  - Long lived radicals on the backbone (from loss of $F^{\bullet}$?)

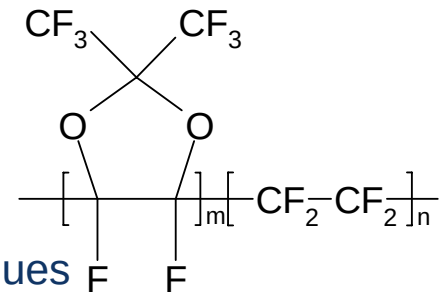
XPS Results



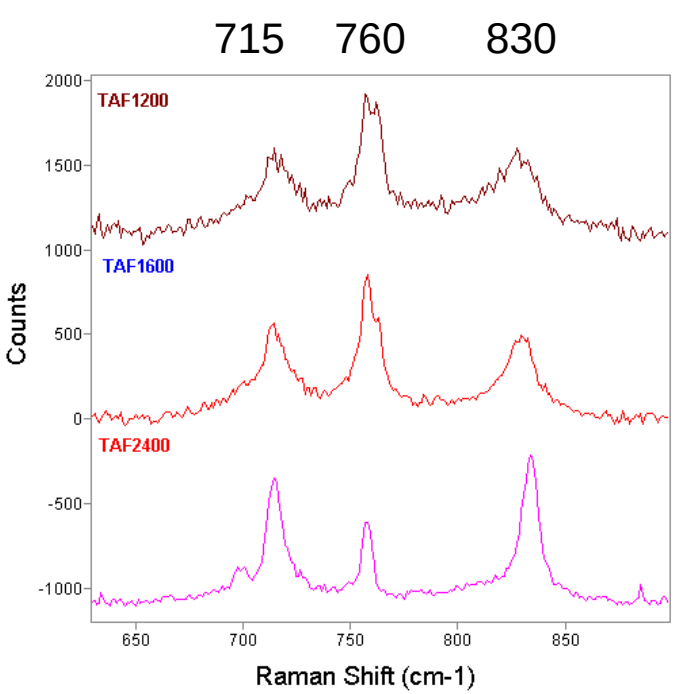


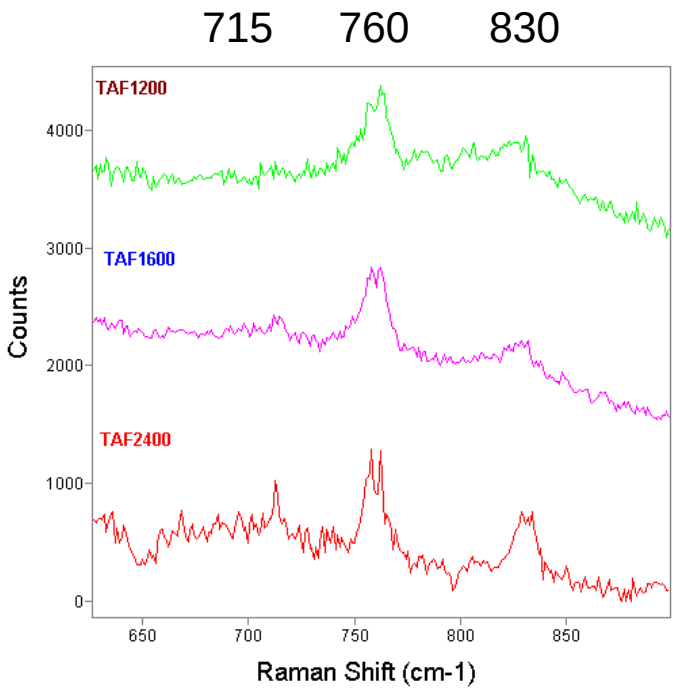


- Dramatic decrease in O\C
  - Infers formation of oxygen containing small molecules
  - Degradation predominantly occurs in dioxole ring
- Decrease in F\C
  - Extensive defluorination and formation of carbonized residues
- -CF_3 degradation products dominate
- Rate of degradation of TAF2400 much faster than for other copolymers

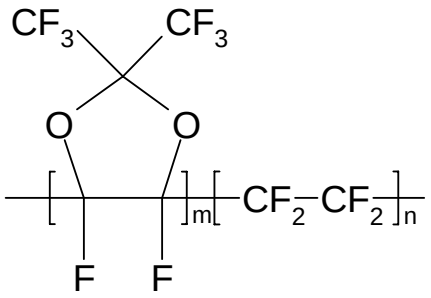


Raman Results





- 715 cm^{-1} peak due to vibration involving $(CF_3)_2$-C-O_2
- 760 cm^{-1} peak due to vibration involving CF_2
- 830 cm^{-1} peak due to vibration involving CF-CF
- Degradation occurs predominately in the dioxole ring
  - $(CF3)_2$-C-O_2 portion in particular, probably via C-O scission
  - Series of dioxole rings are more susceptible to degradation

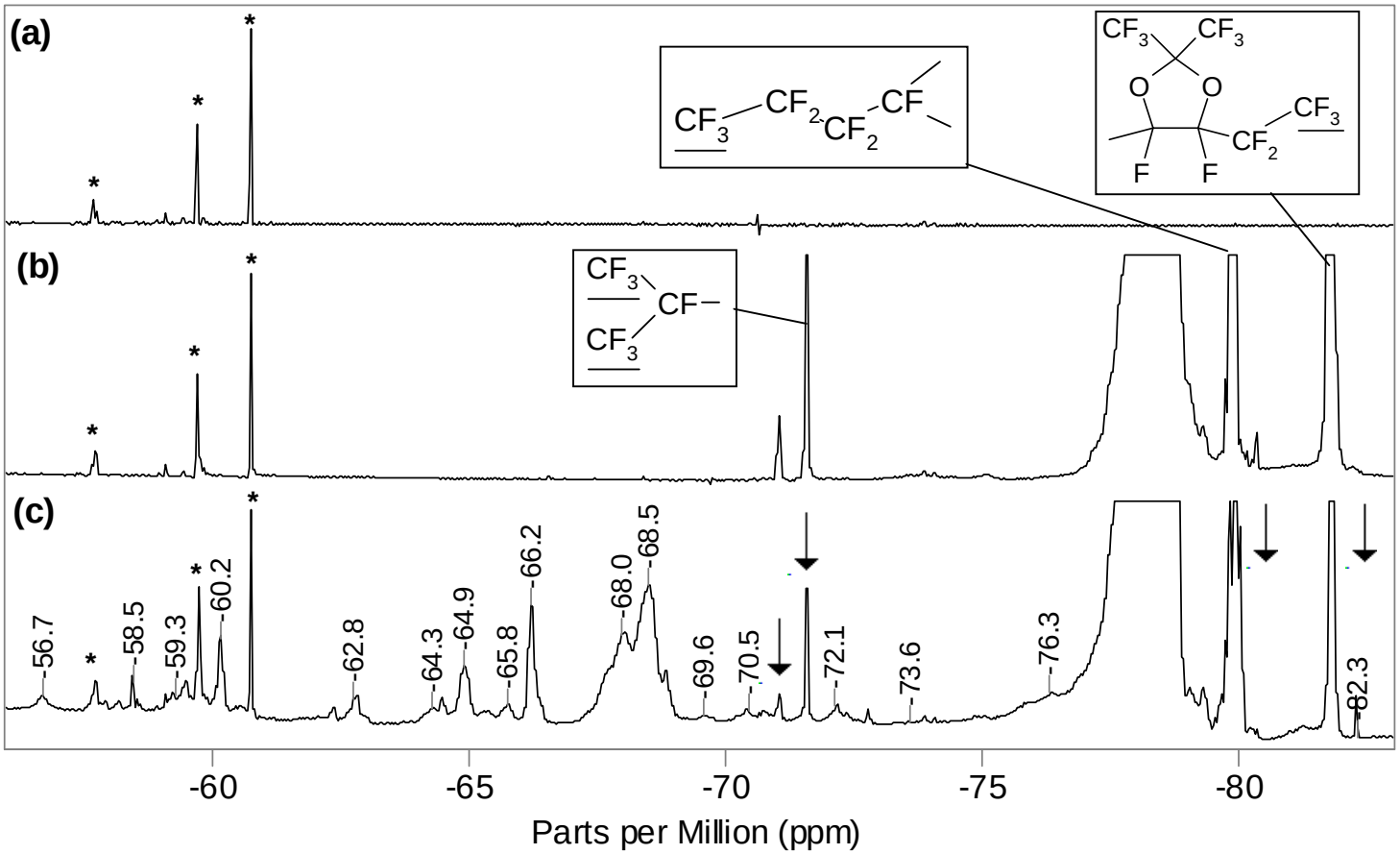


Solution ^{19}F NMR Results

HFB

Virgin TAF1200

157 nm exposed TAF1200 (20J)



- After 157 nm irradiation polymer residues contain a large number of -CF_3 type structures
- Similar scenario for TAF1600 and TAF 2400

^{19}F NMR Peak Assignments

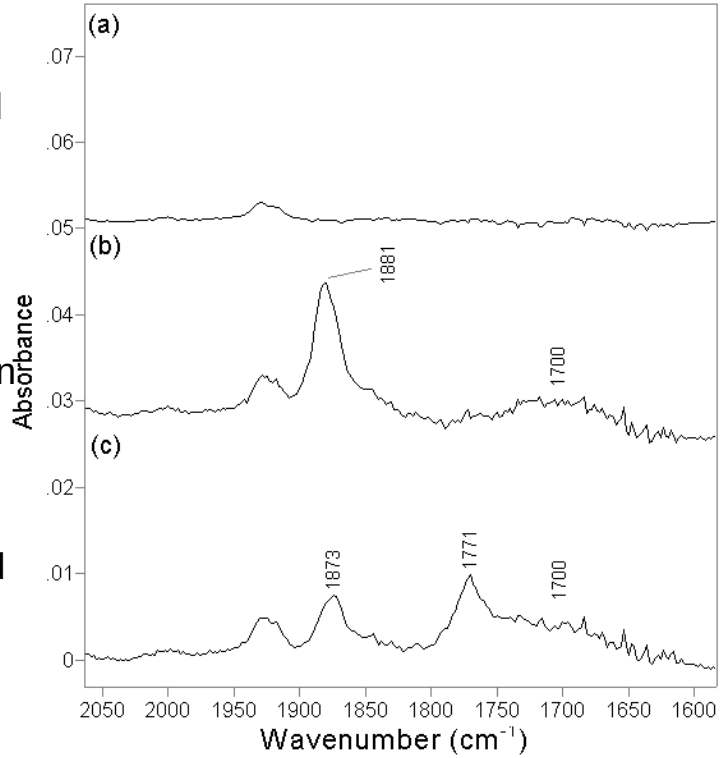
- Peaks were compared to ^{19}F NMR spectral database
  - Peaks present were consistent with $–CF_3$ containing groups
  - Some peaks were consistent with unsaturated groups
  - Presence of $–CF_3$ groups is consistent with XPS data
- Unsaturated products consistent with defluorination that was observed with XPS
- Degradation products are predominately derived from dioxole groups, which is consistent with XPS and Raman data

FTIR Results

Unirradiated Polymer

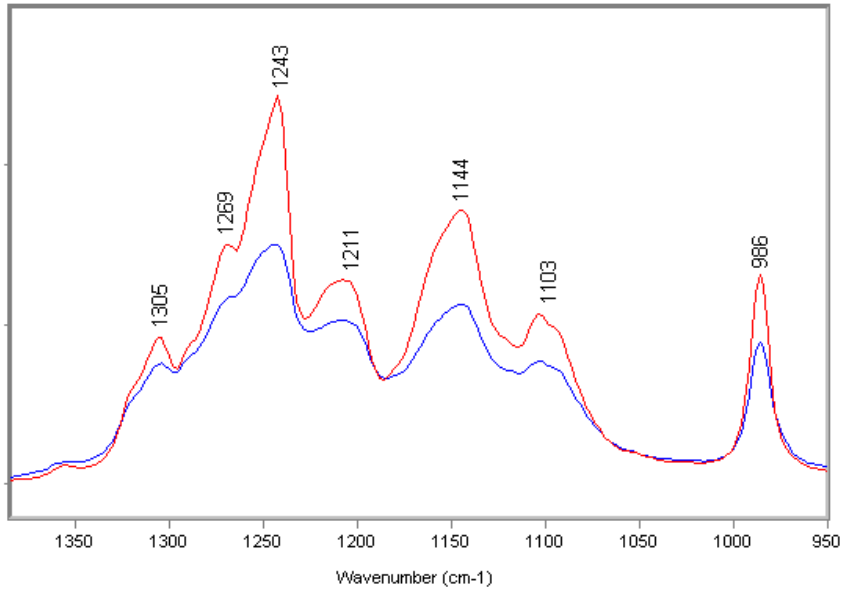
TAF1600 20J, directly after irradiation

TAF1600 20J, exposed to air 16 hrs.



Unirradiated Polymer

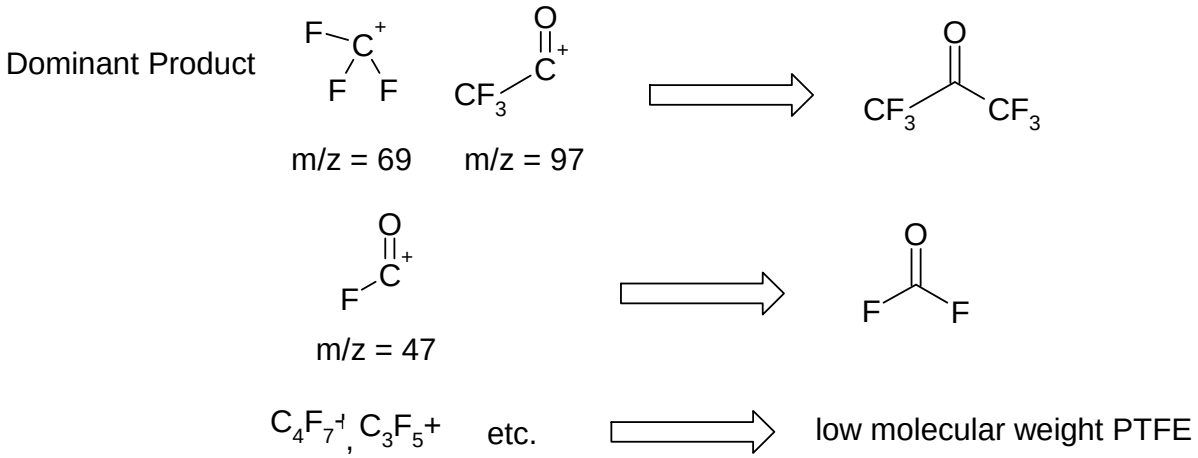
TAF1600 20J



- Observe Acid Fluoride and possibly vinyl group formation
- Acid fluoride at 1873 cm^{-1} confirmed by observing conversion to acid at 1771 cm^{-1}
- Observe dramatic film thinning upon exposure to 157 nm light
- Similar scenario occurs for TAF1200 and 2400
- Acid Fluoride reaches a steady state concentration
  - Indicates that it undergoes secondary reactions

MS Results

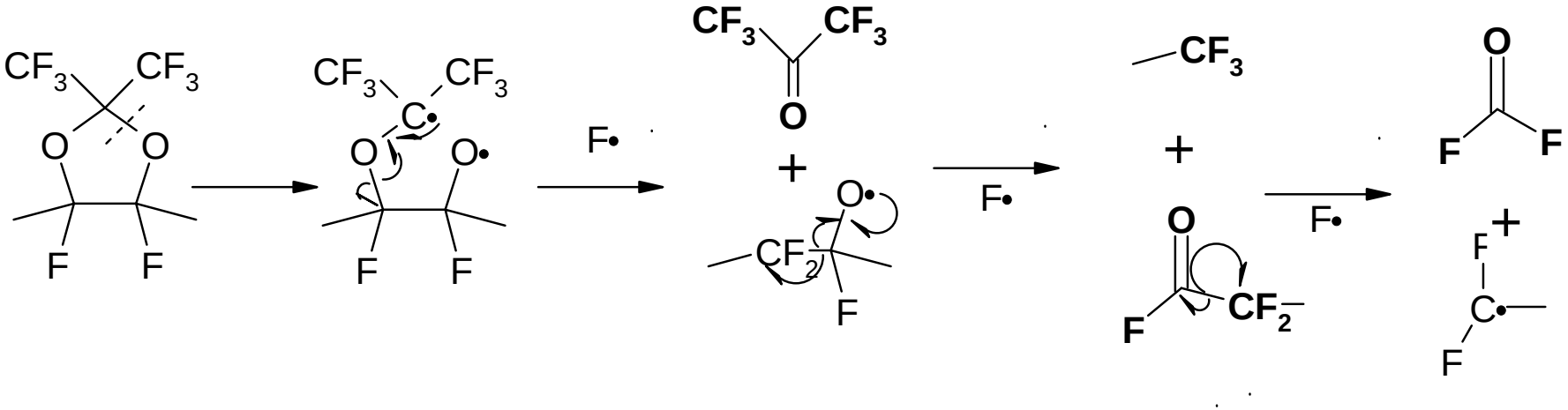
- Nitrogen purge gas from degradation cell was passed through liquid nitrogen cold finger.
- Gas collected was analysed by MS
- Large number of low molecular weight fragments observed (m/z < 200).
  - Eg



Recap of Results

- Mechanism involves
  - Free radicals (ESR)
    - Mobile $–CF_2•$ radicals
  - Degradation predominantly at the dioxole ring (Raman, XPS)
  - Formation of $–CF_3$ end groups (XPS, NMR)
  - Formation of Acid Chlorides (FTIR)
  - Extensive loss of small molecules (FTIR, MS)
  - Formation of unsaturated and graphitic structures (XPS, NMR, FTIR)

Proposed Dominant Mechanism



- Hexafluoroacetone formation consistent with :
  - Forsythe, J. S.; Hill, D. J. T.; Logothetis, A. L.; Whittaker, A. K. *Polym. Deg. Stab.* **1999**, *63*, 95-101.
- Carbonyl difluoride consistent with
  - Tonelli, C.; Tortelli, V. *J. Fluor. Chem.* **2000**, *101*, 117-123

Recap of Results

- Mechanism involves
  - Free radicals (ESR) ✓
    - Mobile $–CF_2•$ radicals ✓
  - Degradation predominantly at the dioxole ring (Raman, XPS) ✓
  - Formation of $–CF_3$ end groups (XPS, NMR) ✓
  - Formation of Acid Chlorides (FTIR) ✓
  - Extensive loss of small molecules (FTIR, MS) ✓
  - Formation of unsaturated and graphitic structures (XPS, NMR)
    Occurs via secondary reactions of primary degradation products

Conclusions

Photodegradation of TAF polymers at 157 nm occurs primarily at the dioxole ring.

- Particularly runs of dioxole units
- Degradation occurs at a much faster rate for TAF2400

- Dioxole ring structure can not be incorporated into future pellicle designs for 157 nm lithography
- Other strategies to break up runs of TFE units need to be used

Other Materials

- Cross-linked PTFE or polyperfluoroethers?
  - Discussed in next talk

Acknowledgements

- International SEMATECH - funding
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