

Electron Beam Irradiation of Polyperfluoroethers: Experimental Analysis of Main-Chain Degradation

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The electron beam irradiation of polyperfluorinated ethers are investigated. Main-chain scissioning is the predominant effect, inducing a weight loss in the bulk materials caused by evolution of small gas molecules such as COF_2 and CF_4 . The G values for main-chain scissioning, mass loss, and gas evolution are determined from experiment and correlated to structural differences. From these results we conclude that unbranched polyperfluoroethers degrade more efficiently and produce more COF_2 than branched polymers when the monomer units contain $-\text{CF}_2-\text{CF}_2-\text{O}-$ and/or $-\text{CF}_2\text{O}-$ in the main chain. With a pendant perfluoromethyl, $-\text{CF}(\text{CF}_3)-\text{CF}_2-\text{O}-$, or an additional carbon atom in the main-chain monomer unit, $-\text{CF}_2-\text{CF}_2-\text{CF}_2-\text{O}-$, the electron beam induced degradation is comparatively less efficient; in the branched polymers, CF_4 evolution competes with COF_2 formation.

Introduction

Polyperfluoroethers are viscous liquids with exceptional chemical and physical properties, consequently, they have extensive applications in industry as lubricants,¹ dielectric fluids,^{2,3} diffusion pump oils,⁴⁻⁶ and as blood substitutes.⁷ More recently, they have been considered for use in drastic environments in aerospace engines and satellite instruments.⁸ Because of their widespread applications, an understanding of degradation mechanisms, both thermally and by high-energy radiation, is required and indeed has been the subject of numerous papers. For example, polyperfluoroethers are widely used in the magnetic recording industry as disk lubricants to provide the desired tribological characteristics between disk and head. Frictional problems during the starting and stopping of the rotary disk causes depletion of the lubricant, consequently, an understanding of their degradation has been an area of active research. In particular, studies on the thermal degradation of a variety of polyperfluoroethers in the presence of metals, metal oxides, and Lewis acids^{1,9} have shown that the stable products ultimately formed are C_3F_6 , CF_3COF , and COF_2 .

The initial interest in the radiation chemistry of polyperfluoroethers was a result of a search for pump oils that did not leave a residue on the walls of a vacuum system when exposed to ionizing radiation. Because they degrade when exposed to ionizing radiation, these materials became attractive for pump fluids in vacuum systems where ionizing radiation was present such as in electron micro-

scopes and plasma processing equipment. Consequently, the effect of radiation on polyperfluoroethers have also attracted a number of studies. Thus, γ -radiolysis on poly(perfluoroethylene oxide) revealed main-chain scission as the primary effect with COF_2 as the main degradation product.¹⁰ Electron beam irradiation studies on a variety of polyperfluoroethers at room temperature under an inert atmosphere have provided similar results, with main-chain scission and mass loss as being the predominant effects suffered by the liquids.^{11,12} These experiments revealed again that the primary product formed upon chain scissioning was COF_2 , although CF_4 was also formed from branched perfluoroethers such as poly(perfluoropropylene oxide). Evolution of CF_4 from the branched polyperfluoroethers is consistent with recent theoretical calculations which predict that the tertiary CF bonds are longer and weaker than the CF bonds in the unbranched perfluoroethers.¹³ In contradistinction, electron beam irradiation of poly(perfluoropropylene oxide) under vacuum¹⁴ resulted in gelation of the liquid, despite observation of mass loss as previously described for the electron beam irradiation of polyperfluoroethers under atmospheric conditions. The proposed mechanism to explain the etching and gelation within the vacuum system was based upon a vacuum-assisted mass loss that depended on the pumping action of the vacuum. In essence, the removal of low molecular weight material by the vacuum pump relaxed the condition for gel formation and permitted it even when the probability for scissioning per monomer per unit dose was 4 times greater than the probability that a monomer unit had an active site for cross-linking per unit dose. Thus, despite main-chain scissioning, the viscosity of the liquid increased instead of decreasing.

In this report we continue our studies on the mechanism(s) of polyperfluoroether degradation induced by

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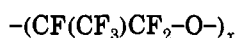
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electron beams. The electron beam is a convenient tool by which main-chain scissioning of the polyperfluorinated ethers is accomplished, after which the degradation of the polymer is readily monitored. Here, a quantitative analysis for the G values for main-chain degradation as a function of temperature are determined using both room- and low-temperature infrared spectroscopy, and these values are compared to G values derived from viscometric measurements. The structures of the polyperfluoroethers used in this study are as follows:

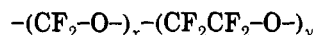
poly(perfluoro- n -propylene oxide), PPFNPO:



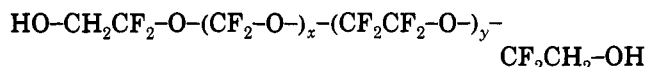
poly(perfluoropropylene oxide), PPFPO:



poly(perfluoromethyleneethylene oxide), PPFMEO:



a PPFMEO copolymer with $-\text{OH}$ end groups, poly(perfluoromethyleneethylene oxide), PPFMEO-OH:



poly(perfluoromethylenepropylene oxide), PPFMPO:



The x to y ratios for the structures illustrated above are provided in the experimental section.

Experimental Section

Materials. All of the polyperfluoroethers were obtained from commercial sources and used directly with no further purification. PPFPO was obtained from E.I. Du Pont De Nemours (Delaware) under the tradename Krytox No. 16256; the number average molecular weight, $M_n = 8500$, and the density $\rho = 1.951 \text{ g/cm}^3$. PPFMPO and PPFMEO were obtained from Montedison USA, Inc., under the trademark Fomblin Fluids, YR ($y/x = 25$, $M_n = 6200$, $M_w = 8600$, $\rho = 1.915 \text{ g/cm}^3$) and Z-15 ($y/x = 0.7$, $M_n = 7200$, $M_w = 13400$, $\rho = 1.845 \text{ g/cm}^3$), respectively. PPFNPO was obtained from Daikin Inc. (Japan) under the tradename DEM-NUMS-100 ($M_n = 5600$, $\rho = 1.878 \text{ g/cm}^3$) and PPFMEO-OH was obtained from Austimont under the tradename ZDOL-2000 ($y/x = 0.7$, $M_n = 2200$, $\rho = 1.750 \text{ g/cm}^3$). As shown in the chemical structures above, PPFMEO-OH differs from the other perfluorinated lubricants by the $-\text{CH}_2\text{OH}$ end groups.

Electron Beam Exposure and Viscosity Measurements. For measuring changes in the viscosity of the polyperfluoroethers, bulk quantities ($\approx 2 \text{ mL}$ or more) of samples were required, and for these purposes, electron beam exposures of the polyperfluoroether samples were achieved using a CB 150 Electron Processor (Energy Sciences, Inc., Woburn, MA) which allowed exposures of the samples to 175-kV electron beam in an atmosphere of nitrogen. A description of the electron beam exposure tools has been given elsewhere.¹¹

Dosimetry. After corrections of the initial 175-kV electron beam for energy loss to the various windows and inert atmosphere that occur between the electron beam gun and the sample, the energy of the electrons incident on the sample is 102 keV. This places restrictions upon the maximum depth the electrons may

penetrate into the liquid, given by the empirical Grün relation:¹⁵

$$R_g = \frac{0.0459}{\rho} E_0^{1.75} \quad (1)$$

where R_g is the Grün range in micrometers, i.e., the maximum electron beam penetration depth perpendicular to the film, ρ is the density of the film in g/cm^3 , and E_0 is the energy of the electron in kiloelectronvolts incident on the film. For densities of $\approx 1.9 \text{ g/cm}^3$, $R_g \approx 80 \text{ }\mu\text{m}$.

The absorbed dose was measured using the aminotriphenylmethane dye-doped nylon plastic films that give rise to an absorption at 510 nm when exposed to high-energy radiation. The films, obtained from Far West Technology Inc.,¹⁶ have a thickness of 50 μm ($R_g = 132 \text{ }\mu\text{m}$ for 102-keV incident electrons on the FWT film). The absorption at 510 and 600 nm has been studied and calibrated against absorbed dose by McLaughlin¹⁷ and Humphreys.¹⁸ The absorbed dose was found by running a dye-containing film in tandem with the sample tray, as described in detail previously.¹¹

Samples of irradiated material in sufficient quantities for viscosity measurements were prepared using a tray made from an aluminum block into which a well, 3 mil deep ($\approx 75 \text{ }\mu\text{m}$) and of area equal to 160 cm^2 was machined. The viscous liquid was placed in the tray to flood the well and the sample thickness was brought to 3 mil by pulling a straight-edge across the sides of the well. After the sample was exposed to the 102-kV electron beam, it was collected and stored under nitrogen in capped plastic bottles for analysis. The exposed samples were found to react with glass but were stable in plastic. Infrared spectra were measured on a Perkin-Elmer Model 983 IR spectrometer equipped with a Model 3600 Data Station. Samples were injected under a nitrogen blanket into KBr liquid cells with a path length of 0.0029 cm. Viscosities were measured with a Brookfield LVTDV-IICP cone and plate viscometer with a 3.0° cone angle. Material transfers to the viscometer cup were performed entirely under nitrogen using a syringe to deliver the liquids from the sealed plastic containers.

Electron Beam Exposure under Vacuum. The apparatus used for 25-kV electron beam exposure of the samples under vacuum and at low temperatures has previously been described in detail.¹⁴ The electron beam induced changes in the samples were followed using IR specular reflection spectroscopy, using a Perkin-Elmer 580 IR spectrometer equipped with a Model 3600 data station. For these purposes, the polyperfluoroethers were spin coated onto Au substrates to thicknesses of 1.0 μm , well below the Grün range R_g of 7 μm , to ensure complete electron beam penetration into the samples. The reflectivity measurements were made in situ by rotation of the sample from the electron beam to the IR beam. All measurements were made with the incident IR beam at 25° from normal to the sample plane.

Electron beam exposures within a vacuum system facilitate the measurement of the current density I (A/cm^2) of the incident beam, using a Faraday cup. The product of I and time t gives q , the incident charge density (C/cm^2) administered to a sample. The incident charge density q is used to determine Q , the total charge density that the thin film experiences from the incident beam and that fraction of the beam backscattered from the substrate. The charge density is defined as

$$Q = (1 + \eta)q \quad (2)$$

where η is the backscattering coefficient of the substrate. All of our experimental results are reported in terms of Q because it is a more precise measure of the number of electrons traversing a thin film.

The absorbed dose, in units of megarad, was determined by use of the following expression:

$$D = E_a/gk \quad (3)$$

where g is the weight of material in grams into which the energy

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E_a (electronvolts) was deposited, and $k = 6.24 \times 10^{19}$ is the factor used to convert from eV/g to Mrad (1 Mrad = 6.24×10^{19} eV/g). For the perfluorinated ether film and film thicknesses studied herein, we have determined that for $Q = 1.0 \mu\text{C}/\text{cm}^2$, $D \approx 2.5$ Mrad.

Gas Evolution from Electron Beam Exposure at 1 Atm.

The gases produced from the electron beam exposure of the polyperfluoroethers were collected in a stainless steel chamber with KBr windows to allow infrared interrogation. The electron beam source used was the 175-kV electron beam apparatus described earlier, and complete details of the gas cell and methodology have been disclosed in an earlier publication.¹²

During the course of the experiments, XPS measurements became necessary in conjunction with the gas evolution measurements, as will be discussed in detail later. XPS measurements on the Ti windows of the gas cell before and after irradiation of the polyperfluoroethers were made on a Surface Sciences SSX 100 Model 5 using an Al K α source. Data were typically acquired with a 50-eV pass energy and a monochromatic X-ray spot size of 600 μm . Pressure in the sample chamber was typically 1×10^{-9} Torr, and the spectral resolution was 1 eV.

Curve fitting to determine binding energies and relative intensities were performed using an iterative least-squares computer program using a combination of Gaussian and Lorentzian lineshapes to best fit the experimental envelope. All binding energies were referenced to the lowest energy C_{1s} line at 284.6 eV (aromatic CC) as is standard practice for (organic) insulating materials.¹⁹ The magnitude of the charge correction was 0.1 eV.

Results and Discussion

A number of different exposures are performed on polyperfluorinated ethers in order to understand the response of the materials to a high-energy electron beam. In our opinion, the most effective means by which the data may be discussed initially is to present a model that fits the experimental observations. Perfluorinated materials typically degrade when exposed to high energy radiation; perfluorinated *ethers* are no exception to this observation. Their primary mode is also degradation, but when a main chain is ruptured, several monomeric units appear to thermally (and/or by radiation) cleave off from the chain. The perfluorinated ethers used in this study have a relatively low molecular weight as far as polymeric materials are concerned and, in addition, have a relatively high vapor pressure for their respective molecular weights. The predominance of main-chain scission, some unzipping, together with the high vapor pressures collectively produce interesting physical and chemical changes upon irradiation.

When polyperfluoroethers are exposed to high-energy radiation, chains are scissioned, thus converting an initially narrow molecular weight distribution to a random one characterized by low molecular weight fragments; thus as the vapor pressure is continually increased, material is vaporized and accompanied by a continual loss of material. Hence, exposures under vacuum exhibit an accelerated weight loss compared to those under atmospheric pressures of inert gas. Concomitantly, after main chain scission some thermal unzipping of monomeric units take place as shown by measurement of G values for formation of gaseous products.

main-chain scission in bulk liquid



bulk liquid loses mass



gases evolved from bulk liquid



-CFO end groups formed in bulk liquid

In this report we combine G value measurements for main-chain scission, mass loss in vacuum and under atmospheric pressures, and formation of gases to support the above model. All of the G values are then compared and correlated with what is understood about the degradation of these materials. The G value is defined as the number of molecules formed or destroyed per 100 eV of absorbed energy and provides a sensitivity scale for radiation-induced damage among various materials.

G Value for Main Chain Scission: Changes in Viscosity. Figure 1a shows the changes in viscosity as a function of absorbed dose for PPFPO, PPFMPO, and PPFMEO. As chains are statistically cleaved, chain length is shortened and viscosity drops. It is not surprising that the largest changes in viscosity occur at the lower dose; it is interesting, however, that the viscosity decrease tails off so rapidly with absorbed dose. (As will be discussed in the next section, when irradiated, small fragments cleave off from the main chain and enter the vapor phase which, if otherwise remained in the bulk liquid, would presumably act to further reduce the viscosity of the liquid. To test this hypothesis, a sample of PPFMPO was irradiated under nitrogen to 111 Mrad and divided into two portions thereafter. One portion was heated in a nitrogen blanket for 20 min at 100 °C to stimulate further vaporization of the smaller fragments out of the liquid film. The second portion was left under a nitrogen blanket at ambient temperatures. No hydrolysis of the acid fluoride groups was evident by infrared for either sample; thus, their viscosities were measured. The viscosity of the second portion was 1640 cps; however, the annealing treatment increased the viscosity of the first portion to 1970 cps, thereby suggesting that small effluents have indeed diffused out of the liquid and, conversely if left in the liquid, may have acted to reduce viscosity.)

The viscosity data allows an evaluation for the number of molecules formed or destroyed per unit energy, i.e., the G value. In a useful form, the G value may be related to changes in the number average molecular weight, M_n , by

$$\frac{1}{M_n} = \frac{1}{M_n^i} + \frac{GD}{100N_A} \quad (4)$$

where M_n^i and M_n are the number average molecular weights initially and after some absorbed dose, D , and N_A is Avogadro's constant. Thus a plot of $1/M_n$ versus D yields G . Here G is the overall G value, i.e., $G = G(s) - G(x)$, whereby $G(s)$ is the G value for scissioning, and $G(x)$ is the G value for cross-linking. Since polyperfluoroethers subjected to electron beam irradiation at room temperature and 1 atm undergo chain scissioning, $G(x) \approx 0$ and $G = G(s)$. It remains to relate the changes in viscosity as a

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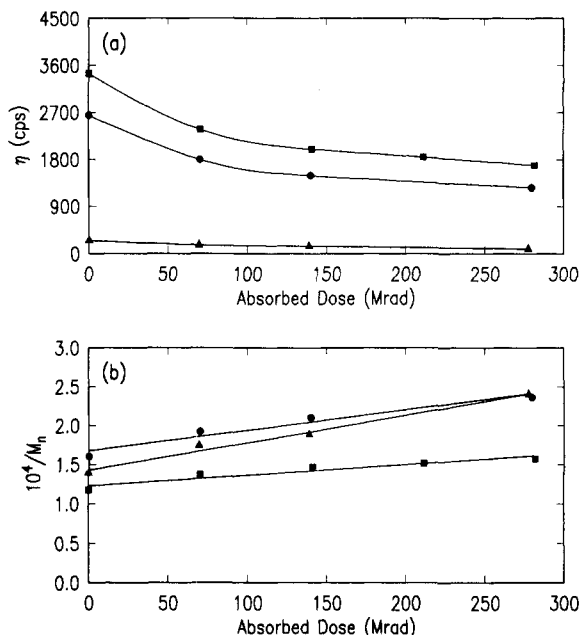


Figure 1. (a) Changes in viscosity of polyperfluoroethers as a function of absorbed dose. (b) Changes in number average molecular weight as a function of absorbed dose. PPFPO ■; PPFMPO ●; PPFMED ▲.

Table I. *G* Values for Main-Chain Scission at *T* = 298 K

polyperfluoroether	viscosity data	thin films (IR) ^a	bulk (IR) ^a
PPFMEO	0.3	0.8	0.8
PPFMPO	0.4	1.7	0.7
PPFPO	0.5	0.7	0.8

^a Divided by 2 (two -CFO end groups per chain).

function of absorbed dose to one of M_n versus dose. The following relationships²⁰ are known for PPFPO, PPFMPO, and PPFMEO before electron beam exposure:

$$\text{PPFPO: } \eta(\text{cps}) = 4.58 \times 10^{-7} \rho M_n^{2.439} \quad (5)$$

where $\rho = 1.951 \text{ g/cm}^3$;

$$\text{PPFMPO: } \eta(\text{cps}) = 1.44 \times 10^{-5} M_w^{2.1} \quad (6)$$

$$\text{PPFMEO: } \eta(\text{cps}) = 1.012 \times 10^{-5} M_w^{1.791} \quad (7)$$

Note that for PPFPO, the viscosity η is related directly to M_n and thus facilitates determination of *G*. In these experiments, only the initial values for the density ρ are known; however, if the *G* value is calculated from the initial slopes shown in Figure 1a at small doses, a reasonable estimate for *G* may be possible. In eqs 6 and 7, the viscosity η is related to M_w and thus, knowledge of the polydispersity index M_w/M_n as a function of dose is required to evaluate M_n . Since the polydispersity index is known²⁰ only initially, we have used this value to allow an estimate for the *G* value taken at the early stages of the irradiation. Under these conditions, using $M_w/M_n = 1.38$ for PPFMPO and 1.87 for PPFMEO, a plot of $1/M_n$ versus absorbed dose is shown in Figure 1b. The *G* values obtained from a least-squares fit of the data are 0.27, 0.44, and 0.49 for PPFPO, PPFMPO, and PPFMEO, respectively, as summarized in Table I. The relative trend in the *G* values tells us that PPFMEO suffers the most electron beam

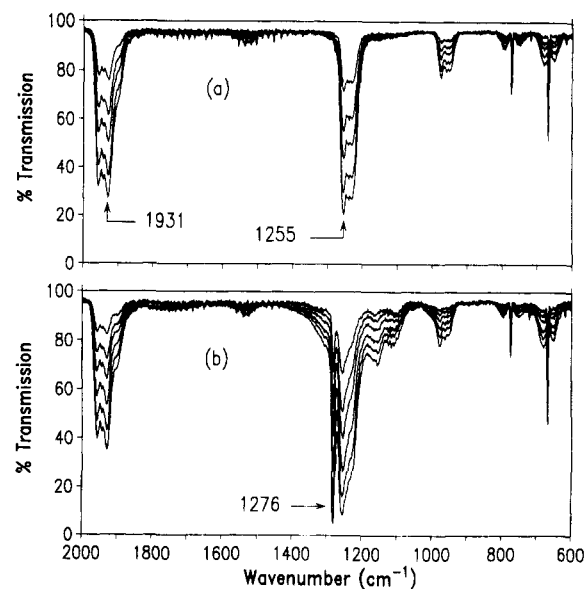


Figure 2. Gas evolution from the 102-kV electron beam irradiation of (a) PPFMEO and (b) PPFMPO at room temperature, 1 atm of argon. (a): 17.8, 35.5, 53.3, 82.9, and 94.8 Mrad. (b): 18.5, 37.0, 55.6, 86.4, and 142.0 Mrad. In (a) and (b), the absorption bands increase with increasing dose.

induced damage, followed by PPFMPO then PPFPO. Structurally, the polymer with the unbranched $-\text{CF}_2\text{CF}_2\text{O}-$ and $-\text{CF}_2\text{O}-$ monomer units scission more efficiently than those with the branched $-\text{CF}(\text{CF}_3)\text{CF}_2\text{O}-$ monomer units.

***G* Value for Gas Evolution from the Bulk Liquids at Atmospheric Pressures.** The electron beam irradiation of the liquid polyperfluoroethers PPFPO, PPFMPO, PPFMEO, PPFMEO-OH, and PPFNPO undergo main-chain scission to produce gases that may be collected in a gas cell designed for interrogation via infrared spectroscopy. COF_2 , CF_4 , and CF_3CFO have been identified by comparison with authentic gases. As an illustrative example, evolution in the gas phase from the electron beam irradiation of PPFMEO and PPFMPO are shown in Figure 2 as a function of absorbed dose. PPFMEO is unbranched with $-\text{CF}_2\text{CF}_2\text{O}-$ and $-\text{CF}_2\text{O}-$ monomer units, while PPFMPO contains primarily the branched CF_3 pendant group in its monomer unit, $-\text{CF}(\text{CF}_3)\text{CF}_2\text{O}-$. As seen in Figure 2a, COF_2 is identified by its characteristic stretching vibrations at 1957, 1931 cm^{-1} ($\text{C}=\text{O}$) and at 1255, 1232 cm^{-1} ($\text{C}-\text{F}$), confirmed via a gas-phase IR spectrum of authentic COF_2 under identical conditions.¹² The absorption band at 668 cm^{-1} is characteristic of carbon dioxide. The same absorption bands are evident in Figure 2b from PPFMPO also; however, there are several other bands not readily observed in Figure 2a. The band centered at 1276 cm^{-1} is unequivocally identified as the $\text{C}-\text{F}$ stretching vibration attributable to CF_4 . In addition, there is a rather broad absorption between 1050 and 1400 cm^{-1} with band centers at 1115 and 1154 cm^{-1} , and a small absorption between 1490 and 1600 cm^{-1} , centered at $\approx 1530 \text{ cm}^{-1}$. We have not been able to unequivocally assign these bands, although absorption in the 1050–1400- cm^{-1} region is characteristic of various $\text{C}-\text{F}$ and $-\text{CF}_2-\text{O}-$ or $>\text{CF}-\text{O}-$ vibrational modes.¹³

A comparison of the *G* values for formation of the various gases is summarized in Table II. To calculate the *G* values a plot of the changes in the integrated absorbance ($\int \log(T_0/T) d\nu$) of an absorption band versus absorbed dose is related to changes in the number of molecules formed or destroyed

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Table II. Summary of G Values for Gas Evolution^a

polyperfluoroether	COF ₂	CF ₄	CF ₃ CFO	total
PPFMEO	7.7 ± 0.5	0.35 ± 0.07		8.1
PPFMEO-OH	6.2 ± 0.3			6.2
PPFMPO	1.7 ± 0.1	1.1 ± 0.2	≈ 0.3	3.1
PPFPO	1.0 ± 0.7	0.70 ± 0.25	≈ 0.1	1.7
PPFNPO	1.2 ± 0.5	0.22		1.4

^a ± obtained from an average of three or more measurements.

per absorbed dose. The G values are then readily calculated in the usual manner¹² and are summarized in Table II for COF₂, CF₄, and CF₃CFO. The G value for formation of COF₂ from electron beam irradiation of PPFMEO and PPFMEO-OH are 7.7 and 6.2, respectively, and drop to ≈ 1–2 for the branched polyperfluoroethers PPFPO and PPFMPO and for PPFNPO. Conversely, the G value for formation of CF₄ is highest for the branched polyperfluoroethers containing pendant –CF₃ units like PPFMPO (G = 1.1), and PPFPO (G = 0.7) and for these polymers, competes with evolution of COF₂. On the basis of the G values, we conclude that the polymers containing perfluoroethylene oxide and perfluoromethylene oxide monomer units are most susceptible to electron beam induced damage and produce the largest quantities of carbonyl fluoride (COF₂). In the branched polyperfluoroethers, PPFPO and PPFMPO, the pendant –CF₃ units in the main chain provide alternative radiation-induced degradation pathways such as evolution of CF₄, and thus COF₂ formation is significantly reduced in comparison. Increasing the number of perfluoromethylene units between the oxygen atoms in the main chain also appears to retard COF₂ fragmentation into the gas phase, as observed for PPFNPO. COF₂ can, under atmospheric conditions, hydrolyze to the very corrosive hydrogen fluoride, consequently, main-chain scission of the relatively inert polyperfluoroethers renders the physical and chemical properties of these materials considerably different from their initial properties and thus may effect device applications.

Several generalizations may be drawn from the above data. For all of the systems studied main-chain scission is the major route for decomposition which leaves radical sites on the ends of the fragmented chains; bonds β to the radical sites are considerably weakened and susceptible to thermal scission, thus enabling the evolution of small gaseous molecules like COF₂. This “unzipping” or β -cleavage reaction apparently stops at some point in the chain where activation energies are too large in comparison to the kT available at room temperature; at this point the acid fluoride end groups may be formed.

G Value from Mass Loss Measurements at Atmospheric Pressures. As discussed in the previous section, at room temperature in the absence of a vacuum environment, electron beam irradiation of polyperfluoroethers produce small gas molecules such as COF₂ that can be collected and observed via infrared in the gas phase. Additionally, changes in the bulk liquid film are also observed as a result of electron beam irradiation and these data are discussed next. The major changes observed is mass loss and the formation of a –CFO acid fluoride absorption band in the infrared which persists in the liquid film. The transmission infrared spectra for PPFPO as a function of absorbed dose is shown in Figure 3 as an illustrative example. In Figure 3a, the transmission spectrum of a thin film of PPFPO, 2.6 μ m, is shown as a function of absorbed dose. Several major changes are

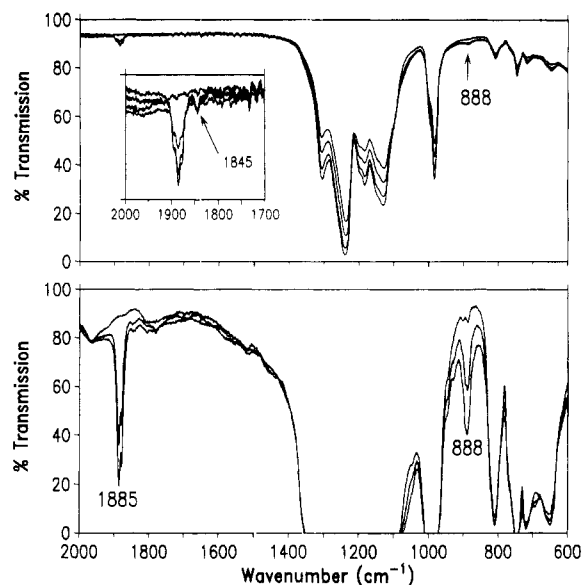


Figure 3. Transmission infrared spectra of PPFPO films as a function of absorbed dose at room temperature, 1 atm of nitrogen. Top figure: initial film thickness 2.6 μ m; 0, 38.0, 76.0, and 114.0 Mrad. All of the absorption bands decrease with increasing dose, except for the 1885- and 888-cm⁻¹ bands which result from the irradiation. The inset presents the 1885-cm⁻¹ region in greater detail. Bottom figure: film thickness 0.029 mm; 0, 111, and 222 Mrad. The thicker film presents the increase in the absorption bands at 1885 and 888 cm⁻¹ as a function of absorbed dose.

evident in the infrared spectrum of PPFPO as a result of electron beam exposure. First, there is a decrease in the integrated area of the major absorption bands characteristic of the polymers. Second, there is evolution of a band centered at ca. 1885 cm⁻¹, the carbonyl absorption of an acid fluoride group, which persists in the liquid and is attributed to stable oligomer(s) with a –CFO end group, perhaps produced by main-chain scission and subsequent thermal rearrangement; that the 1885-cm⁻¹ band contains a –CFO end group has been confirmed via hydrolysis experiments in the infrared.¹¹

To facilitate detection of other important electron beam induced fragments and/or products, thicker films of the perfluorinated ethers were also investigated. In Figure 3b, the infrared spectrum of PPFPO in a 0.029-mm fixed-path-length liquid cell is shown as a function of absorbed dose. Here the evolution of the stable 1885-cm⁻¹ carbonyl absorption is readily observed. Additionally, a new absorption band at 888 cm⁻¹ is also observed concomitant with the evolution of the acid fluoride band, which may be a C–O and/or C–F vibrational mode associated with the oligomeric product. In this section we limit our discussion to data pertaining to electron beam induced mass loss, such as shown in Figure 3a; discussions pertaining to the evolution of the 1885-cm⁻¹ entity is deferred to a later section. To calculate the G value from the infrared mass loss data, knowledge of the changes in mass as a function of absorbed dose is required. The changes in the integrated absorbance as a function of absorbed dose was related to changes in mass first by establishing a standard curve relating integrated absorbance to film thickness, and then relating the film thickness to mass via the initial density of the liquid, valid at small doses. In Figure 4, a plot is presented for the number of moles of monomer lost per unit weight, as a function of absorbed dose. These data reveal that monomer units are lost from PPFMEO-OH and PPFMEO most efficiently,

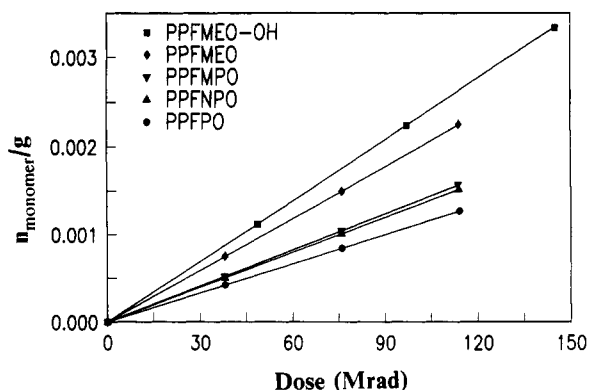


Figure 4. Number of moles of monomer per unit weight lost as a function of absorbed dose from transmission infrared data.

Table III. *G* Values from Infrared Data and Weight Loss Measurements^a

polyperfluoroether	transmission IR, 1 atm N ₂	weight loss data, 1 atm N ₂	reflectance IR, vacuum
PPFMEO	19.0 ± 5.4	22.8 ± 0.6	40.7
PPFMEO-OH	18.9 ± 3.5		34.0
PPFMPO	13.3 ± 1.2	11.5	27.2
PPFNPO	12.8 ± 1.9		26.0
PPFPO	10.7 ± 2.9	10.5 ± 1.9	25.9

^a ± obtained from an average of three or more measurements.

followed by PPFMPO, PPFNPO, and PPFPO. These data correlate well with the *G* values measured for gas evolution (Table I). From the data presented in Figure 4, the *G* values are presented in Table III. These data reveal that the *G* values are of the order of ≈ 20 for PPFMEO and PPFMEO-OH and drop significantly to ≈ 11 –13 for PPFMPO, PPFNPO, and PPFPO, with PPFPO having no perfluoromethylene monomer units, having the lowest overall *G* value. Comparison with the *G* values for gas evolution presented in Table II indicate, for example, for PPFMEO, that while a total of 19 monomer units may be scissioned per 100 eV of absorbed energy (Table II), either as monomeric or oligomeric units, only 8 COF₂ units are detected in the gas phase (Table II). This implies that not all of the fragmented pieces decompose to stable small gases like COF₂ and enter the gas phase, but instead, larger oligomers may simply condense on the walls inside the gas cell. Evidence for such condensation has been obtained using X-ray photoelectron spectroscopy and will be discussed in a later section.

To corroborate the *G* values obtained from the infrared mass loss data (Figure 3), films of the polyperfluoroethers were spin-coated onto Si wafers and their weight was measured as a function of absorbed dose. For these experiments, the film thicknesses were 18–35 μm . These data are presented in Figure 5. It is observed that the normalized weight loss as a function of absorbed dose is greatest for PPFMEO and smallest for PPFPO, consistent with the spectroscopic measurements. From the initial slopes of the curves, the *G* values were found to be 23, 12, and 11 for PPFMEO, PPFMPO and PPFPO, respectively, as summarized in Table III. The *G* values from direct weight loss measurements are consistent with the *G* values obtained from infrared detection of mass loss of thin films, i.e., 19, 13, and 11 for the same polyperfluoroethers, respectively.

***G* Values from Mass Loss Measurements under Vacuum.** A final set of experiments for weight loss

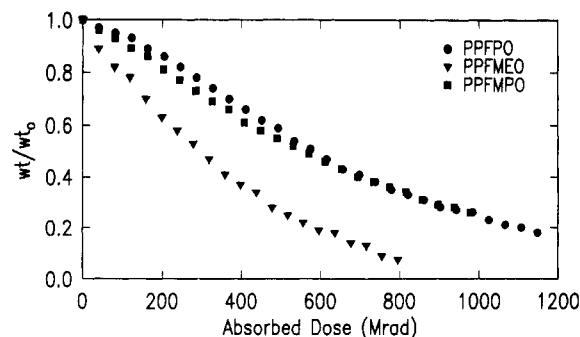


Figure 5. Normalized weight loss of polyperfluoroethers as a function of absorbed dose. Data obtained by direct weight measurements.

measurements was performed via specular reflectance infrared spectroscopy in a vacuum environment, at room temperature. Thus films of the polyperfluoroethers were spin coated onto gold substrates (typically 1–2 μm) and their infrared spectra measured as a function of electron beam exposure. The changes in the percent reflectivity was related to changes in the film thickness via a dispersion analysis²¹ and converted to mass lost by multiplication of the film thicknesses by the initial density of the polyperfluoroethers. The density of the liquids was assumed not to change significantly since only the initial slopes of the mass loss versus incident charge density plots were utilized in calculating the *G* values. The *G* values obtained from these measurements are summarized in Table III. As observed previously, the *G* values are highest for the unbranched polyperfluoroethers like PPFMEO and PPFMEO-OH, and lowest for PPFPO. The *G* values vary from 41 to 26 and in general are twice as high as the transmission infrared and weight loss measurements. Under the vacuum environment, smaller oligomeric fragments are pumped away immediately by the vacuum system¹⁴ which might otherwise persist in the liquid film at 1 atm, thus the *G* values are higher.

In summary of the mass loss data, we interpret the results as meaning that the polyperfluoroethers which contain the unbranched perfluoromethylene oxide and perfluoroethylene oxide monomer units scission more readily than the branched polymers like PPFPO. Increasing the number of carbon atoms between the oxygen atoms in the monomer units, i.e., PPFNPO, appears to minimize chain degradation as well.

***G* Value for Formation of R-CFO Oligomers in the Bulk Liquid at Atmospheric Pressures.** We observed in Figure 3 that concomitant with the mass loss of the polyperfluoroethers, evolution of bands centered near 1885 cm^{-1} that persisted in the liquid were also observed after electron beam irradiation. These absorption bands are different from gases like COF₂ in that they are most probably stable oligomeric R-CFO units whose vapor pressure at room temperature and 1 atm is low enough such that the oligomers do not enter the vapor phase. The evolution of the acid fluoride absorption as a function of absorbed dose in the liquid-phase transmission infrared spectrum of the polyperfluoroethers are summarized in Figure 6 for the various polyperfluoroethers and allow

(21) Pacansky, J.; England, C. D.; Waltman, R. J. *Appl. Spectrosc.* 1986, 40, 8.

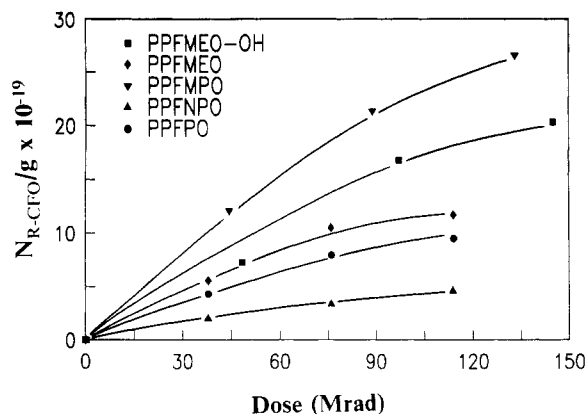


Figure 6. The number of molecules of R-CFO oligomers produced per unit weight of polyperfluoroether, as a function of absorbed dose. Data from transmission infrared spectra of thin films.

Table IV. *G* Values for Formation of R-CFO in Bulk Liquid^a

polyperfluoroether	thin films, IR, 1 atm argon	bulk films, IR, 1 atm argon
PPFMEO	1.63 ± 0.08	1.5
PPFMEO-OH	2.01 ± 0.11	1.6
PPFMPO	3.47 ± 0.23	1.3
PPFNPO	0.65 ± 0.02	
PPFPO	1.44 ± 0.04	1.5

^a ± obtained from an average of three or more measurements.

evaluation of the *G* value:

$$G = 100 \frac{\int \log(T/T_0) d\nu N_A}{A_{\text{CFO}} l D \rho} \quad (8)$$

where $\int \log(T/T_0) d\nu$ is the integrated absorbance (cm^{-1}), N_A is Avogadro's number, A_{CFO} is the integrated molar absorption coefficient (cm/mole), l is the path length (cm), ρ is the density (g/cm^3), and D is absorbed dose in eV/g ($6.24 \times 10^{19} \text{ eV}/(\text{g Mrad})$). The integrated molar absorption coefficient for RCFO is $A_{\text{CFO}} = 7.86 \times 10^6 \text{ cm}/\text{mol}$ as determined from the molecule $\text{OFC}-\text{CF}_2\text{CF}_2\text{CF}_2\text{OCF}(\text{CF}_3)\text{CFO}$, and this value is used to calculate the *G* value for the formation of the oligomeric -CFO fragments left in the liquid polyperfluoroether films. From data such as shown in Figure 6, the *G* values were determined. The data are summarized in Table IV and are ≈ 1 –3 for the various polyperfluoroethers. To corroborate the thin film measurements (Figure 3a), thick films of the polyperfluoroethers were also studied. For the latter, liquid cells with fixed path lengths of 0.029 mm were used to facilitate detection of the oligomeric R-CFO absorption (see Figure 3b, for example). The *G* values from these measurements are summarized in Table IV and are 1.5, 1.6, 1.3, and 1.5 for PPFMEO, PPFMEO-OH, PPFMPO, and PPFNPO, respectively, and are consistent with the values derived from the thin film measurements. These values are all consistent with the *G* values calculated from EPR and viscosity studies by Barnaba et al.,¹⁰ for example, $G = 1.8$ for poly(perfluoroethylene oxide) homopolymer.

Correlation of *G* Values Obtained From Viscosity, Gas Evolution and Mass Loss Measurements. *Mass loss and gas evolution:* Consider first the *G* values determined from the mass loss and gas evolution experiments of the various polyperfluoroethers at room temperature and 1 atm; Tables II and III contain the appropriate data. The *G* values range from ≈ 11 to 22, depending

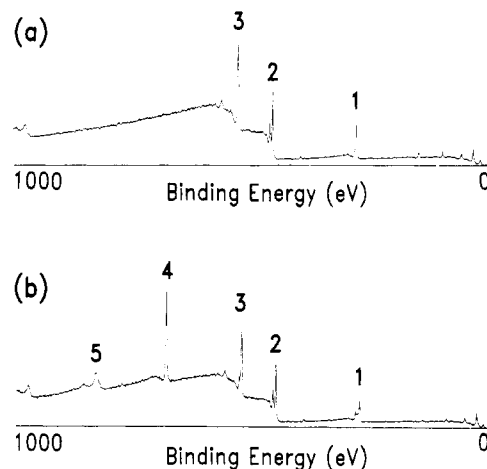


Figure 7. Survey XPS scans of Ti foils used in the gas evolution studies: (a) virgin Ti; (b) Ti used as a window in the gas cell irradiation of PPFMPO. For both spectra: 1, C 1s; 2, Ti 2p_{1/2}; 2p_{3/2}; 3, O 1s; 4, F 1s; and 5, F auger.

upon the polymer, as found by both spectroscopy and direct weight loss measurements. This stipulates, for example, that 19 monomer units are lost per 100 eV absorbed energy in PPFMEO. The *G* value for total detectable gases from PPFMEO, under these conditions, is 8 (Table II). Consequently, there is mass lost from the bulk of the liquid that is unaccounted for in the gas phase. Part of the discrepancy is evident in Figure 2b, for example. The broad bands between 1050 and 1400 cm^{-1} with band centers at 1115 and 1154 cm^{-1} , and a small absorption between 1490 and 1600 cm^{-1} , centered at $\approx 1530 \text{ cm}^{-1}$ remain unidentified but do account for some fraction of the mass lost. Without knowledge of the entities responsible for these absorption bands, nor of their oscillator strengths, then the *G* values tabulated in Table II are more precisely the *G* values for gases that could be identified in the gas phase. However, we might expect these contributions to be small since COF_2 and CF_4 appear to be the dominant stable gases produced, and this is particularly evident at small absorbed doses (Figure 2). During the course of the gas evolution studies, we also observed that the broad absorption band centered at 1530 cm^{-1} (Figure 2) was due to material condensing and/or reacting with the KBr windows of the gas cell. Since the gas cell used to collect the gas products from electron beam exposure of the polyperfluoroethers has a surface area of $\approx 130 \text{ cm}^2$, the possibility that some of the "missing" mass was condensing on the walls of the gas cell was considered. Thus one of the KBr window ports of the gas cell was replaced with a virgin Ti foil (13 μm) and a polyperfluoroether irradiated in the usual manner. The Ti foil was then removed from the gas cell and, along with another piece of virgin Ti, was interrogated using X-ray photoelectron spectroscopy (XPS). The results of the survey scans are shown in Figure 7. The virgin Ti foil, shown in Figure 7a, shows the characteristic TiO_2 2p_{1/2}, 2p_{3/2} core ionization lines at 458.6 and 464.3 eV, respectively, with the 5.7-eV split characteristic of the oxide.¹⁹ Carbon- and oxygen-containing surface contaminants are also evident at 284.6 (C 1s) and 530 eV (O 1s). Note the absence of any signals in the 688-eV range which would indicate the presence of any fluorine (F 1s) containing compounds. In Figure 7b, the Ti foil used in the gas evolution studies is shown. The most dramatic change observed in the survey scan is the presence of a strong line at 688.3 eV, attributable to the

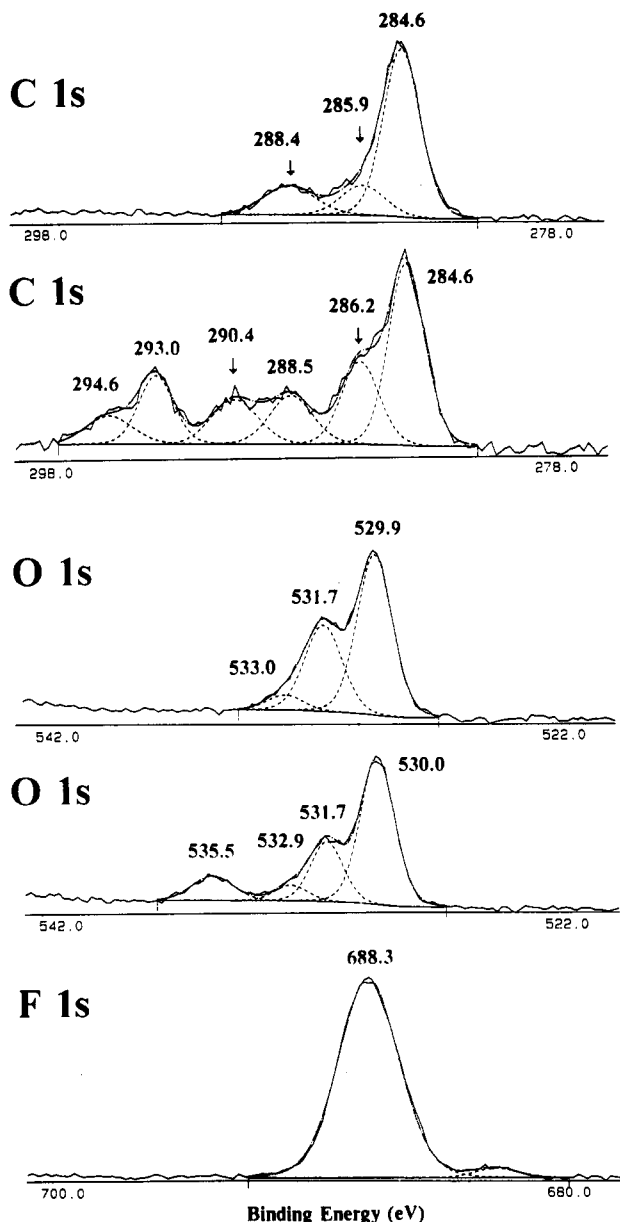


Figure 8. C 1s, O 1s, and F 1s core ionization lines for Ti foil before and after use in gas cell. The top C 1s and O 1s spectra are for the virgin Ti foil, while the corresponding bottom figures, and the F 1s spectrum, are after use in the gas cell.

F 1s core ionization of organic fluorine. The other new line at 835 eV is a fluorine auger transition. Thus it is apparent that fluorinated materials are indeed condensing on the inside walls of the gas cell, which are not detected via gas-phase infrared. To characterize these condensates, the C 1s, O 1s, and F 1s core ionization lines of the Ti foils before and after use in the gas evolution experiments are shown in Figure 8. In Figure 8, new C 1s lines are observed at 290.4, 293, and 294.6 eV which are attributed to carbon atoms with fluorine and oxygen neighbours, i.e., $-\text{CF}_2-$ and $-\text{O}-\text{CF}_2-\text{C}$ entities.²² A new core ionization line at 535.5 eV in the O 1s region is characteristic of $-\text{CF}_2-\text{O}-\text{CF}_2-$. Finally, the F 1s line at 688 eV is compelling evidence that perfluorinated material is condensing on the gas cell walls. We also observe a minor line at 684 eV characteristic of F^- entity. Thus, on the basis of the XPS results, and the G values summarized in Tables I and II, we conclude

that the electron beam exposure of the liquid polyperfluoroethers cause main-chain scission whereby oligomeric fragments and small gas molecules are split off. Stable products like COF_2 enter the gas phase and are readily detectable via infrared; larger fragments that are split off have lower vapor pressures and consequently condense to the walls inside the gas cell. Since these materials are not detected in the gas phase transmission infrared, their masses have not been accounted for and this may in part reflect the G value differences observed between Tables II and III.

Main-chain scission: When an electron beam breaks a bond in the main chain of a polyperfluoroether, it is reasonable to expect that radical sites on the ends of the fragmented chains are created. Bonds β to the radical sites are considerably weakened and susceptible to thermal scission, thus enabling the evolution of small gaseous molecules like COF_2 . This "unzipping" or β -cleavage reaction apparently stops at some point in the chain where activation energies are too large in comparison to the kT available at room temperature; at this point the acid fluoride end groups may be formed. The G values for evolution of the acid fluoride groups thus reflect main chain scission, and these data were summarized previously in Table IV. The G values were generally of the order of about 1.5 for the evolution of R-CFO units. If we assume that for every bond broken, two R-CFO units are produced, then the G value for main chain scission would be 1.5 divided by 2, or ≈ 0.8 . These data are summarized in Table I. In comparison, the G values for main-chain scission from the viscosity measurements ranged from 0.3 to 0.5, approximately a factor of 2 less than the values obtained from spectroscopic measurements. We believe the viscosity-derived G values underestimate the spectroscopically determined G values for the following reasons. First, as discussed above, the use of eqs 5–7 assumes a polydispersity index that does not change with absorbed dose, since only the initial values were used to relate the changes in the viscosity to the number average molecular weight needed for the analysis. It is generally accepted that main-chain degradation of a polymer leads to a random distribution of its molecular weight, i.e., $M_w/M_n \rightarrow 2$. If this is accounted for in eqs 5–7 for the polyperfluoroethers, this will have the effect of increasing the G value. For example, for PPFMPO, the G value was 0.4 as determined from Figure 1, using $M_w/M_n = 1.38$. If electron beam irradiation causes the molecular weight distribution of PPFMPO to approach a random distribution, then the following G values may be obtained instead. Thus, in this example, if $M_w/M_n = 1.5$, $G = 0.67$; if $M_w/M_n = 1.75$, $G = 1.15$; if $M_w/M_n = 2.00$, $G = 1.63$. We observe the sensitivity of the G value to distributions in the molecular weight. Thus a proper accounting for changes in the polydispersity index as a function of electron beam irradiation can affect the G value significantly and may explain the observed variance between the G values obtained from infrared and viscosity data (Table I).

Conclusion

Electron beam irradiation of polyperfluoroethers causes main-chain degradation characterized by unzipping and evolution of small molecules like COF_2 , leaving behind $-\text{CFO}$ terminated oligomers in the liquid. Since main-chain scission predominates, the initial narrow molecular

(22) Miller, D. C., this laboratory, private communication.

weight distribution moves to a random one characterized by low molecular weight fragments with high vapor pressure. Thus the response of the materials to high-energy radiation differs dramatically when exposures are performed under vacuum or under atmospheric conditions. Nevertheless, the materials inherently degrade upon exposure and release gases, most of which are toxic and/or corrosive, and all of which are accompanied by a loss of sample weight.

The G values for main-chain degradation of five polyperfluoroethers, PPFMEO, PPFMPO, PPFPO, PPFNPO, and PPFMEO-OH were determined from spectroscopic, mass loss, and viscometric measurements. While G values were extracted from the experimental work with great care and in most cases, each experiment repeated three or more times to provide relative error; nevertheless, several assumptions were necessarily incorporated to obtain the final G values. In analyzing the viscosity data, it was necessary to limit evaluation of the data to the initial slopes of the curves in the M_n versus absorbed dose plots since the polydispersity relationship after irradiation was not

known. Therefore, those G values should be considered to be estimates.

The G values for weight loss ranged from 11 to 22, depending upon the polymer. The G values for gas evolution, COF_2 and CF_4 , ranged from 1 to 8, depending upon the polyperfluoroether. The G values for main-chain scission ranged from 0.3 to 1.7, depending upon the polymer. In general, it was observed that unbranched polyperfluoroethers with two carbon atoms between each oxygen in the main chain, i.e., PPFMEO and PPFMEO-OH, produced the most carbonyl fluoride and had the highest G values for mass loss. The unbranched polymer PPFNPO with three carbon atoms between each oxygen in the main chain, generally had the lowest G values for both mass loss and gas evolution. The branched polyperfluoroethers PPFPO and PPFMPO also had relatively low G values for mass loss and gas evolution compared to PPFMEO. Thus the structure and combinations of the monomer units apparently has a profound effect on the scissioning of the polyperfluoroethers and the overall stability to radiation-induced damage and the distribution of gaseous products evolved.