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Degradation and Crosslinking of Perfluoroalkyl Polyethers Under X-Ray Irradiation in Ultrahigh Vacuum

Shigeyuki Mori
and Wilfredo Morales

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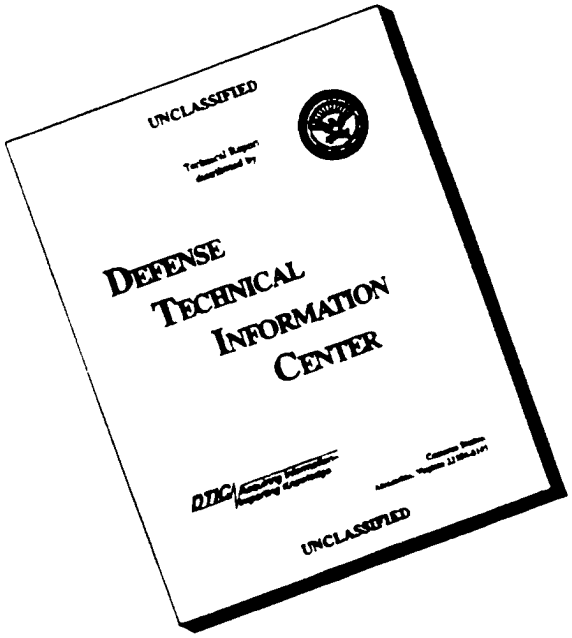

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16. Abstract

Degradation of three types of commercially available perfluoroalkyl polyethers (PFPE)—Demnum S200, Fomblin Z25, and Krytox 16256—by x-ray irradiation was studied by using x-ray photoemission spectroscopy (XPS) and a mass spectrometer under ultra-high-vacuum conditions. The carbons in the polymers were characterized by chemical shifts of C_{1s} binding energies. Gaseous products containing COF_2 and low-molecular-weight fluorocarbons were formed. From Fomblin Z25, which has acetal linkages ($-OCF_2O-$), a large quantity of COF_2 gas was evolved. Liquid products became tacky after a long irradiation time, and some did not dissolve in Freon. High-pressure liquid chromatography (HPLC) showed that molecular weight distribution became broader and that higher molecular weight polymers were formed from Demnum and Krytox. We concluded from these results that degradation and cross-linking took place simultaneously. Demnum crosslinked more easily than the other fluids. The time dependence of both XPS spectra of C_{1s} and mass spectra showed that C-O-bonded carbons in PFPE's were removed faster than other carbons. There was no substrate effect on the degradation reaction because the first-order rate constants calculated from the change of gaseous products were similar when stainless steel (440C) and gold-coated surfaces were used. Metal fluorides were formed on stainless steel during the reaction. A mechanism for the degradation of PFPE's is discussed on the basis of their molecular structures.

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Summary

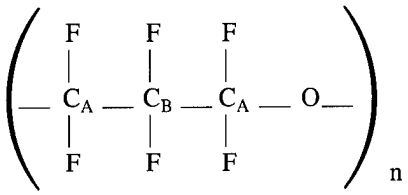
Degradation of three types of commercially available perfluoroalkyl polyethers (PFPE)—Demnum S200, Fomblin Z25, and Krytox 16256—by x-ray irradiation was studied by using x-ray photoemission spectroscopy (XPS) and a mass spectrometer under ultra-high-vacuum conditions. The carbons in the polymers were characterized by chemical shifts of C_{1s} binding energies. Gaseous products containing COF_2 and low-molecular-weight fluorocarbons were formed. From Fomblin Z25, which has acetal linkages ($-OCF_2O-$), a large quantity of COF_2 gas was evolved. Liquid products became tacky after a long irradiation time, and some did not dissolve in Freon. High-pressure liquid chromatography (HPLC) showed that molecular weight distribution became broader and that higher molecular weight polymers were formed from Demnum and Krytox. We concluded from these results that degradation and crosslinking took place simultaneously. Demnum crosslinked more easily than the other fluids. The time dependence of both XPS spectra of C_{1s} and mass spectra showed that C–O-bonded carbons in PFPE's were removed faster than other carbons. There was no substrate effect on the degradation reaction because the first-order rate constants calculated from the change of gaseous products were similar when stainless steel (440C) and gold-coated surfaces were used. Metal fluorides were formed on stainless steel during the reaction. A mechanism for the degradation of PFPE's is discussed on the basis of their molecular structures.

Introduction

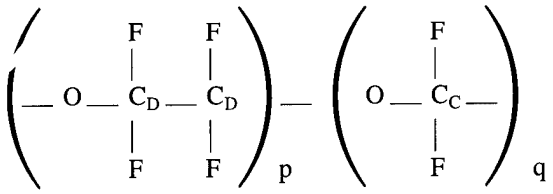
Perfluoroalkyl polyethers (PFPE) have physical and chemical properties, such as extremely low vapor pressure and high chemical inertness (refs. 1 and 2), that allow their use as vacuum pump oils (ref. 3), as lubricants for magnetic recording media (ref. 4), and as lubricants for instrument ball bearings aboard satellites (ref. 5).

The three commercially available PFPE fluids have the following molecular structures:

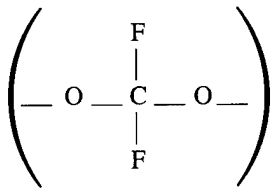
Demnum S200



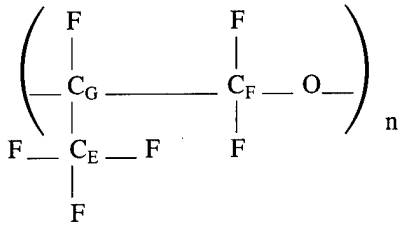
Fomblin Z25



p/q = 0.6 to 0.7. Note: Only Fomblin contains "acetal" structure.



Krytox 16256



The subscripts on the carbon atoms denote their different bonding arrangements. Thus C_A, for Demnum, denotes a carbon atom bonded to an oxygen atom, to two fluorine atoms, and to another carbon atom. On the other hand, C_B denotes a carbon atom bonded to two other carbon atoms and to two fluorine atoms. Fomblin has two different carbon atoms—C_C and C_D; Krytox has three different carbon atoms—C_E, C_F, and C_G. The chemical activities of the PFPE fluids differ as a result of their different molecular structures (refs. 6 and 7). The acetal linkage in Fomblin is explicitly indicated in figure 1 for the later reference.

PFPE fluids have been characterized by various analytical tools such as infrared spectroscopy (refs. 8 and 9), HPLC (ref. 10), mass spectroscopy (ref. 11), electron paramagnetic resonance (EPR) (ref. 12), and XPS (refs. 4, 13, and 14). XPS is a useful tool for characterizing chemical bonds, especially surface chemical bonds. One of the disadvantages of XPS analysis, however, pertains to polymer samples—polymers under study may be damaged by x-ray irradiation (refs. 15 and 16). Perfluoroethyl polyether degradation under x-ray irradiation has been reported (ref. 12). In addition PFPE degradation under irradiation from low-energy electrons (ref. 11), high-energy electrons (refs. 8 and 9), and ion beams (ref. 17) have all been reported.

Although some researchers have used XPS for characterizing PFPE fluids, they did not report on the possible degradation of the fluids due to the x-ray irradiation. The objectives of this investigation were to characterize the three commercial PFPE fluids by XPS and to investigate the possible chemical effect of the x rays on the PFPE fluids during XPS measurements.

Experimental Procedure

Materials

Three commercially available PFPE fluids were used:

(1) Demnum S200—a poly(perfluoropropylene oxide)

(2) Fomblin Z25—a copolymer of perfluoromethylene and perfluoroethylene oxides

(3) Krytox 16256—a poly(perfluoropropylene oxide) with pendent $-CF_3$ groups

Their properties are listed in table I.

A cotton swab was used to coat the surface of a metal substrate (440C stainless steel with a diameter of 9.5 mm) with each of the PFPE fluids. The metal substrates were rinsed with acetone in an ultrasonic bath after polishing with diamond pastes (6 μm followed by 1 μm). Gold-coated metal substrates were also used. The gold film was about 0.1 μm thick. The fluid sample mass on the metal substrate varied between 10 and 100 μg, and the corresponding average film thickness varied between 0.08 and 0.8 μm.

TABLE I.—PROPERTIES OF PFPE FLUIDS

Property	Fluid		
	Demnum S200	Fomblin Z25	Krytox 16256
Average molecular weight	8400	9500	11 000
Kinetic viscosity at 20 °C, cS	500 + 25	255	2717
Viscosity index	210	355	------
Pour point, °C	−53	−66	−15
Density at 20 °C, g/ml	1.894	1.851	1.92
Surface tension at 20 °C, dyne/cm	19	25	19
Vapor pressure, torr:			
At 20 °C	5×10^{-11}	2.9×10^{-12}	3×10^{-14}
At 100 °C	1.0×10^{-7}	1.0×10^{-8}	1×10^{-9}

XPS Measurement

The XPS spectrometer used was equipped with a MgK_α x-ray source (conditions: 25 mA, 12 kV). The distance between the metal surface and the x-ray anode was about 30 mm; the takeoff angle toward the metal was 0° (fig. 1). The electron detector window was 3 mm by 6 mm. The binding energies of C_{1s}, O_{1s}, and F_{1s} were determined from high-resolution spectra (fixed pass energy, 25 eV). The binding energies were calibrated with a pure copper surface that was cleaned by argon ion sputtering under ultrahigh vacuum ($Cu_{2p_{3/2}} = 932.4$ eV and $Cu_{3p_{3/2}} = 74.9$ eV). Compensation for charging up was not attempted. The C_{1s} spectra were resolved by a curve resolver.

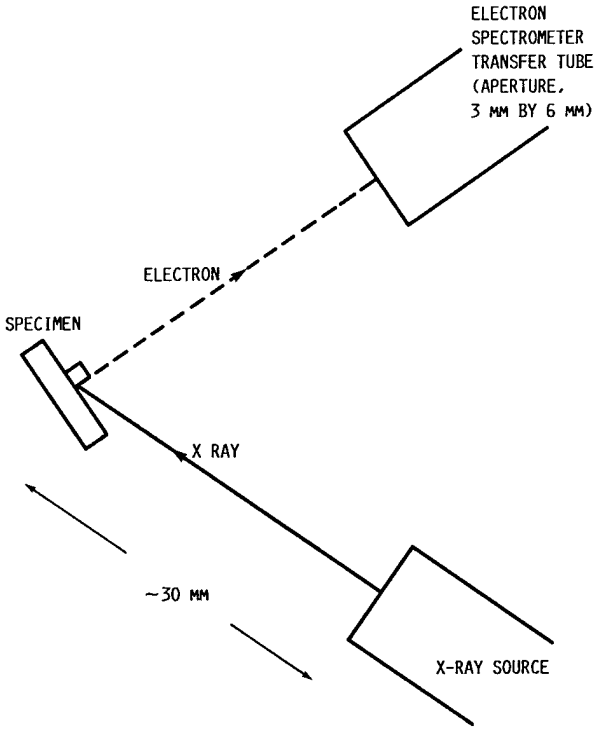


Figure 1.—Schematic diagram of x-ray photoemission spectrometer.

The vacuum chamber was evacuated to less than 5×10^{-9} torr with an ion pump (pumping speed, 140 liters/sec for N_2). Pressure changes due to gas evolution during x-ray irradiation were monitored by a nude-ion gage. Gaseous products formed during x-ray irradiation were monitored with a quadrupole mass spectrometer.

Characterization of Products

After an x-ray irradiation experiment the metal surface was rinsed with pure 1,1,2-trichlorotrifluoroethane (TCF), separating TCF-soluble material from TCF-insoluble material. The TCF-soluble rinse was collected for size exclusion analysis by high-pressure liquid chromatography (HPLC). Details of this HPLC analysis have been reported elsewhere (ref. 10). The TCF-insoluble material left on the metal surface was examined by Fourier transform infrared (FTIR) emission spectroscopy at 175 °C.

Mass Balance

Mass balances were estimated for all three PFPE fluids by placing approximately 2.5 mg of a sample fluid on a preweighed 440C metal specimen (diameter, 19 mm) and then weighing the metal specimen a second time to give the precise mass of the fluid. The fluid was then irradiated for 3 hr. After irradiation the metal specimen was weighed a third time to give the weight loss of the fluid, which corresponds to the amount of gaseous products formed. Finally, the metal surface was rinsed with 3 ml of TCF and the metal specimen was weighed a fourth time. The weight difference before and after the rinse was the amount of TCF-soluble product that was analyzed by HPLC. The remaining material on the metal surface was TCF-insoluble material. The mass balance data are summarized in table II.

TABLE II.—MASS BALANCE FOR DEGRADATION OF FLUIDS

[After 3-hr x-ray irradiation under conditions of MgK, 12 kV, and 25 mA, pressure increase due to gas evolution was 5×10^{-8} torr.]

Product	Fluid					
	Demnum S200		Fomblin Z25		Krytox 16256	
	Amount					
	mg	Percent	mg	Percent	mg	Percent
Gas	0.60	29	0.44	18	0.51	21
Liquid[a]	.78	38	1.91	76	1.68	70
Polymer[b]	.68	33	.15	6	.21	9
Total	2.06	100	2.50	100	2.40	100
Polymer/gas ratio	1.1		0.3		0.4	

[a]TCF-soluble material.
[b]TCF-insoluble material.

Results and Discussion

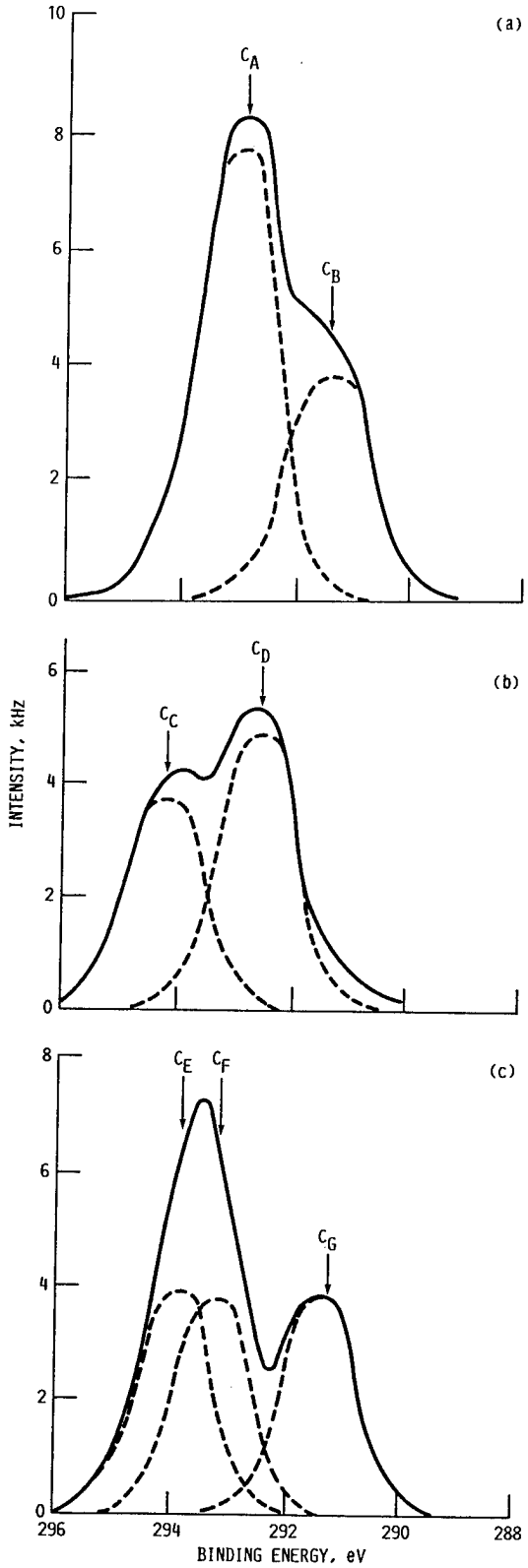
Characterization of PFPE Fluids by XPS

The initial C_{1s} spectra for the PFPE fluids are shown in figure 2. According to the binding energies, Demnum and Fomblin each have two different bonding carbon atoms, whereas Krytox has three different bonding carbon atoms. The binding energies and their relative intensity for the PFPE fluids, on both 440C steel and gold-coated metal substrates, are summarized in table III. In general, higher electronegativities of bonded atoms will shift binding energies to higher values. The binding energies summarized in table III were assigned from their chemical shifts.

The C_{1s} binding energies for Demnum (on the 440C metal substrate) are 292.9 and 291.4 eV. As was mentioned previously, there are two different types of bonding carbon atoms in the Demnum molecule. One (C_A) is bonded with two fluorine atoms, an oxygen atom, and another carbon atom. The other (C_B) is bonded with two fluorine atoms and two other carbon atoms. Since the electronegativity of an oxygen atom is higher than that of a carbon atom, the binding energy of carbon C_A was expected to be higher than that of carbon C_B. The intensity ratio of the 292.9-eV peak to the 291.4-eV peak is 2; this result agrees with the ratio of the number of C_A carbon atoms to the number of C_B carbon atoms.

Fomblin has two different types of bonding carbon atoms—C_C and C_D. The number of C_D carbon atoms is approximately 1.3 times the number of C_C carbon atoms (calculated from its chemical formula). Since the C_C carbon atom is bonded with two oxygen atoms and the C_D carbon atom is bonded with an oxygen and a carbon atom, it was expected that the C_C binding energy would be higher than the C_D binding energy. The experimental C_{1s} binding energies for Fomblin were 294.2 and 292.6 eV; the intensity of the higher binding energy peak was 1.3 times that of the lower binding energy peak. Thus the binding energies for the C_C and C_D atoms were assigned as 294.2 and 292.6 eV.

Krytox has three types of bonding carbon atoms—C_E, C_F, and C_G. The relative numbers of these three carbon atoms in the Krytox molecule are the same. The resolved XPS spectrum (fig. 2(c)) shows three C_{1s} peaks, at 293.8, 293.2, and 291.4 eV. The intensities of the three peaks are nearly equal. Since the C_E atom is bonded to three fluorine atoms, the binding energy of this carbon atom is expected to be the highest of the three carbon atoms. The C_F atom is bonded directly to two fluorine atoms, and the C_G atom is bonded to a trifluoromethyl group instead of a fluorine atom. Since the



(a) Demnum S200.
(b) Fomblin Z25.
(c) Krytox 16256.

Figure 2.—C_{1s} XPS spectra. Substrate, 440C stainless steel.

TABLE III.—BINDING ENERGIES OF C_{1s} AND THEIR INTENSITY RATIOS

Fluid	Substrate				Assignment	
	440C		Gold		Carbon	Intensity ratio
	Binding energy, eV	Intensity ratio	Binding energy, eV	Intensity ratio		
Demnum S200	292.9 291.4	2 1	292.4 291.0	2 1	C_A C_B	2 1
Fomblin Z25	294.2 292.6	1 1.3	293.3 291.9	1 1.3	C_C C_D	1 1.3
Krytox 16256	293.8 293.2 291.4	1 1 1	293.1 292.3 290.6	1 1 1	C_E C_F C_G	1 1 1

directly bonded fluorine atoms shift the C_{1s} binding energy to higher values than the trifluoromethyl group (ref. 19), the binding energy of the C_F atom was expected to be higher than that of the C_G atom. It was concluded that the binding energies of the C_E, C_F, and C_G atoms were 293.8, 293.2, and 291.4 eV, respectively.

The C_{1s} binding energies of the gold-coated metal substrate are also summarized in table II. Lower binding energies were measured on the gold surfaces than on the 440C steel surfaces. Although these results may be explained by surface effects such as charging up, since the 440C steel is covered with an oxide layer, further work is needed to clarify the difference in binding energies between the two surfaces. The order of binding energies on the gold surfaces is, nevertheless, similar to the order on the 440C steel surfaces. The binding energy order is as follows for the 440C steel substrate:

$$C_C > C_E > C_F > C_A > C_D > C_B = C_G$$

After a long irradiation time (380 min), a new F_{1s} peak appeared at 684.5 eV (fig. 3) that corresponds to metal fluorides (refs. 14 and 20). The metal fluoride could be formed by the reaction of COF_2 or fluorocarbon radicals (products from PFPE irradiation) with the 440C surface oxide.

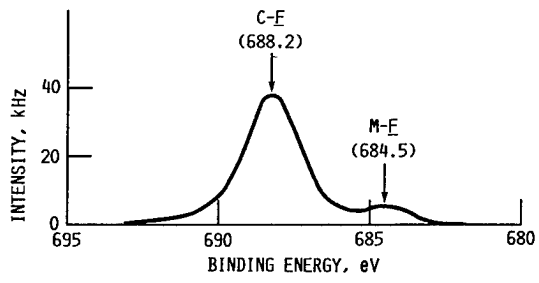


Figure 3.—F_{1s} XPS spectra of Krytox 16256. Substrate, 440C stainless steel; irradiation time, 380 min.

Time Dependence of XPS Spectra

Figure 4 shows the time dependence of the Demnum C_{1s} spectra during x-ray irradiation. The intensity of the peak at 292.9 eV decreased with irradiation time, providing evidence that Demnum changed chemically during x-ray irradiation. This peak corresponds to C_A, the oxygen-bonded carbon atom, and it is apparent from the figure that it is removed substantially from the Demnum molecule.

The C_{1s} XPS spectra for Demnum, Fomblin, and Krytox are shown in figure 5 after approximately a 1-hr irradiation. The resolved peaks have been identified with the same nomenclature as in figure 2, but the exact positions of these resolved peaks are slightly different because of the deconvolution procedure. Notice that for Fomblin (fig. 5(b)) the C_C peak intensity decreased substantially in relation to the C_D peak intensity. In addition, for Krytox (fig. 5(c)) the intensity of both the C_F and C_G peaks decreased faster than that of the C_E peak. The C_A, C_C, C_D, C_F, and C_G carbon atoms are all bonded to oxygen atoms. These results suggest that the C–O-bonded carbons are more easily removed from the PFPE molecules than the C–C-bonded carbons (C_B and C_E); moreover, the acetal-bonded ($-OCF_2O-$) carbon, C_C, in the Fomblin molecule undergoes the greatest peak intensity decrease.

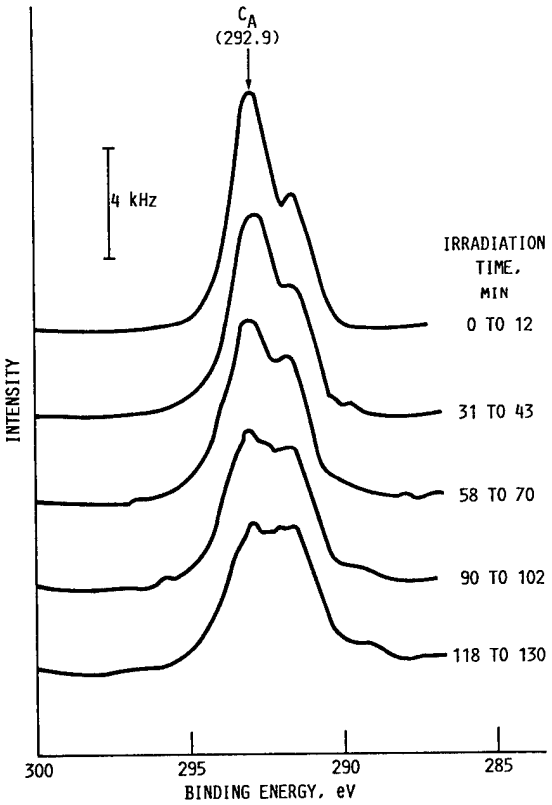
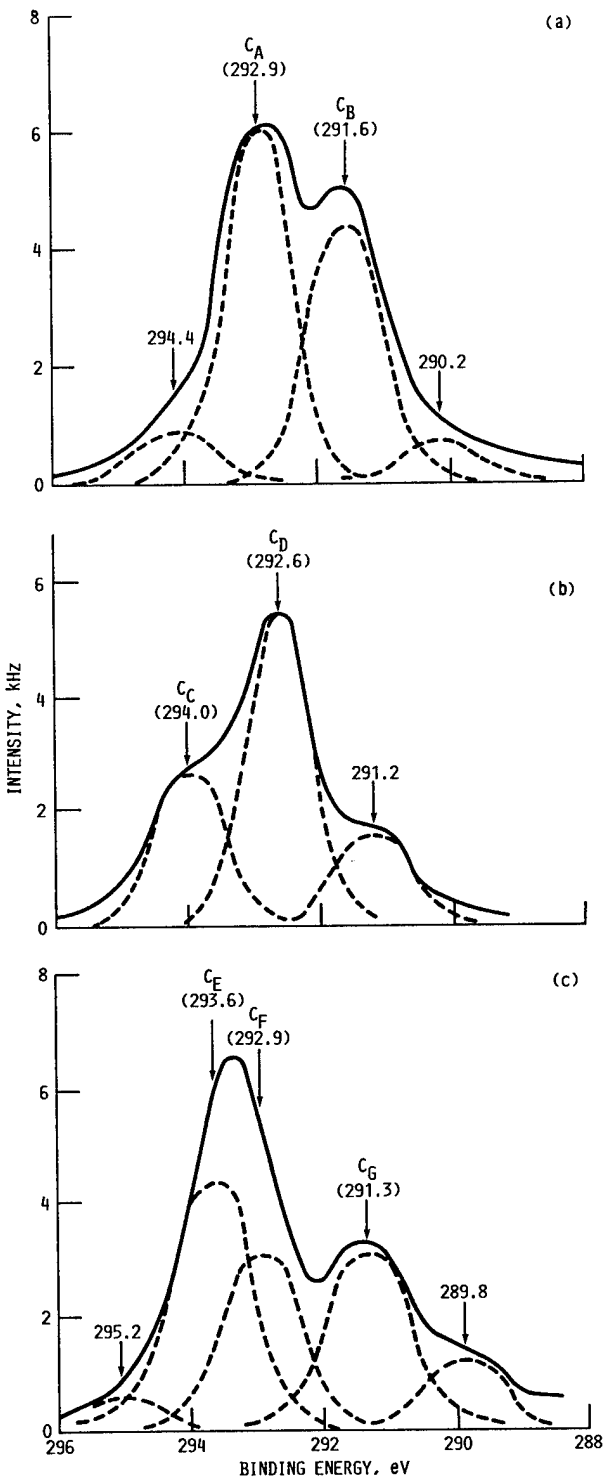


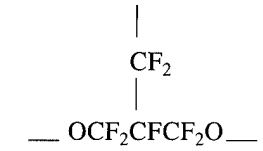
Figure 4.—Time dependence of C_{1s} spectra of Demnum S200 during x-ray irradiation.



(a) Demnum S200.
(b) Fomblin Z25.
(c) Krytox 16256.

Figure 5.—Change of C_{1s} XPS spectra by x-ray irradiation. Substrate, 440C stainless steel; irradiation time, 60 to 72 min.

In addition to the intensity changes of the existing peaks, new peaks appeared at both higher and lower binding energies. One explanation for the peak formation at the higher binding energy is the formation of a trifluoromethyl group such as $-OCF_2CF_3$ or $-OCF_3$. The formation of the peak at the lower binding energy can be explained by the formation of a branched carbon group by crosslinking (ref. 16).



Gas Evolution

Figure 6 shows the pressure changes inside the vacuum chamber due to gas evolution from the PFPE fluids as a function of time during x-ray irradiation. For all three fluids the pressure at the initial stage of irradiation increased to a maximum and then decreased gradually. The pressure behavior at the initial stage of irradiation can be explained by the accumulation of gaseous products or intermediates in the PFPE liquid phase. The pressure change at the maximum pressure P_{max} is dependent not only on the type of PFPE fluid used but on the fluid amount as well. Figure 7 shows the effect of the initial fluid weight on P_{max}. It was found that gaseous products formed more easily from Fomblin than from Demnum or Krytox. One of the reasons for the large pressure change (P_{max}) occurring from the Fomblin irradiation is the generation of a substantial amount of COF_2 in addition to other low-molecular-weight gaseous products. The amounts of gaseous products from Demnum and Krytox were similar to each other.

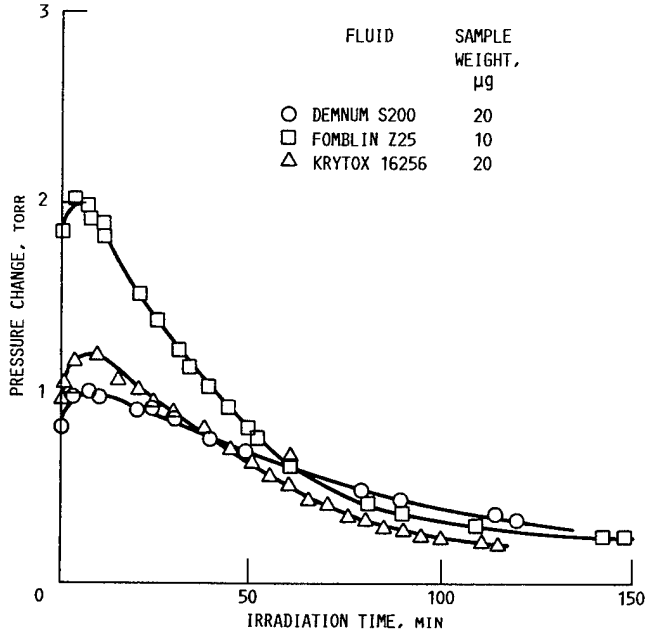


Figure 6.—Pressure change owing to gas evolution.

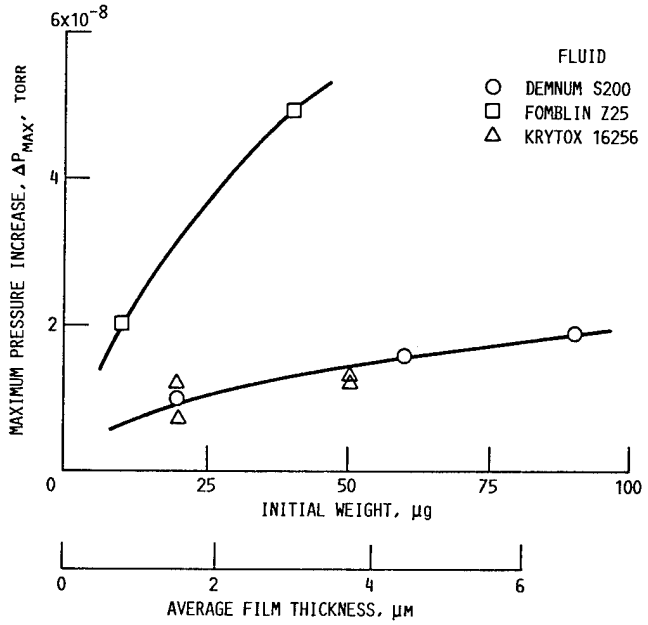


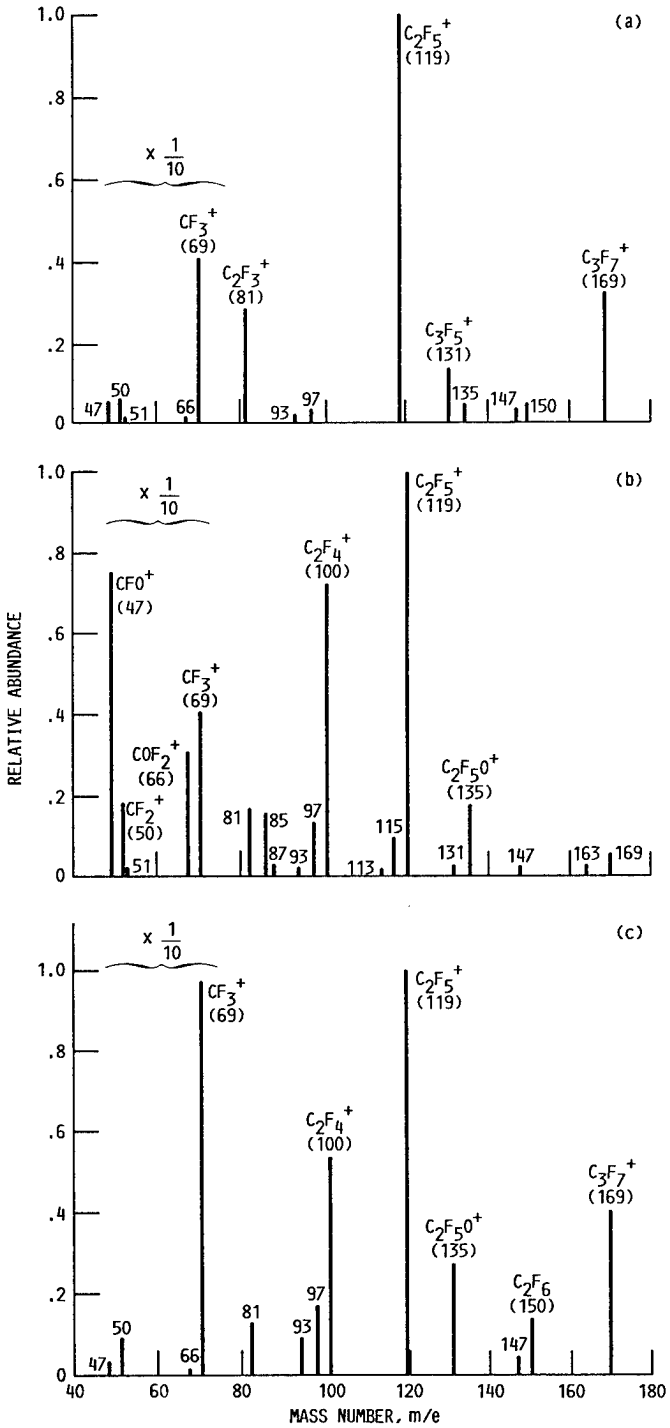
Figure 7.—Effect of sample weight on maximum pressure increase.

Mass Spectra of Gaseous Products

Figure 8 shows the mass spectra of the gaseous products; table IV gives relative values of the principal spectral intensities from the three PFPE fluids. The main peak from Demnum (fig. 8(a)) was CF_3^+; in addition, other fluorocarbons such as $C_2F_4^+$, $C_2F_5^+$, and $C_3F_7^+$ were also detected. A small amount of COF_2 was also formed since fragments of COF^+ and COF_2^+ were detected. The mass spectra of the Krytox and Demnum gas products (fig. 8(c)) were similar except for the higher intensity of CF_3^+ for Krytox. This result was probably due to the presence of the CF_3 pendent groups in Krytox.

The mass spectrum for Fomblin gas products (fig. 8(b)) shows very high intensities of COF^+ and COF_2^+. The former peak was the main fragment of COF_2 gas. We also noted that the $C_3F_7^+$ peak intensity was much lower than those for the Demnum and Krytox fluids.

Figure 9 shows the time dependence of the mass intensities of the gaseous products from the three PFPE fluids during x-ray irradiation. The decreasing intensities of the mass fragments were similar to the total pressure decrease shown in figure 6. Figure 10 shows the time dependence of intensity ratios of gaseous products. The intensity ratios of COF_2^+/CF_3^+ and $C_2F_5^+/CF_3^+$ decreased with time (fig. 10(b)). The high decreasing rate of the C_C carbon atom suggested that COF_2 gas formed readily from the acetal-linked carbon atom (C_C) in Fomblin.



(a) Demnum S200.
(b) Fomblin Z25.
(c) Krytox 16256.

Figure 8.—Mass spectra of gaseous products. Substrate, 440C stainless steel; irradiation time, 5 to 10 min.

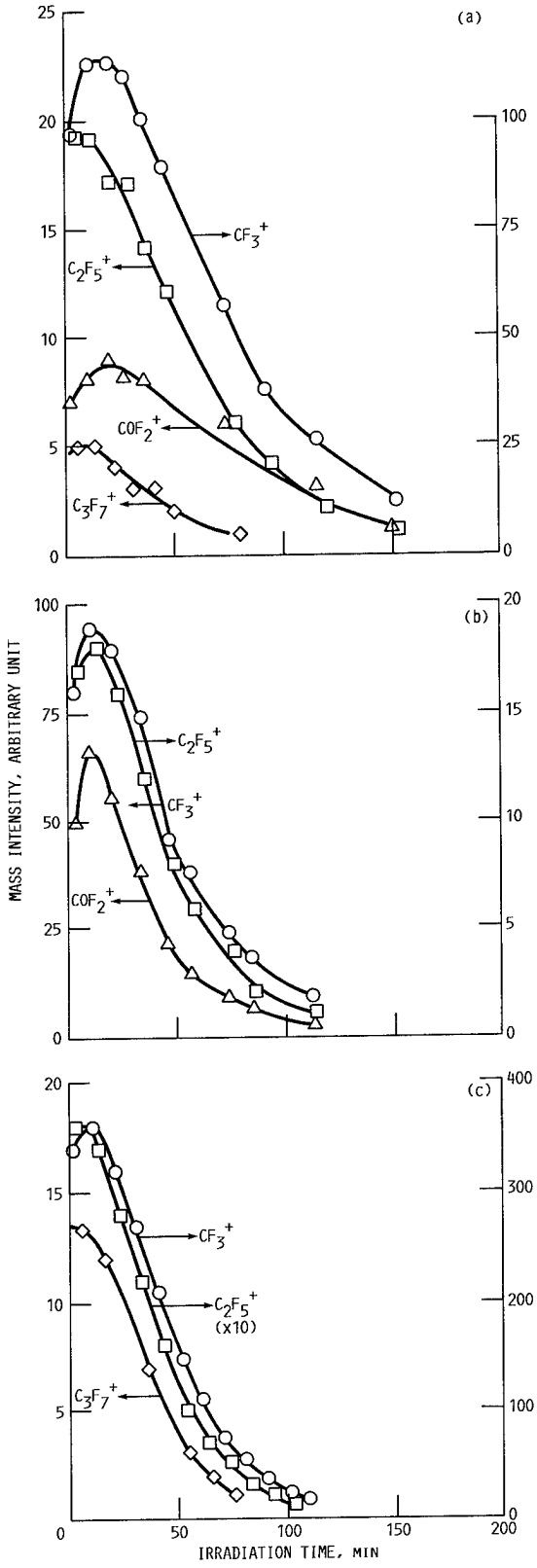
TABLE IV.—COMPARISON OF RELATIVE ABUNDANCE OF GASEOUS PRODUCTS DETECTED BY MASS SPECTROMETRY TAKING $C_2F_5^+$ FRAGMENT PRODUCT (MASS NUMBER, 119) AS 100 PERCENT

Mass number, *m/e*	Fragment	Fluid		
		Demnum S200	Fomblin Z25	Krytox 16256
		Relative abundance, percent		
47	CFO^+	55	740	30
50	CF_2^+	52	180	90
66	CF_2O^+	16	300	8
69	CF_3^+	400	400	950
81	$C_2F_3^+$	28	17	13
85	CF_3O^+	---	15	---
93	$C_3F_3^+$	2	1	9
97	$C_2F_3O^+$	3	13	17
100	$C_2F_4^+$	---	71	52
113	$C_2F_3O_2^+$	---	2	---
119	$C_2F_5^+$	100	100	100
131	$C_3F_5^+$	13	3	---
135	$C_2F_5O^+$	5	16	27
147	$C_3F_5O^+$	4	2	4
150	$C_3F_6^+$	5	---	13
163	$C_2F_5O_2^+$	---	1	---
169	$C_3F_7^+$	32	5	38

Characterization of Liquid Products

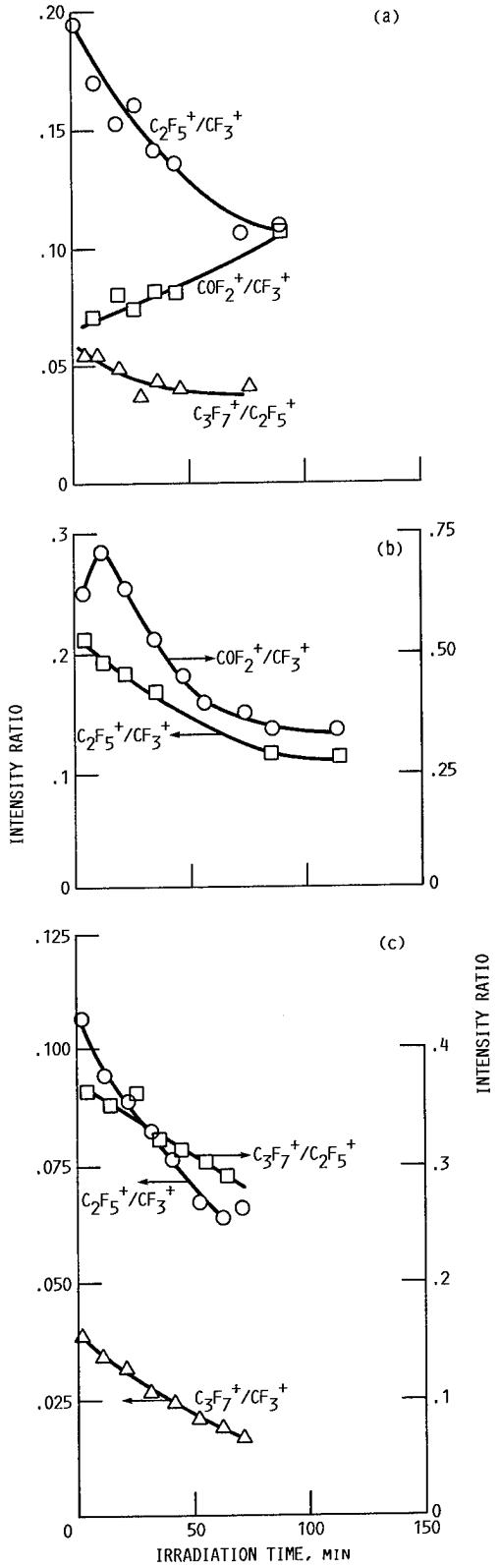
The PFPE fluids became tacky after x-ray irradiation. This suggested that the polymerization or crosslinking of the fluids may have occurred. XPS spectra, as shown in figure 5, also suggested crosslinking of the irradiated liquids. Crosslinking of Krytox (refs. 8 and 9) under high-energy electron irradiation and of polyperfluoroethylene oxide (ref. 12) under γ-ray irradiation has been reported. After a 3-hr x-ray irradiation the PFPE fluids on the metal surfaces were rinsed with 3 ml of TCF solvent. The TCF-soluble products were examined with both FTIR and HPLC; the TCF-insoluble product was analyzed by infrared (IR) emission spectroscopy and XPS.

The FTIR spectrum of the TCF-soluble products from Krytox fluid is shown in figure 11. The spectrum shows the existence of CF_3 and CF_2 groups at 1300 cm^{-1} and a C–O bond at 1100 cm^{-1}. An isolated peak at 980 cm^{-1} is associated with a CF_3 group (ref. 8). The FTIR spectrum of the unused Krytox fluid was identical to figure 11. The FTIR spectra of the TCF-soluble products from Demnum and Fomblin also did not change after irradiation. Pacansky (ref. 8) found that a new band at 1885 cm^{-1} appeared when Krytox was exposed to a 175-kV electron beam. This band indicates carbonyl absorption of an acid fluoride group, which easily converts to a carboxylic acid group upon exposure to moist air. In this study there was no evidence for the formation of a carbonyl group. We concluded from the FTIR spectra that chemical bonds such as C–F and C–O were retained after x-ray irradiation.



(a) Demnum S200.
(b) Fomblin Z25.
(c) Krytox 16256.

Figure 9.—Time dependence of mass intensity. Substrate, 440C stainless steel.



(a) Demnum S200.
(b) Fomblin Z25.
(c) Krytox 16256.

Figure 10.—Time dependence of intensity ratios of gaseous products. Substrate, 440C stainless steel.

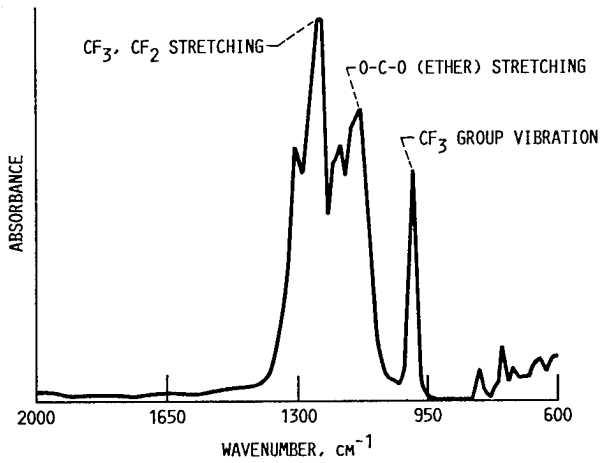
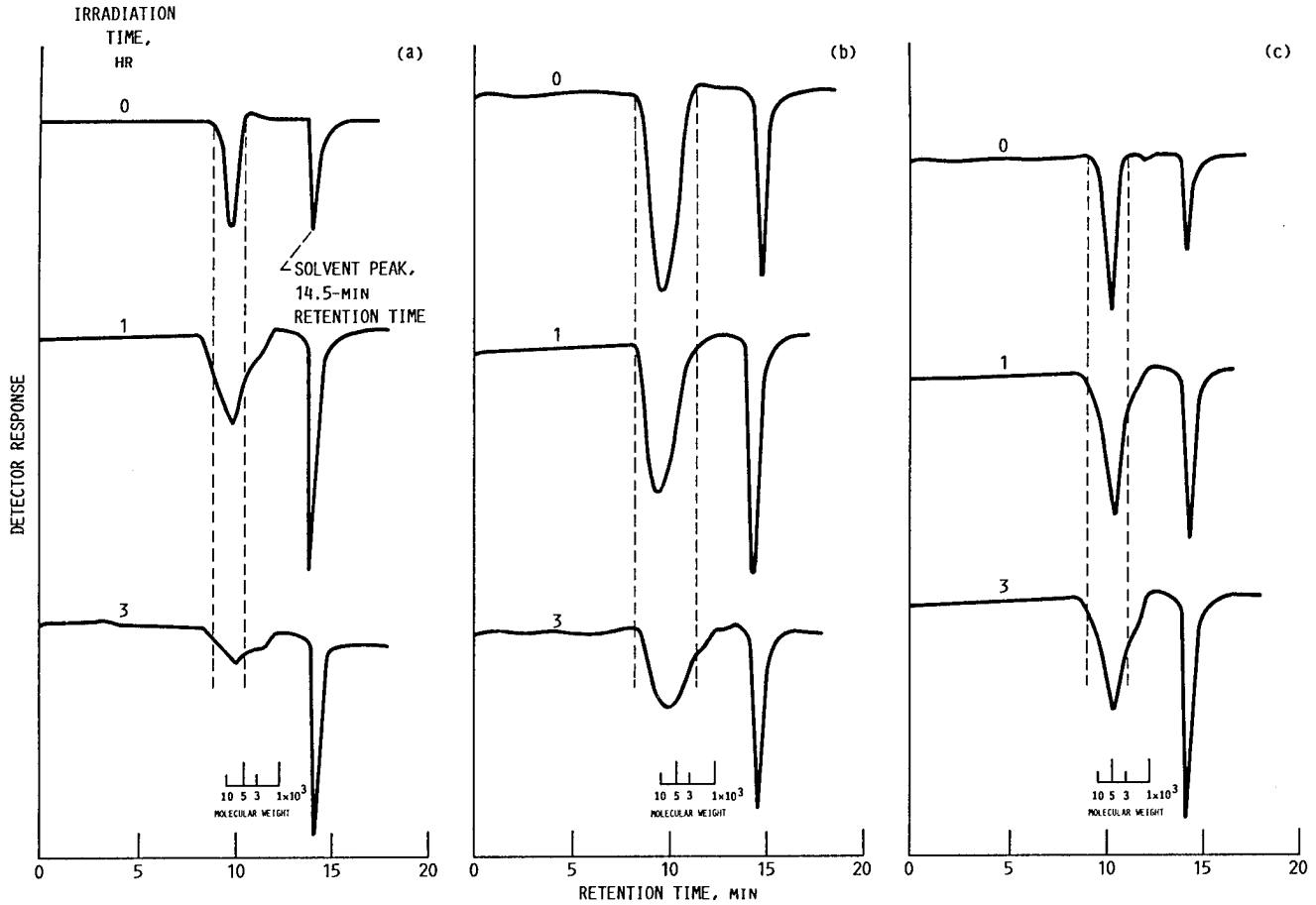


Figure 11.—FTIR spectrum of TCF-soluble matter formed from Krytox 16256.

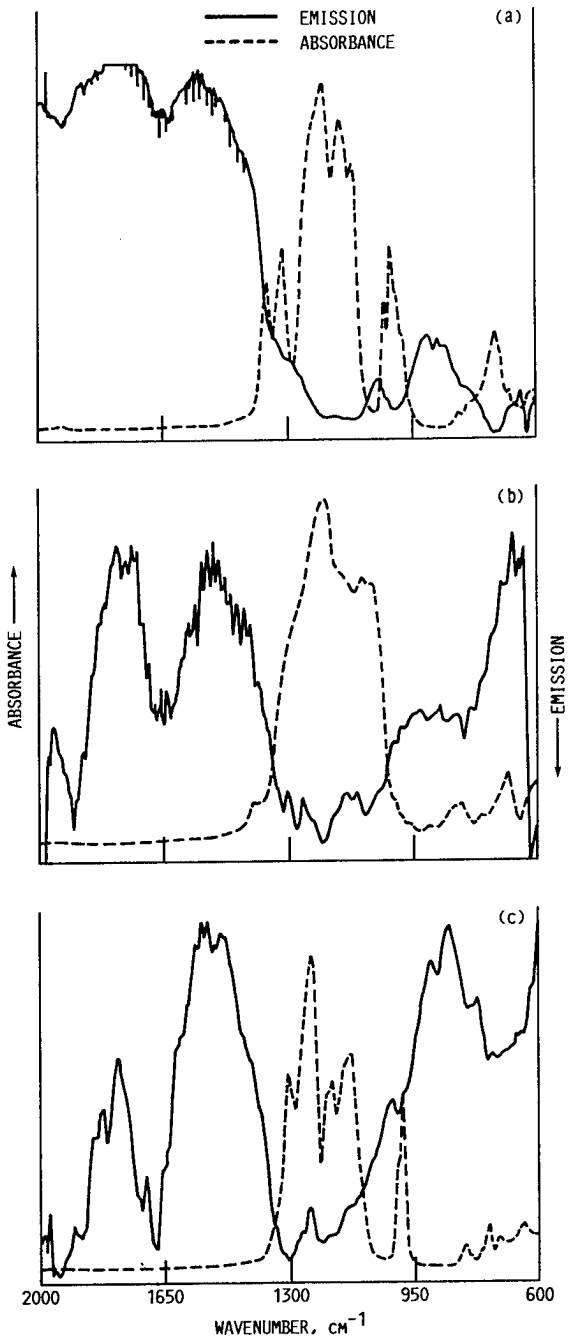
HPLC chromatograms of the TCF-soluble products are shown in figure 12. Since the size exclusion mode was used, the retention times are inversely related to the molecular weight of the samples. The large peak at 14.5 min is a characteristic solvent peak. As can be seen from figure 12 the peaks from the unused PFPE fluids are relatively sharp, indicating a narrow molecular weight distribution range. The PFPE peaks of all three fluids used became broader after x-ray irradiation. In particular, the peaks shifted to the lower molecular weight range with the appearance of a shoulder; this indicates that degradation of the fluids, induced by the x-ray irradiation, resulted in the formation of lower molecular weight liquid products. In addition to the formation of lower molecular weight products, the HPLC chromatograms of Demnum (fig. 12(a)) and Krytox (fig. 12(c)) reveal the presence of higher molecular weight products. These results indicate that polymerization (crosslinking) occurred during the x-ray irradiation of Demnum and Krytox. The Fomblin chromatograms (fig. 12(b)) do not show the presence of higher molecular weight products.

The TCF-insoluble material was analyzed by FTIR emission spectroscopy (fig. 13). This technique involves heating the sample to a temperature (in this case 175 °C) where infrared emission from the sample can be analyzed by an infrared spectrometer. In addition to the FTIR emission spectra,



(a) Demnum S200.
(b) Fomblin Z25.
(c) Krytox 16256.

Figure 12.—HPLC chromatograms of TCF-soluble material.



(a) Demnum S200.
(b) Fomblin Z25.
(c) Krytox 16256.

Figure 13.—FTIR emission spectrum of TCF-insoluble materials.

figure 13 shows the corresponding FTIR transmission spectra (absorbance vs wave number) of the unused PFPE fluids. (Notice that an emission trough corresponds to an absorbance peak.) The FTIR emission spectra of all three TCF-insoluble products reveal a broad emission of C–F and C–O bonds in the range 1350 to 950 cm^{-1}. XPS spectra also reveal that the TCF-insoluble material contained C–F and C–O bonds and that the intensity ratio of O_{1s}/C_{1s} was lower than that of the original PFPE fluid. As shown in figure 9(b) the amount of COF_2 in the gaseous products from Fomblin decreased with irradiation time, suggesting a smaller amount of C–O bonding in the TCF-insoluble material than in the unused fluid. We concluded from these results that the TCF-insoluble material was basically fluoroalkyl ethers but that their oxygen content was lower than that in the unused fluids.

Kinetic Considerations

The pressure change ΔP detected in the vacuum chamber corresponds to the rate at which gaseous products are formed from the PFPE fluids. The initial pressure P in the vacuum chamber was determined by a mass balance between the gas desorbed from the chamber walls (rate, r_d, mole/sec) and the pumping speed F at the vacuum chamber outlet. This mass balance can be written as

$$RTr_d = FP \tag{1}$$

where R and T are the gas constant and the absolute temperature, and the product FP is an effective pumping speed. When the gaseous products evolve from the PFPE fluid at the rate of r_g (mole/sec) and the pressure increases to P', the mass balance becomes

$$RTr_d + RTr_g = FP' \tag{2}$$

From equations (1) and (2) the evolution rate can be estimated from the pressure change ΔP,

$$r_g = \frac{F\,\Delta P}{RT} \tag{3}$$

At the initial stage of x-ray irradiation the pressure increased readily to a maximum and then decreased exponentially. This behavior can be explained by the accumulation of intermediate or gaseous products in the PFPE liquid phase. After reaching equilibrium, the evolution rate is proportional to the production rate in the liquid phase.

If the production rate is proportional to the rate of destruction of the parent molecules, then a first-order reaction equation can be written as

$$\Delta P = -k_1 \frac{dN}{dt} \tag{4}$$

where N is the amount of the irradiated PFPE fluid. Since the x-ray flux is constant,

$$\frac{dN}{dt} = -kN \tag{5}$$

This leads to

$$N = N_0 \exp(-kt) \tag{6}$$

and consequently

$$\Delta P = \Delta P_0 \exp(-kt) \tag{7}$$

or

$$\ln\left(\frac{\Delta P}{\Delta P_0}\right) = -kt \tag{8}$$

If we use the maximum pressure change ΔP_{max} as an initial pressure increase ΔP_0, equation (8) becomes

$$\ln\left(\frac{\Delta P}{\Delta P_{max}}\right) = -kt \tag{9}$$

The data from figure 6 were replotted according to equation (9), and the results are shown in figure 14. Linear relationships were obtained for all three PFPE fluids. Pacansky (refs. 8 and 9) also obtained a linear relationship for the first-order reaction of Krytox under high-energy electron beam irradiation. The first-order rate constants (independent of the fluid's initial weight) for both 440C steel and gold substrates are listed in table V. The rate constant for Demnum is almost half that of Fomblin and Krytox. There is no substrate effect on the decomposition of the PFPE fluids, which means that the secondary electrons emitted from the substrates by the x rays did not affect the decomposition reaction.

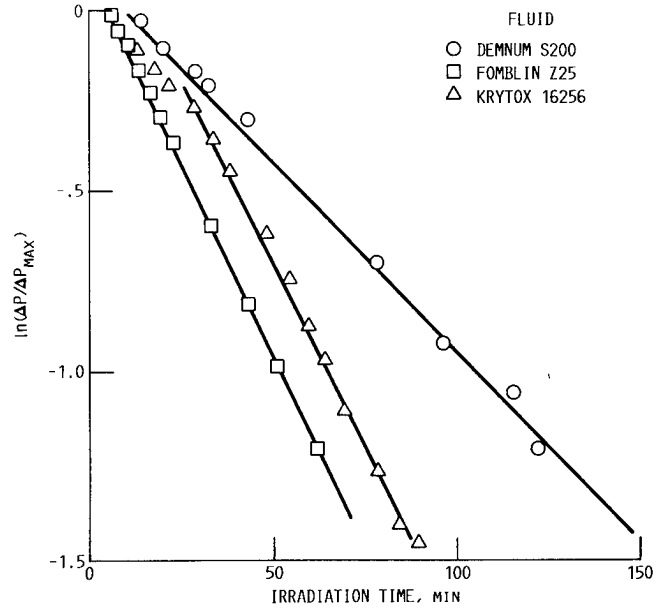


Figure 14.—Semilogarithmic relation of pressure change with irradiation time. Substrate, 440C stainless steel.

TABLE V.—FIRST-ORDER RATE CONSTANTS

Substrate	Fluid		
	Demnum S200	Fomblin Z25	Krytox 16256
	Rate constant, min^{-1}		
440C	1.0×10^{-2}	2.2×10^{-2}	2.1×10^{-2}
Gold	1.1	1.8	1.9

Mass Balance

There are three types of decomposition products: gaseous, TCF soluble, and TCF insoluble. From table II it can be seen that the percentage amounts of the three types of products were about the same for Fomblin and Krytox, whereas the percentage amounts for Demnum differed substantially. Notice that the amount of TCF-soluble products from Demnum was lower than from the other fluids and that the amount of its TCF-insoluble products was very high in relation to the other fluids. The ratio of TCF-insoluble products to gaseous products for Demnum was more than three times that for Fomblin. Since the experimental evidence suggested that the main component of the TCF-insoluble product could be crosslinked polymers, the mass balance data indicated that crosslinking occurred more readily for Demnum than for the other fluids.

Chemical Reactions of PFPE Fluids Under X-Ray Irradiation

It has been reported that fluorine radicals are formed when fluorinated carbon molecules are exposed to high-energy photons such as x rays and γ rays (ref. 24). These very reactive fluorine radicals can attack the main carbon molecular chain, resulting in main chain scission—fluorocarbon radicals have been detected by electron paramagnetic resonance (EPR) (ref. 12). The fluorocarbon radicals are as follows:

(1) $-OCF_2\dot{C}FO-$
(2) $-OCF_2CF_2O-$
(3) $-OCF_2CF_2-$
(4) $-CF_2\dot{C}FCF_2-$
(5) $-OCF_2\dot{C}FCF_2O-$

Different fluorocarbon radicals have different stabilities; for example, chain radical 1 is more stable than radicals 2 and 3 (ref. 12). For polytetrafluoroethylene (PTFE) it has been reported that the chain radical 4 is the most stable radical (ref. 25).

The experimental results indicate that fluorine radicals were formed during x-ray irradiation of the PFPE fluids, which then caused main chain scission. For Fomblin the main chain scission resulted in a radical that propagated through the acetal linkages, generating large quantities of COF_2 gas in addition to lower molecular weight products as follows:

(1) $CF_3(OCF_2CF_2)_p-(OCF_2)_q-OCF_3 \rightarrow F\cdot$ Under x-ray irradiation fluorine radicals are formed from Fomblin.

(2) $F\cdot + CF_3(OCF_2CF_2)_p-(OCF_2)_q-OCF_3 \rightarrow CF_3(OCF_2CF_2)_pCF_3 + \cdot OCF_2OCF_2OCF_2-$

Very reactive fluoride radicals will then attack Fomblin, generating long-chain-containing radicals.

(3) $\cdot OCF_2OCF_2OCF_2- \rightarrow COF_2 + \cdot OCF_2OCF_2- \rightarrow COF_2 + \cdot OCF_2-$

An unzipping mechanism occurs, generating COF_2. For Demnum a stable radical (radical 5) was probably formed. This radical resembles the stable chain radical 4 of PTFE. Because of their stability these radicals can crosslink with other radicals rather than decompose.

For Krytox if a fluorine radical attacks a pendent group ($-CF_3$), tetrafluorocarbon could be formed. This is reflected in the high intensity of CF_3^+ ($m/e = 69$) in the gaseous products from the Krytox fluid.

Conclusions

Three different commercial perfluoroalkyl polyethers (PFPE)—Demnum S200, Fomblin Z25, and Krytox 16256—were irradiated by x rays under ultra-high-vacuum conditions. The following conclusions were reached:

1. X-ray emission spectroscopy (XPS) measurements distinguished different bonding carbon atoms for the PFPE fluids from the chemical shift of the C_{1s} binding energies.

2. All three PFPE fluids decomposed under x-ray irradiation, generating gaseous products such as COF_2.

3. High-pressure liquid chromatography (HPLC) measurements revealed the formation of lower-molecular-weight liquid products for all three decomposed PFPE fluids. HPLC also revealed that higher-molecular-weight liquid products formed from the decomposed Demnum S200 and Krytox 16256. A TCF-insoluble material was formed from the decomposition of all three PFPE fluids. The experimental results indicated the material to be crosslinked polymers.

4. Fomblin Z25 and Krytox 16256 decomposition rates, based on gas evolution, were approximately twice that of Demnum S200. PFPE decomposition and the resulting reaction products are dependent on the particular molecular structure of the PFPE fluid.

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National Aeronautics and Space Administration
Cleveland, Ohio, January 9, 1989

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