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Mechanism of 157 nm Photodegradation of Poly[4,5-difluoro-2,2-bis(trifluoromethyl)-1,3-dioxole-*co*-tetrafluoroethylene] (Teflon AF)

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ABSTRACT: The photodegradation at 157 nm of thin films of a series of Teflon AF copolymers has been comprehensively examined using electron spin resonance, NMR, FTIR, and Raman spectroscopies, mass spectrometry and X-ray photoelectron spectroscopy. The mechanism of degradation involves reaction at the dioxole units, and as a consequence the sensitivity to degradation increases across the series Teflon AF 1200, 1600, and 2400. A major volatile product is hexafluoroacetone formed by degradation at the dioxole unit. NMR and volatile product analysis confirm that degradation occurs largely at the dioxole unit leading to an array of new chain-end species. Main-chain and chain-end carbon-centered radicals were identified as arising from abstraction reactions and main-chain cleavage, respectively. In addition to loss of the dioxole units, XPS analysis indicates extensive char formation at the film surface, providing evidence of loss of fluorine atoms which in turn may react with free radical intermediates to form stable products identified by NMR. The implications for design of materials for 157 nm photolithography are discussed.

Introduction

Copolymerization of 4,5-difluoro-2,2-(trifluoromethyl)-1,3-dioxole (PDD) with tetrafluoroethylene (TFE) results in copolymers with a range of desirable properties, many of which differ greatly from those of poly(tetrafluoroethylene) (PTFE). For instance, the incorporation of the cyclic PDD unit into the polymer backbone serves to disrupt sequences of TFE units, leading to amorphous copolymers[1,2] with high optical transparency that can extend well into the vacuum ultraviolet (VUV) region,[3] high glass transition temperatures (T_g) that can be as high as 240 °C[2] and high permeability to gases[4,5] and small molecules.[6,7] They also possess properties of other perfluorinated polymers such as low dielectric constants (∼1.9),[8] low refractive indices (∼1.3)[3] and a high degree of chemical inertness.[3] Some of these properties for three copolymer compositions are listed in Table 1.

These favorable properties have led to poly[4,5-difluoro-2,2-bis(trifluoromethyl)-1,3-dioxole-*co*-tetrafluoroethylene] (Teflon AF) copolymers having a wide range of applications, including playing a critical role in the production of integrated circuits by photolithography. Their high optical transparency, high glass transition temperatures and photostability at 248 and 193 nm have enabled them to be used as pellicles, protective membranes whose critical function is to protect the photomask from particulate contamination during the manufacture of integrated circuit. However, the optical properties of Teflon AF copolymers are generally insufficient for use in 157 nm lithography, due to poor photostability and high absorbance. Hence, a need has arisen to find transparent and photostable polymers for use as pellicles at this wavelength.[9] Although partially fluorinated polymers with sufficient transparency have been produced, they have been shown to deteriorate rapidly when exposed to 157 nm light.[9−11] In fact, perfluorinated polymers such as Teflon AF and Cytop have been demonstrated to be significantly more photostable at 157 nm, despite the higher absorbance of these polymers at that wavelength.[10,11] For this reason the photochemistry of Teflon AF and Cytop needs to be better understood, so that these families of polymers can be re-formulated or redesigned to meet the needs of the semiconductor industry if 157 nm lithography is pursued in the future. The semiconductor industry is currently investigating second and third generation 193 nm immersion lithography and EUV lithography as technologies to achieve the 32 nm node and beyond. If either or both of these technologies fail there will be a reexamination of the use of 157 nm photons to achieve low critical dimension patterning, and information on the stability of fluoropolymers to exposure will therefore be important for design of both pellicles and resists.

Table 1. Composition and UV Absorbance (at 157 nm) of Teflon AF Copolymers

Teflon AF grade	mole % PDD	mole % TFE	$A_{157\ \mathrm{nm}}$ (μm^{-1})	T_g (°C)
1200	52	48	0.64	120
1600	65	35	0.42	160
2400	89	11	<0.01	240

Recently, Lee et al.[12] have studied the VUV degradation of model fluoroalkanes in a bid to better understand the effects of VUV radiation on perfluorinated compounds. The stated aim was to enable discovery of more stable polymers for use as 157 nm lithography pellicles. Prior to this Jahan and co-workers reported the effects of γ[13] and X-ray[14] radiation on Teflon AF in air, and related the increase in optical density to the formation of main-chain peroxy radicals. In addition, we have recently

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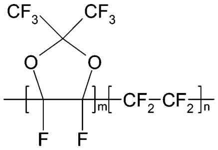


Figure 1. Generic structure of the Teflon AF copolymers.

presented initial results of a study of the effect of 157 nm light on Teflon AF 1600 to gain a better understanding of the mechanisms of the VUV degradation of Teflon AF copolymers.[15] In this current paper we present a comprehensive study of the photodegradation of a series of Teflon AF copolymers with 157 nm light and discuss possible mechanisms of degradation.

Finally the mechanism of interaction of VUV photons with polymers is of interest as irradiation of polymer surfaces is emerging as a potential method of modifying surface topography and chemistry. In particular, irradiated polymers are being investigated because of the increased propensity of cells to adhere to undergo attachment and growth compared with virgin materials.[16] Most of this work has been performed at longer wavelengths, however access to F_2 laser facilities has led to increased interest in 157 nm irradiation, and opens the opportunity for modification of polymers that are transparent at other more-accessible wavelengths such as 193 and 248 nm. Recently, Takao et al. investigated the effects of 157 nm radiation on the surface of silicones, and reported changes in chemistry and topography of the material as a function of threshold dose.[17] Before this Costela and co-workers[18] reported the effect of 157 nm photons on a number of polymeric materials, including PTFE. Modification of the surface of fluoropolymers is especially interesting as usually this class of materials is highly resistant to cell adhesion. As shown by Makohliso et al.[19] changes in surface topography of Teflon AF through micropatterning can have a profound effect on the proclivity of cells to adhere to the polymer surface.

Experimental Section

Polymers and Sample Preparation. Copolymers of 4,5-difluoro-2,2-(trifluoromethyl)-1,3-dioxole (PDD) and tetrafluoroethylene (TFE) were obtained from DuPont. The grades were Teflon AF 1200, 1600 and 2400. The composition and important properties of these polymers are detailed in Figure 1 and Table 1. Thin films of Teflon AF were prepared by spin-coating 1−3 wt % solutions of polymer in Fluorinert 75 onto VUV grade calcium fluoride windows. A spin program of 500 rpm for 9 s followed by 2000 rpm for 60 s was used. The thickness of the films was of the order of 1−2 μm. These spin-cast films were irradiated with 157 nm light as described below and analyzed by XPS, FTIR, and Raman spectroscopy. For ESR, ^{19}F NMR and MS volatile analysis, slightly thicker films (∼2 μm) were prepared by casting of polymer solutions onto VUV calcium fluoride windows.

The initial absorbance of Teflon AF films at 157 nm is on the order of 0.4 μm^{-1},[11] and therefore, films of the thickness prepared in these studies will absorb appreciable amounts of energy. The films of thickness 1−2 μm will transmit just 40 and 20% of the incident photons, respectively. In this work we report results from measurements using a range of analytical techniques, and in particular, we measure the relative proportion of products formed. No attempt is made to compare absolute yields of products from technique to technique due to difficulties in determining absolute energies incident on the samples prepared with slightly different geometries.

157 nm F_2 Laser Irradiation. The films were irradiated with a Lambda Physiks, Optex 157 nm F_2 excimer laser where the beam was directed into a glovebox purged with dry nitrogen gas. The concentration of oxygen in the reaction chamber was maintained below a maximum of 2 ppm, and was monitored with a Thermox CG1000 oxygen detector. Films were irradiated at a dose rate of 0.1 mJ cm^{-2} per pulse to a range of doses from 5 to 50 J cm^{-2}. The energy was monitored using a Scientech PHF25 detector with a Scientech Vector D200 controller. For all analytical measurements apart from ESR measurements, the samples were ultimately exposed to atmospheric oxygen.

Electron Spin Resonance (ESR). Films of Teflon AF were irradiated to a total dose of 5 or 20 J cm^{-2} in a Harrick cell in which the oxygen concentration was maintained to less than 2 ppm by purging with ultrapure nitrogen in a nitrogen purged glovebox. After irradiation the films were transferred to sealable ESR tubes inside the glovebox at an oxygen concentration of less than 50 ppm. Continuous wave (CW) ESR spectra were recorded on a Bruker Elexsys E580 continuous wave/FT spectrometer fitted with an X-band Super High Q resonator. Variable temperature (100−298 K) regulation was achieved through the use of a liquid nitrogen flow-through cryostat coupled with a Eurotherm B−VT-2000 temperature controller. Typical acquisition parameters were as follows: power 0.2 to 50 mW; modulation amplitude 0.1 to 0.8 mT; sweep time 84 s; 2048 or 4096 points.

X-ray Photoelectron Spectroscopy (XPS). XPS was conducted on a KRATOS AXIS ULTRA. Survey spectra were collected using an analyzer pass energy of 160 eV while the high-resolution spectra of individual elements were taken with a pass energy of 20 eV and a step increment of 0.1 eV. An X-ray power of 150 W was used (10 mA anode current, 15 kV).

^{19}F Nuclear Magnetic Resonance (NMR) Spectroscopy. ^{19}F high-resolution NMR spectra were collected on a Bruker DRX500 at 298 K using a BBi probe without lock or decoupling. The polymers were dissolved in hexafluorobenzene. The spectra were run for a minimum 128 scans. A total of 128K data points collected, and were zero filled to 256K prior to Fourier transformation.

The NMR spectra reported here were assigned by reference to several large databases of ^{19}F chemical shifts.[20−25] In addition a number of previous studies have reported the ^{19}F chemical shifts in spectra of synthetic fluoropolymers.[26,27] Note that other authors have used the chemical shift of extended sequences of $-CF_2-$ units equal to −120 ppm as an internal chemical shift reference. We follow the recent convention of Scheler[28] and use −122 ppm. In general the reported literature chemical shifts are accurate to within ±2 ppm due to the significant solvent effect often reported in ^{19}F NMR. Caution should be exercised in use of the extensive tables of chemical shifts for this reason.

Raman Microspectroscopy. Raman spectra of irradiated thin film samples were acquired using a Renishaw Raman microscope (System 1000). A Spectra Physics 633.2 nm helium−neon laser (model 127) was used, which delivered 8 mW to the sample. The laser was not attenuated and was focused using the 50× objective, giving a spatial resolution of approximately 1 μm. For the spectra obtained in this study, the instrument was run in "snapshot mode" where the diffraction grafting was centered at 1000 cm^{-1}. This gave a spectral range for the 633 nm laser from approximately 520 to 1420 cm^{-1}. The acquisition time for each spectrum was 30 s. The spectral resolution was 3.6 cm^{-1}, which was calculated by measuring the full-width at half-maximum of the nitrogen gas band in air at 2331 cm^{-1}. The instrument was run in confocal mode where confocal operation was achieved by setting the slit width to 15 μm and by masking the charge-coupled device (CCD) detector to an image height of 4 pixels. The diffraction grating was calibrated against the Si−Si stretch from a silicon wafer at 520.1 cm^{-1}. When spectral mapping was performed, the sample was mounted on the computerized X−Y translational mapping stage and spectra were taken at 2 μm intervals to produce a matrix of spectra.

Fourier Transform Infrared (FTIR) Spectroscopy. FTIR spectra of irradiated thin film samples were collected in transition mode with a Perkin-Elmer 2000 spectrometer, with a resolution of 4 cm^{-1}.

Mass Spectrometry (MS). For analysis of volatile products the polymer films were mounted in a Harrick liquid cell fitted with VUV grade calcium fluoride windows. The cell was purged with

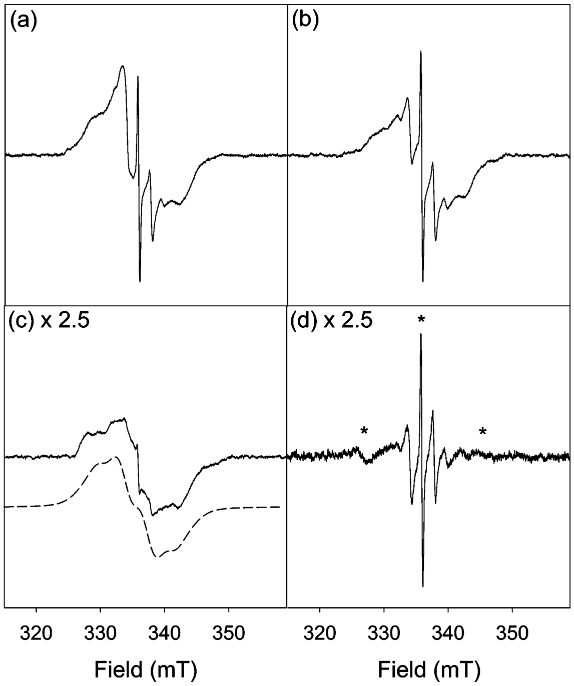


Figure 2. ESR spectra recorded at 298 K of Teflon AF 1200 (a) exposed to a total dose of 5 J cm^{-2} immediately after irradiation, (b) exposed to a total dose of 20 J cm^{-2} immediately after irradiation, and (c) exposed to a total dose of 20 J cm^{-2} 71 h after irradiation and (d) the short lifetime component obtained by the weighted spectral subtraction of spectrum c from spectrum b.

ultrapure nitrogen gas. During 157 nm irradiation of the polymer the purge gas was passed through a cold finger that was maintained at a temperature of 77 K, to collect the volatile photoproducts. The collected volatile photoproducts were analyzed using a Balzers MSC200 Thermocube quadrupole mass spectrometer gas analyzer with static gas inlet system with molecular leak valve.

Results and Discussion

The degradation of fluorinated polyethers under UV irradiation has been previously suggested to proceed via a Rydberg excited-state which dissociates at the ether bond to form free radical products.[12] For this reason we investigate in this study the effect of changes in the dioxole content in Teflon AF on the degradation. Furthermore, the identification of radical intermediates in the degradation of the model polyethers necessitates a study of these products by electron spin resonance spectroscopy.

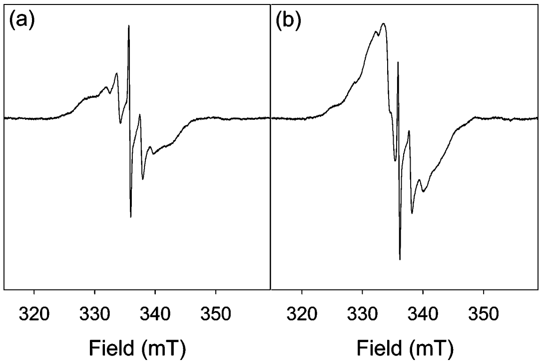


Figure 3. ESR spectra recorded at 298 K of (a) Teflon AF 1600 after being exposed to a total dose of 20 J cm^{-2} of irradiation and (b) Teflon AF 2400 after being exposed to a total dose of 20 J cm^{-2} of irradiation. Both spectra were acquired immediately after irradiation.

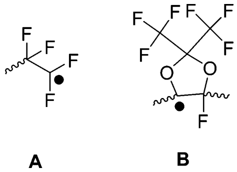


Figure 4. Proposed radical species identified as two components observed in the ESR spectra of Teflon AF copolymers irradiated with 157 nm light.

Free Radical Products (ESR). The ESR spectra of Teflon AF copolymers irradiated with a 157 nm laser exhibit complex splitting patterns. For example, in Figure 2, parts a and b, the ESR spectra obtained from Teflon AF 1200 irradiated to total doses of 5 and 20 J cm^{-2} respectively are presented. These spectra appear to consist of at least two components, namely a sharp central triplet and a broad underlying multiplet. It is evident that the broad component is more intense in the spectrum obtained from the sample irradiated to a dose of 5 J cm^{-2} than in the spectrum of the sample irradiated to a dose of 20 J cm^{-2}. This behavior was also observed in the spectra obtained from irradiated samples of Teflon AF 1600 and Teflon AF 2400 (data not shown). It is also apparent that the free radicals responsible for the broad ESR signal are more stable at room temperature than those giving rise to the narrow signal. The ESR spectrum of Teflon AF 1200 irradiated to a dose of 20 J cm^{-2} and allowed to stand for 72 h at room temperature after irradiation is shown in Figure 2c. It is clear that the sharp central triplet has decayed in intensity, such that only the long-lived broad multiplet signal can be observed. The difference spectrum shown in Figure 2d demonstrates that the signal which has decayed is in fact a triplet of triplets; the position of the weak outer components of the triplet has been marked in Figure 2d with asterisks. The outer components of the triplet are broad and poorly resolved as reported by Toriyama and Iwasaki for irradiated PTFE.[29] Finally the ESR spectra obtained from Teflon AF 1600 and 2400 irradiated to a dose of 20 J cm^{-2} are presented in Figure 3, parts a and b. It is evident that the broad component is most intense in the spectrum of irradiated Teflon AF 2400, while the sharper component is more prominent in the spectra of Teflon AF 1200 and 1600.

It is widely reported that the ESR spectra of irradiated fluoropolymers are often broad and complicated, as a result of (1) overlapping signals from more than one type of radical and (2) the often very large anisotropy of the hyperfine coupling constants with the fluorine nuclei. Despite these difficulties it is possible to assign with some certainty the ESR spectra of the irradiated Teflon AF samples. The broad signal which persists for long time (Figure 2c) is largely due to $>C^{\bullet}$ radicals (Figure 4 B) formed by loss of a fluorine atom from the tertiary carbon of PDD units. This radical species is analogous to the main-chain radical formed on argon plasma treatment[30] or γ-irradiation of PTFE.[31,32] The spectrum in Figure 2c can be well simulated by assuming the isotropic hyperfine coupling constants similar to those reported by Kuzuya and co-workers[30] for plasma-irradiated PTFE. The simulated spectrum shown as a dashed line in Figure 2c was generated assuming $a_{\beta}(1) = 3.0$ mT, $a_{\beta}(2) = 3.8$ mT, $a_{\gamma}(4) = 0.32$ mT, 80% Lorentzian line shape of width = 3.0 mT. These values compare with $a_{\beta} = 3.15$ mT, $a_{\gamma} = 0.32$ mT used by Kuzuya et al.[30] The broad signal is not consistent with hyperfine coupling to fluorine nuclei in the α position, which is on the order of 7−10 mT. It should be noted that all the materials in this study are glassy at ambient temperature, and that the consequent low chain mobility may contribute to the substantial line width in the spectrum. Oshima et al.[33] have reported increased ESR line width in irradiated cross-linked PTFE compared with uncross-linked polymer.

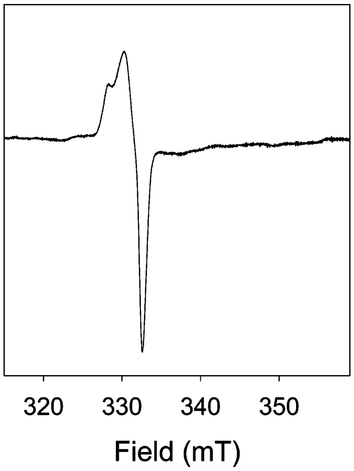


Figure 5. ESR spectrum recorded at 298 K of Teflon AF 1200 irradiated to a total dose of 5 J cm^{-2} in an inert atmosphere and then exposed to the atmosphere.

The triplet of triplets, with a splitting of 1.7 mT for the central triplet and a splitting of the triplets of ∼10 mT, has been assigned to a chain-end $-CF_{2(\beta)}-CF_{2(\alpha)}^{\bullet}$ radical shown in Figure 4 C). The weak peaks with splitting around 10 mT arise from coupling to the two α-fluorine nuclei, and the 1.7 mT hyperfine splitting is due to splitting with the two β-fluorine atoms. Similar signals have been observed for argon plasma treated[30] and for γ irradiated[29,31,32] PTFE, and also for γ irradiated Teflon AF 1600.[34] Toriyama and Iwasaki[29] have reported the temperature dependence of the hyperfine coupling constants for degraded PTFE.

The ESR spectrum of Teflon AF 1200 after irradiation to 5 J cm^{-2} followed by exposure of the sample to the atmosphere is shown in Figure 5. The pattern observed is attributed to the formation of peroxy radicals, which results from the reaction of the carbon-based radicals with oxygen. This radical transformation confirms that the radicals observed in the absence of oxygen were carbon-centered radicals. The spectra are very similar to those reported by Jahan et al.[14] in their study of the formation of peroxy radicals in X-irradiated Teflon AF 1600 and 2400.

Analysis of Surface Chemistry. As reported by French and co-workers,[12] irradiation of fully or partially fluorinated films with 157 nm photons results in rapid photochemical darkening, and hence the photochemistry f these materials occurs largely on the surface of the films. Changes in the surface chemistry of the irradiated Teflon AF films is therefore of much interest. Figure 6 shows the high-resolution C 1s XPS spectra of Teflon AF 1200 exposed to a range of total doses from 0 to 50 J cm^{-2}. For the unexposed material the C 1s spectrum exhibits two peaks at 293 and 290.5 eV. The peak at 293 eV is assigned to carbons in -CF_3 groups[35] while the broader peak at 290.5 eV is consistent with binding energies of carbon atoms in $-CF_2-$, $-CF<$ and $[-O_2-C-(CF_3)_2]$ groups.[35] The spectra of samples exposed to 157 nm radiation exhibit a decrease in the intensity of the peak at 290.5 eV with increasing dose. Furthermore, a broad asymmetric peak with a maximum at 286 eV was observed with increasing dose and was attributed to carbons in structures resulting from defluorination of the polymer chain and loss of the PDD group. The ratios of fluorine-to-carbon and oxygen-to-carbon were also observed to decrease with increasing dose (data not shown), consistent with defluorination and photodegradation at the perfluorodioxole ring. In contrast to these changes, the intensity of the peak assigned to the carbons in $-CF_3$ groups (293 eV) does not change significantly. Similar changes in the XPS spectra were observed to occur for the Teflon AF 1600 and 2400 on irradiation.

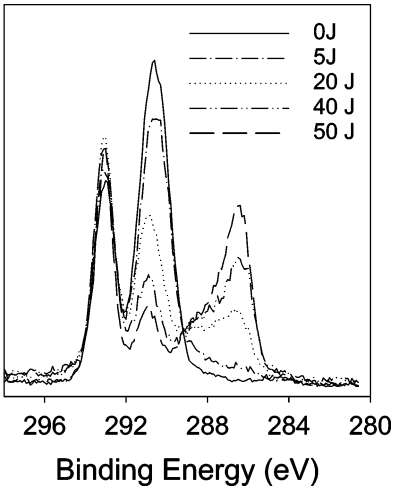


Figure 6. XPS spectra of Teflon AF 1200 exposed to total doses of 0, 5, 20, 40, and 50 J cm^{-1}.

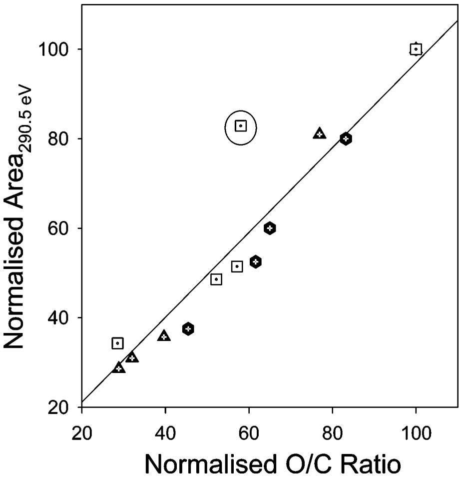


Figure 7. Change in normalized area of the peak in the XPS spectra at 290.5 eV as a function of the O/C ratio (normalized to total intensity) for Teflon AF 2400 (▲), 1600 (⬢), and 1200 (□) after exposure to 157 nm radiation at 0, 5, 20 30, and 40 J cm^{-1}. The solid line is the line of best fit having an r^2 equal to 0.97. The circled point was not included in regression analysis of the data.

In Figure 7, the normalized area of the 290.5 eV peak is plotted against the O/C ratio for each of the polymers and at all exposure doses. A highly linear relationship is observed with an r^2 value of 0.97. This indicates that the decrease in the peak at 290.5 eV is largely due to loss of carbons adjacent to oxygen, i.e., $-CF<$ and $[-O_2-C-(CF_3)]$. Further evidence for this is the small increase in binding energy of the peak at 290.5 eV consistent with a higher proportion of $-CF_2-$ groups remaining after irradiation. Thus, it appears that the major photochemical processes on irradiation are occurring at the PDD group. Despite this the intensity of the $-CF_3$ peak at 293 eV does not change significantly, despite the fact that loss of $O_2-C-(CF_3)$ should also lead to a decrease in the fluoromethyl content. It is thus apparent that new $-CF_3$ groups, most likely chain ends, are being formed at a similar rate to the breakdown of the PDD ring.

Analysis of Bulk Chemistry. NMR spectroscopy is regarded as the most informative analytical tool in polymer science, and has been applied to the study of the radiation chemistry of polymers over many years.[36] To generate sufficient sample for the ^{19}F solution-state NMR spectra reported here approximately

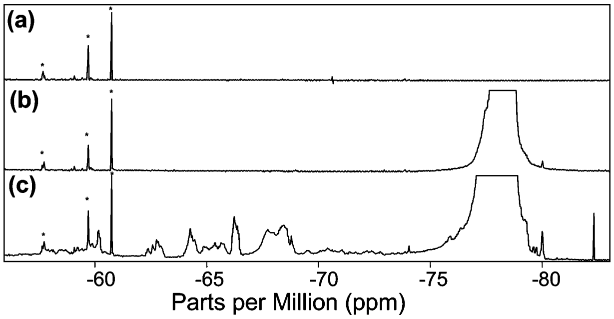


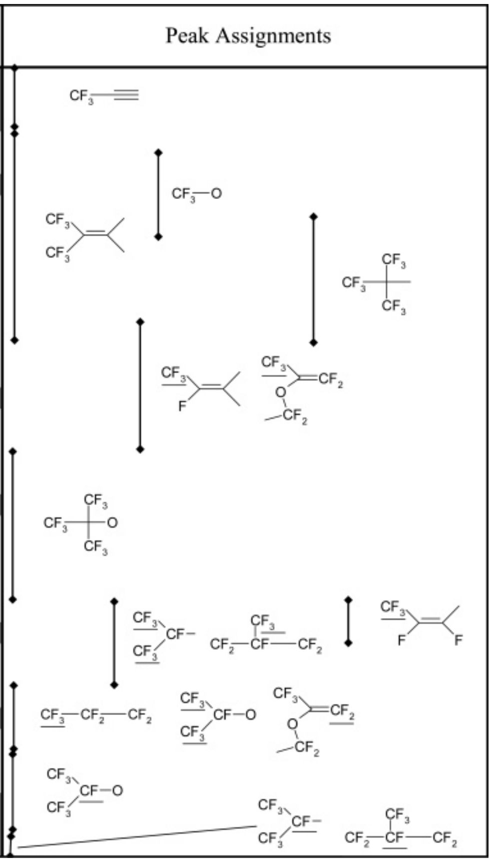
Figure 8. ^{19}F solution-state NMR spectra of (a) hexafluorobenzene (HFB), (b) Teflon AF 2400 dissolved in HFB, (c) Teflon AF 2400 irradiated to a total dose of 20 J cm^{-2} dissolved in HFB. The subspectra from −82 to −55 ppm are plotted only. The vertical scales of spectra b and c have been scaled to equal intensity of the main peak at 78 ppm.

20 thin films (4 cm^2 area, ~1 μm thick) were each irradiated to a dose of 20 J cm^{-2}. Following irradiation the films were soaked in hexafluorobenzene (HFB) to remove them from the calcium fluoride substrate. Because of experimental limitations the entire film could not be irradiated, and hence contributions from the unirradiated polymer appear in the NMR spectra. Nonetheless, a large number of new resonances are observed in the ^{19}F NMR spectra of Teflon AF copolymers after 157 nm irradiation, particularly in the region from −50 to −85 ppm in the spectra. The ^{19}F solution-state NMR spectra (the subspectrum from −50 to −85 ppm is plotted only) for (a) the solvent HFB, (b) unirradiated Teflon AF 2400, and (c) Teflon AF 2400 irradiated with a 157 nm laser to a dose of 20 J cm^{-2} are presented in Figure 8. In this region of the spectrum, the HFB solvent has three peaks due to impurities which have been marked with asterisks. The spectrum of the unirradiated polymer shows major peaks at −78.1 and −78.6, which can be assigned to the $-CF_3$ groups in the PDD ring.[7] Note that in Figure 8 the vertical scale of the spectrum has been expanded so that the splitting into the individual peaks cannot be seen. Small peaks at −80 and −79.5 ppm are also present, and they are due to $-CF_3$ end groups in the unirradiated polymer.

In contrast to these simple spectra, the spectrum of the exposed material shows a large number of new resonances which can be attributed to $-CF_3$ groups in various structures. The observation of a proliferation of fluoromethyl groups on irradiation is consistent with the XPS results described above. The appearance of $-CF_3$ containing structures is not unexpected, as they have also been observed in NMR spectra of γ-irradiated poly(tetrafluorethylene-*co*-perfluorovinyl ethers),[8,9] poly(tetrafluoroethylene-*co*-hexafluoropropylene) (FEP),[10] poly(tetrafluoroethylene-*co*-perfluoropropyl vinyl ether) (PFA)[11] and poly(tetrafluoroethylene) (PTFE).[12,13] Furthermore, $-CF_3$ containing structures are observed to be formed in other high-energy processes involving fluorinated polymers, such as electron-beam irradiated vinylidene fluoride−TFE copolymers,[14] PTFE oligomers prepared by reaction with F_2 gas at high temperatures[15] and plasma-polymerized fluorocarbon films.[16,17] However, it was not possible to make definite assignments of the degradation products for 157 nm degraded Teflon AF 2400 due to the large number of overlapping peaks in the NMR spectra and the poor resolution resulting from the limited mobility of the polymer chains in solution. Attempts to confirm assignments of these peaks using 2D COSY ^{19}F NMR were unsuccessful, primarily due to the broad line widths obtained from the polymer solutions and the low concentrations of degradation products in the sample. However, to support tentative assignments made below and to indicate the types of structures likely to be formed as a result of 157 nm irradiation, we have listed the ^{19}F chemical shifts of a number of structures reported in several large databases in the literature (Table 2).[20−25] In addition a number of previous studies have reported the ^{19}F chemical shifts in spectra of synthetic fluoropolymers. Furthermore, a semiquantitative assessment has been made for each of the peaks to identify from which component of the polymer the peak originated. In Table 2, the dominant component indicates whether the structure giving rise to the peak is derived from the TFE or the dioxole component, based on the chemical shift and the relative intensities of the peaks for the three irradiated Teflon AF samples having different initial composition.

Table 2. Assignments to the ^{19}F Solution-State NMR Spectra of 157 nm Degraded Teflon AF

Peak Position (ppm)	Dominant Component
54.4	TFE
56.7	TFE
57.9	TFE
58.2	Dioxole
58.4	Dioxole
58.9	TFE
59.3	Dioxole
59.4	Dioxole
60.2	Dioxole
60.5	Dioxole
62.4	Dioxole
62.6	Dioxole
62.8	Dioxole
64.3	Dioxole
64.5	Dioxole
64.9	TFE
65.4	Dioxole
65.8	Dioxole
66.2	Dioxole
67.7	Dioxole
68	TFE
68.5	Dioxole
68.8	Dioxole
68.5	
68.8	
70.5	Dioxole
72.1	TFE
75.9	Dioxole
76.3	Dioxole
79.7	Dioxole
79.8	TFE
82.3	Dioxole
142.5	Dioxole
142.9	Dioxole
143.3	TFE
143.6	TFE
184.2	TFE



In addition to NMR analysis of the polymers in solution, the irradiated samples were examined using FTIR. Typically, vibrational modes associated bonds that have a large dipole moment, such as carbonyls, are most readily observed by infrared spectroscopy. Figure 9 shows the transmission FTIR spectra in the 1575 − 2075 cm^{-1} region from (a) unirradiated Teflon AF 1600, (b) Teflon AF 1600 irradiated to a total dose of 50 J cm^{-2} with 157 nm radiation, and (c) Teflon AF 1600 irradiated to a total dose of 50 J cm^{-2} and then exposed to the atmosphere for 16 h. The spectrum of the unirradiated polymer (Figure 9a) exhibits only a weak overtone band at 1925 cm^{-1}. Following irradiation to a dose of 50 J cm^{-2} a peak at 1881 cm^{-1} appears, consistent with the formation of perfluorinated acid fluorides.[34,37,38] Irradiation took place in an inert atmosphere, so formation of acid fluorides must occur via photoinduced chain scission reactions involving the PDD ring. A broad peak centered at 1700 cm^{-1} was also observed and is assigned to $-CF{=}CF-$ and $CF_2{=}CF-$ unsaturated groups, which are usually observed at 1740 and 1680 cm^{-1} respectively.[37] In addition an overall decrease in the intensity of the peaks in the

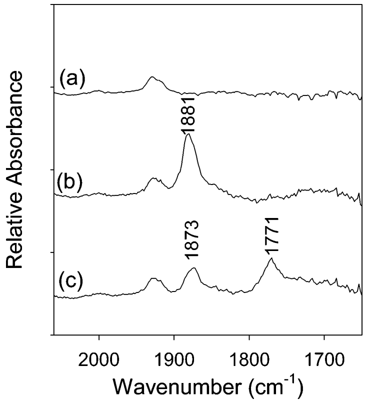


Figure 9. Transmission FTIR spectra of Teflon AF 1600 (a) unirradiated and (b) after 157 nm irradiation to a total dose of 50 J cm^{-2} and (c) after 157 nm irradiation to a total dose of 50 J cm^{-2} and the post irradiation exposure to the atmosphere for 16 h.

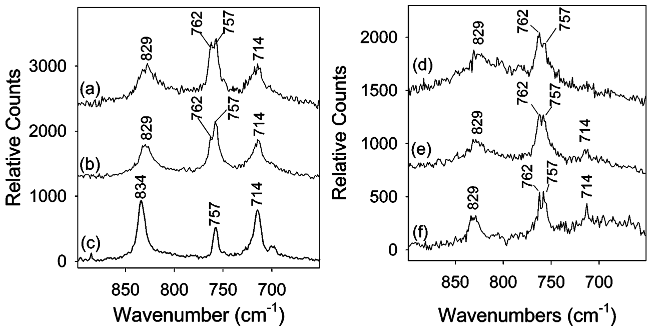


Figure 10. Raman spectra of thin films of unexposed (a) Teflon AF 1200, (b) Teflon AF 1600, and (c) Teflon AF 2400 and samples irradiated to a dose of 30 J cm^{-2}: (d) Teflon AF 1200, (e) Teflon AF 1600, and (f) Teflon AF 2400.

spectrum from 1000 to 1575 cm^{-1} (data not shown) was observed with increasing irradiation dose, and indicates that ablation of the polymer occurs during irradiation. The peaks in this region can be attributed to C−C, C−F, and C−O stretching vibrations,[37] but further analysis was made difficult because of the extensive coupling of these vibrations.

Raman spectroscopy is complementary to FTIR spectroscopy in that symmetrical vibrational modes are most readily observed. In Figure 10, the Raman spectra of virgin polymers (a) Teflon AF 1200, (b) Teflon AF 1600, and (c) Teflon AF 2400 and of these three polymers exposed to 30 J cm^{-2} of 157 nm radiation are presented. In the 620−900 cm^{-1} region there are three main peaks for Teflon AF type polymers at 715, 757, and 829 cm^{-1}. However, the positions of the peak maxima for the bands at 757 and 830 cm^{-1} appear to be dependent on polymer composition. Legeay et al.[39] have reported the Raman spectrum of Teflon AF 1200; however, they were unable to definitively assign three main bands.

In Figure 10a−c, the bands at 715 and 829 cm^{-1} are observed to increase in area with increasing PDD content, so are assigned to vibrational modes of PDD repeat units. No change in position with PDD content was observed for the band at 715 cm^{-1}. However, the band at 829 cm^{-1} was observed to be comprised of two components, the first at 829 cm^{-1} which is relatively more intense at low PDD content and the second at 834 cm^{-1} which was more intense at higher PDD content. It is clear the sequence distribution of PDD groups will, as with other copolymers, be dependent on copolymer composition.[11,40] For example, Teflon AF 1200, which has a TFE content of 52 mol %, has 42% of the TFE units in runs of 3 repeat units or more, while Teflon AF 2400, which has a TFE content of 11 mol % has only 5% of its TFE units in runs or 3 repeat units or more.[11]

With increasing PPD content in the copolymers, the probability of adjacent PDD units will increase. We can see that around 830 cm^{-1}, the peak at 834 cm^{-1} increases in intensity over that at 829 cm^{-1} at higher PDD contents. We therefore assign the vibrations associated at 834 cm^{-1} and 829 cm^{-1} to the CF group within T*P*P + P*P*P and T*P*T triads, respectively. Vibrations of the $[O_2{-}C{-}(CF_3)_2]$ portion of the PDD unit should be less sensitive to copolymer sequence, and therefore the peak at 715 cm^{-1}, which did not change in position with copolymer composition, was assigned to a vibrational mode involving this group. The peak at 757 cm^{-1} was assigned to the C−C−C stretching mode of the TFE unit.[41] It should be noted that for PTFE this peak occurs at 731 cm^{-1}. This peak has two components, the intensities of which were dependent on PDD concentration. The intensity of the partly resolved peak at 762 cm^{-1} increased with PDD content, and so was assigned to T*T*P and P*T*P triads, while the peak at 757 cm^{-1} is relatively more intense for polymers with lower PDD content and thus is assigned to T*T*T triads.

Upon exposure to 157 nm light to a dose of 30 J cm^{-2} profound changes were observed in the Raman spectra. The most notable change was almost the complete disappearance of the peak at 715 cm^{-1}, which in the discussion above was assigned to the $[O_2{-}C{-}(CF_3)_2]$ portion of the PDD ring. The peak at approximately 829 cm^{-1} was also observed to decrease relative to the peak at 760 cm^{-1}. For Teflon AF 2400, this peak was observed to shift from 830 to 825 cm^{-1} after irradiation at 157 nm. This clearly indicates that sequences of PDD repeat units are more labile than isolated PDD units. In a similar manner the intensity of the peak at 762 cm^{-1} due to TFE units adjacent to PDD units was observed to decrease in intensity on irradiation more rapidly than the component with a maximum at 757 cm^{-1}, which we have assigned to runs of TFE units. This again indicated that the PDD group is substantially more susceptible to radiolysis at 157 nm.

Analysis of Volatile Products. The volatile products formed during 157 nm irradiation were collected in a cold finger cooled to 77 K and subsequently analyzed by mass spectrometry. The list of major ions observed in the mass spectra, the relative intensities for each of the copolymers, and the assignments to the fragments are presented in Table 3. As for the ^{19}F NMR analysis a complex array of degradation products has been observed.

The principal fragments from the volatile products of radiolysis of the Teflon AF materials are CF_3^+ and COF^+ as well as fragments arising from low molecular weight TFE oligomers. In Table 3, we have proposed the identity of the parent molecules or reaction; the mechanisms of formation are discussed in the next section.

The Mechanism of Photodegradation. The most important conclusions of the comprehensive examination of the degradation of the Teflon AF are listed below.

•The mechanism of degradation involves free radicals (ESR). The major stable free radical at ambient temperature is associated with the PDD units (ESR).

•Scission of the polymer backbone occurs to generate $-CF_2^{\bullet}$ radicals (ESR).

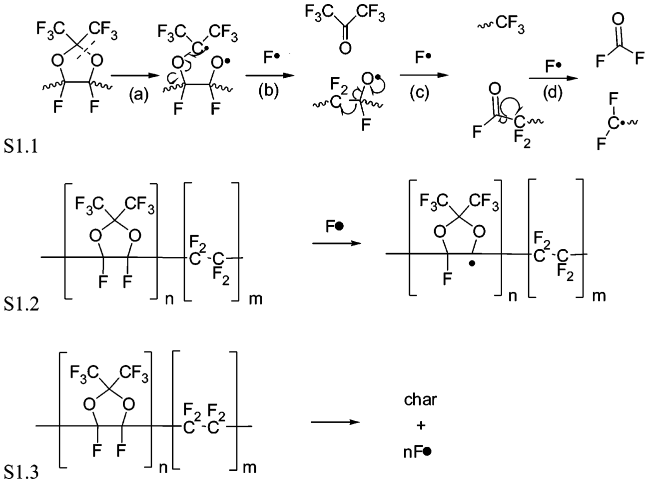
•Defluorination of the backbone occurs, eventually yielding a char (XPS).

•The major site for photochemical changes is the perfluorodioxole ring (XPS, Raman, ESR, ^{19}F NMR).

Table 3. Summary of Results of Mass Spectroscopic Analysis of Volatile Products of Radiolysis of Teflon AF at 157 nm

fragment	*m/z*	I_{1200}	I_{1600}	I_{2400}	source
COF	47	7.6	12.4	14.0	radical chain end scission
CF_3	69	100	100	100	PDD, hexafluoroacetone
$CF_2{=}CF$	81	9.5	7.7	7.9	TFE, oligomers
$CFC-CF_2$	93	10.4	6.8	6.9	HFP, TFE oligomers
CF_3CO or CF_2COF	97	1.5	2.8	3.4	radical chain end scission
$CFC-CF_3$	112	0.9	2.1	1.7	HFP, TFE oligomers
CF_3CF_2	119	4.6	6.6	8.7	TFE, oligomers
$CF_2{=}CF-CF_2$	131	4.0	6.8	8.7	HFP, TFE, oligomers
$CFC-CF_2-CF_2$	143	0.5	1.1	1.1	TFE, oligomers
CF_3CF_2CO or CF_3COCF_2	147	0.8	1.5	1.8	radical chain end scission
$CF_2{=}CF-CF_2-CO$ or $CF_2{=}CF-CO-CF_2$	159	0.8	1.8	1.4	radical chain end scission
$CF_3-CF_2-CF_2$	169	2.6	4.3	4.5	TFE, oligomers
$CF_2{=}CF-CF_2-CF_2$	181	6.3	12.6	9.9	TFE, oligomers
$CFC-CF_2-CF_2-CF_2$	193	0.2	0.5	0.5	TFE, oligomers
$CF_3CF_2CF_2CO$ or $CF_3COCF_2CF_2$ or $CF_3CF_2COCF_2$	197	0.5	0.9	1.2	radical chain end scission

Scheme 1. Proposed Major Pathways for the Photodegradation of Teflon AF under 157 nm Radiation



•A complex array of photodegradation products is generated (^{19}F NMR, MS).

•The stable species formed include acid fluorides (FTIR), unsaturated species (FTIR, ^{19}F NMR, MS), char (XPS), hexafluoroacetone (MS), carbonyl difluoride (MS), low molecular weight PTFE oligomers (MS), and structures containing $-CF_3$ (XPS, ^{19}F NMR).

In light of these results, we have proposed that the mechanisms depicted in Scheme 1 are the major pathways for the photochemical degradation at 157 nm of Teflon AF copolymers. The ESR and XPS results in particular indicate that irradiation with 157 nm photons leads to significant defluorination of the polymer to form a char (Scheme 1.3) and thus it is expected that there will be a constant flux of $F^{\bullet}$ radicals available for addition to chain ends and other radical intermediates, and indeed in other reports on the radiation degradation of perfluorinated compounds, $F^{\bullet}$ radicals are suggested to be readily formed.[42]

In the reaction Scheme S1.1, it is proposed that a major event is cleavage of the carbon−oxygen bond of PDD units as indicated by the dashed line. This can be followed by elimination of hexafluoroacetone to form an alkoxy radical. The formation of hexafluoroacetone was previously proposed by Forsythe et al.[34] as a major pathway for the degradation of Teflon AF 1600 under γ-radiolysis. It is expected that the alkoxy radical will be unstable and undergo β-scission to yield acid fluoride and perfluoromethyl end groups. The constant flux of $F^{\bullet}$ radicals referred to above is available for addition reactions to the free radical products. The acid fluoride can subsequently undergo secondary degradation to yield carbonyl difluoride and chain-end radicals (Figure 4B) observed by ESR. Addition of fluorine to the $\sim CF_2^{\bullet}$ chain-end radicals, or abstraction reactions, will lead to methyl groups observed by ^{19}F NMR spectroscopy. The photolysis of acid fluorides leads to the formation of carbonyl difluoride and alkyl radicals which can undergo addition or combination reactions.[43] The tertiary, carbon-centered radical (Figure 4A), observed using ESR spectroscopy, is most likely formed by abstraction of the fluorine atom (Scheme S1.2), and can undergo further reaction to also form hexafluoroacetone and oxygen-containing or unsaturated chain ends, although the radicals in Figure 4A are persistent at room temperature as determined by ESR measurement. As mentioned above the XPS measurements indicate the formation of char as a result of extensive defluorination (Scheme S1.3); these reactions will provide a flux of fluorine radicals available for addition reactions in Scheme S1.1.

The mechanisms proposed above furthermore account for the decrease in the O/C ratio with increasing extent of degradation observed in XPS, the generation of acid fluoride observed by FTIR, the formation of CF_3 groups verified by ^{19}F NMR and XPS, and the radicals products observed by ESR. However, the plethora of photochemical products observed by NMR and MS in particular teach us that the photochemistry of the Teflon AF copolymers is more complicated than indicated above, and likely involves secondary reaction of the degradation products described above. Despite this, the mechanisms account for overwhelming majority of the photochemical degradation products that we have observed in Teflon AF copolymers irradiated with 157 nm light.

From the results and mechanism presented above it is apparent that the photosensitivity of Teflon AF copolymers at 157 nm is due to the presence of the perfluorodioxole group. Partly, this is because hexafluoroacetone is a good leaving group, and this drives the degradation toward the formation of chain-scission products. It is clear therefore that future attempts to design polymers that are photostable at 157 nm should take the photosensitivity of the PDD unit into account.

The ability of Teflon AF to be spin-coated into thin films, its optical clarity resulting from its amorphous nature, and its creep resistance have made this polymer an attractive material for the selective adhesion of cells for use in biosensor applications.[19] To achieve this goal methods for the selective surface modification of Teflon AF are required. Methods such as reactive ion etching,[19] and irradiation with broad band VUV[35] light have been utilized previously to modify the surfaces of Teflon AF. The sensitivity of Teflon AF to irradiation with 157 nm light also presents a facile method for the modification and patterning of the surfaces of these polymers with acid fluoride and carboxylic acid functionalities. This study is the first attempt to characterize the complex sequence of photochemical events occurring during exposure to VUV photons.

Conclusions

The photodegradation at 157 nm of a series of Teflon AF copolymers has been studied using a range of techniques including ESR, ^{19}F NMR, FTIR, Raman, MS volatile analysis, and XPS. Analysis of the degradation products and the product distribution as a function of copolymer composition has led to the conclusion that the photochemical degradation initiates at the perfluorodioxole ring. The resultant photochemical reactions lead to a diverse array of degradation products. In broad terms photodegradation at the dioxole ring leads to chain scission, resulting in the formation of acid fluorides, and $CF_2^{\bullet}$ end groups, which can lead to the formation of CF_3 end groups. It has been concluded that to design new polymers with greater stability at 157 nm changes to the structure of the perfluorodioxole group will need to be made. The results from this study may also provide methods for the generation of Teflon AF surfaces that are functionalized with carboxylic acid groups.

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