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# Electron Beam Irradiation of a Perfluoroalkoxy Fluorocarbon Resin: Tetrafluoroethylene/Perfluoromethyl Vinyl Ether Copolymer

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ABSTRACT: Tetrafluoroethylene/perfluoromethyl vinyl ether copolymer was exposed to electron beams and analyzed for structural changes and volatiles generated via infrared spectroscopy. When the copolymer is irradiated, gases are produced, mass loss is induced, and acid fluoride end groups are formed in the bulk. $CF_4$, $COF_2$, $CO_2$, and $CF_3OCF_3$ are produced with *G* values of 0.93, 0.31, 0.055, and 0.14, respectively. The sum of the *G* values for gas formation, 1.43, provides an upper limit estimate for side chain cleavage. The *G* value for formation of acid fluoride in the bulk is 0.34 and provides a lower limit estimate for main chain scission. Hence, most of the side chain scissioning leads to reactions that do not produce acid fluoride end groups.

## Introduction

Polyperfluorinated ether liquids have enjoyed widespread technological applications because of their unique physical and chemical properties. In particular, these materials are excellent lubricants because of their intrinsic stability to temperature and chemical attack and comparatively low vapor pressures. They are linear polymers composed primarily of homo- and/or copolymers of perfluoroalkoxy materials, e.g., $-CF_2O-$, $-CF_2CF_2O-$, $-CF_2CF_2CF_2O-$, and $-CF(CF_3)CF_2O-$ monomer units. In these materials, the −C−O−C− alkoxy ether linkage occurs in the main chain. After an initial radiation or thermally induced scission, these materials are observed to degrade to lower molecular weights with evolution of volatile gases such as $COF_2$, $CF_3CFO$, and simple perfluoroalkanes.[1−4]

Perfluorinated ethers containing the alkoxy ether linkage in the side chain instead of in the main chain are also technologically important materials. These are typically melt processible copolymer solids that exhibit excellent chemical and mechanical properties at elevated temperatures and, consequently, are useful in the chemical processing industry. Some materials characteristics include chemical inertness, heat resistance, flexibility and toughness, stress-crack resistance, low surface energies, low moisture absorption, and exceptional dielectric properties. They are known in the industry as perfluoroalkoxy (PFA) fluorocarbon resins, and to distinguish these types of materials from the polyfluorinated ether liquids discussed above, we will retain this nomenclature throughout. Tetrafluoroethylene/perfluoromethyl vinyl ether copolymer, hereafter called TFE−PFMVE, is one such copolymer whose chemical structure is shown below. It is a copolymer

$$\text{-(-}CF_2CF_2\text{-)-///-(-}CF[OCF_3]CF_2\text{-)-}$$

containing tetrafluoroethylene and perfluoromethyl vinyl ether monomer units. The perfluorinated ether side chains are randomly distributed along a fluorocarbon backbone in the main chain. Logothetis[5] has recently reported the compression set, tensile strength, and chemical resistance of TFE−PFVME O-rings that were cross-linked via electron beam irradiation. A gel content of 95% was reported after 10−15 Mrad. During the course of the investigation, he also found that TFE−PFVME undergoes a measurable weight loss as a function of absorbed dose. When TFE−PFVME is scissioned, cleavage of both C−C and C−O bonds is possible. The presence of the C−O ether bond as a side chain may lead to different products and/or distribution of products compared to scission processes in tetrafluoroethylene polymer and polyperfluorinated ethers. Hence, we report the electron beam induced scissioning of TFE−PFMVE copolymer and characterize the scission products that are produced. Thus TFE−PFMVE was exposed to electron beams and analyzed for structural changes and volatiles generated via infrared spectroscopy. TFE−PFMVE was exposed to a 25 kV electron beam under vacuum at $T = 20$ K and changes in its infrared spectrum were monitored including warmup to 290 K. Another set of samples were exposed to a 175 kV electron beam under argon at room temperature and the gases collected and interrogated via transmission infrared spectra. The weight loss as a function of absorbed dose at 298 K was also followed using the 175 kV electron beam. *G* values for polymer decomposition and evolution of gaseous products are reported. The *G* value is defined as the number of molecules formed or destroyed per 100 eV of absorbed energy. $COF_2$, $CF_4$, $CO_2$, and $CF_3OCF_3$ are observed in the gas phase.

## Experimental Section

TFE−PFVME was kindly provided by Dr. A. Logothetis of the DuPont Experimental Station, Wilmington, DE. The random copolymer is composed of tetrafluoroethylene/perfluoromethyl vinyl ether monomer units in a 2:1 mole ratio, respectively. It is amorphous with a $T_g$ of −5 °C and $M_n \simeq 60\,000$. $COF_2$, $CF_4$, and $CF_3OCF_3$, used for gas identification purposes, were obtained from commercial sources and used directly. The stated purity of $CF_3OCF_3$ was 70%; a gas chromatogram identified the major impurities to be $CF_3H$ and $CO_2$. The impurity bands attributed to $CF_3H$ are identified in the infrared spectrum presented in Figure 6, bottom figure.

The apparatus used for the 25 kV electron beam exposure of the samples under vacuum and at low temperatures is shown in Figure 1. It consists of a stainless steel vacuum chamber connected to an electron beam gun. The chamber was sequentially pumped down with a Teflon vane pump, nitrogen-cooled sorption pumps, and an Air Products closed-cycle cryopump with an 8 in. cold surface while the electron

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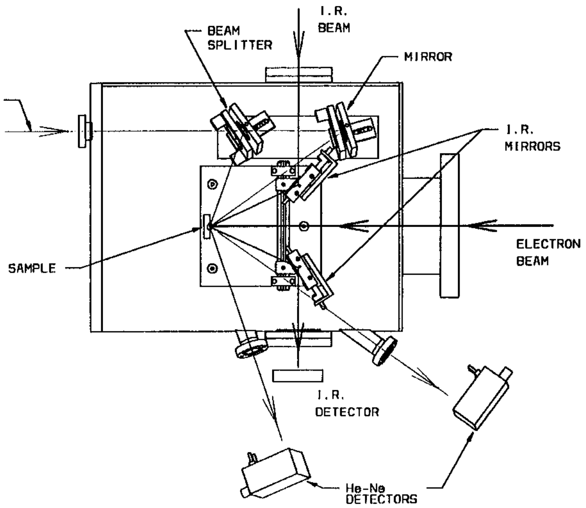

**Figure 1.** Diagram of experimental setup for electron beam gun, vacuum chamber, and FT-IR.

beam gun was pumped with two 20 L/s ion pumps. The electron beam gun operates from 0 to 30 kV and the beam is focused with a magnetic lens. The current in the electron beam was measured with a Faraday cup connected to a Keithly 480 picoammeter. The Faraday cup could be positioned in the path of the beam. For these experiments, a constant current density of 64 nA/cm$^2$ was used. The light from an infrared spectrometer is brought into the chamber through a series of mirrors and reflects off of the sample substrate to an externally located detector. Changes in the infrared spectrum could then be monitored concurrently with electron beam irradiation. For these purposes, a Bruker Model IFS 88 FTIR spectrometer is used. The light from a He−Ne laser is brought into the sample chamber, passed through a beam splitter, and reflected off a second mirror to coincide upon the sample substrate. The beams were then reflected off the substrate to photodiode detectors. In this manner, changes in film thicknesses could be measured from the resultant interferograms.

Electron beam exposures at 175 kV were achieved using a CB 150 electron processor (Energy Sciences, Inc., Woburn, MA) which allowed exposures of the samples to a 175 kV electron beam in an atmosphere of nitrogen. After corrections for beam energy losses to the various window foils and inert atmosphere, the energy incident on the samples was either 88 or 102 kV, depending upon sample cell configuration. The methodology used to collect and measure the infrared spectra of the gases evolved has been described elsewhere.[2] Transmission infrared spectra were measured on a Perkin-Elmer Model 983 IR spectrometer equipped with a Model 3600 data station.

Films for infrared analysis were prepared by heating the polymer to 250 °C between a polished stainless steel substrate and a polyimide releasing film backed by a stainless steel plate and pressing to ≃8000 psi. For the 25 kV electron beam exposures, a ≃4 *μ*m thick film was used. The electron penetration depth is described by Grün[6] as

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

where $R_g$ is the Grün range in *μ*m, i.e., the maximum electron beam penetration depth perpendicular to the film, $\rho$ is the density of the film in g/cm$^3$, and $E_0$ is the energy in kV incident on the film. For $E_0 = 25$ kV, with a film density[7] of ≃1.7 g/cm$^3$, $R_g = \simeq 8$ *μ*m.

## Results

**Low-Temperature IR Data.** The changes in the infrared spectrum of TFE−PFMVE before and after exposure to a 25 kV electron beam under vacuum at $T = 20$ K are shown in Figure 2. The spectrum before irradiation is shown in Figure 2a; the broad absorption bands between 1400 and 1000 cm$^{-1}$ are attributed to the C−C, C−F, and C−O stretching vibrations. The band near 890 cm$^{-1}$ is usually a combination of C−C, CF$_2$, and CF$_3$ stretching vibrations, and valence angle bends are usually observed below 800 cm$^{-1}$ in these materials.[8] When exposed to an electron beam, several changes in the infrared spectrum are observed. Six new absorption bands are clearly identified at 2343, 1935, 1907, 1885, 1790, and 967 cm$^{-1}$. The shape of the broad absorption region between 1400 and 1000 cm$^{-1}$ is also observed to change. Many of these absorption bands have also been observed previously in the infrared spectrum of the structurally analogous polyperfluorinated ethers[2] after exposure to an electron beam and thus facilitate the band assignments here. Based upon these data, the 1935 and 1907 cm$^{-1}$ absorption bands are attributed to the C=O stretching frequency in carbonyl fluoride or COF$_2$.[9] These two bands have been observed previously in the infrared and Raman spectrum of authentic liquid COF$_2$.[10] The 1885 cm$^{-1}$ band is attributed to the carbonyl stretching vibration of an acid fluoride group, R−CFO. This is verified by exposing the irradiated material to moist air, which causes the hydrolysis of the 1885 cm$^{-1}$ R−CFO to an acid R−COOH, with a characteristic infrared frequency centered at 1770 cm$^{-1}$, as also observed previously in polyperfluorinated ethers.[1] Since evolution of CF$_3$CFO is not observed in the gas phase after electron beam irradiation of TFE−PFVME, discussed below in Figure 4, R must be a larger fragment than CF$_3$, and thus R−CFO is most probably an oligomer or polymer with an acid fluoride end group formed by electron beam induced scissioning. CO$_2$, at 2343 cm$^{-1}$, may be produced from the electron beam induced decomposition of TFE−PFVME itself as well as from the electron beam irradiation of its radiation products COF$_2$ and R−CFO.[2] The absorption band at 967 cm$^{-1}$ is attributed to the CF$_3$ and FCO bending mode[8] of CF$_3$OCF$_3$, its subsequent identification to be discussed below (Figure 5). The absorption band at 1790 cm$^{-1}$, Figure 2, was not observed previously in the electron beam irradiation of

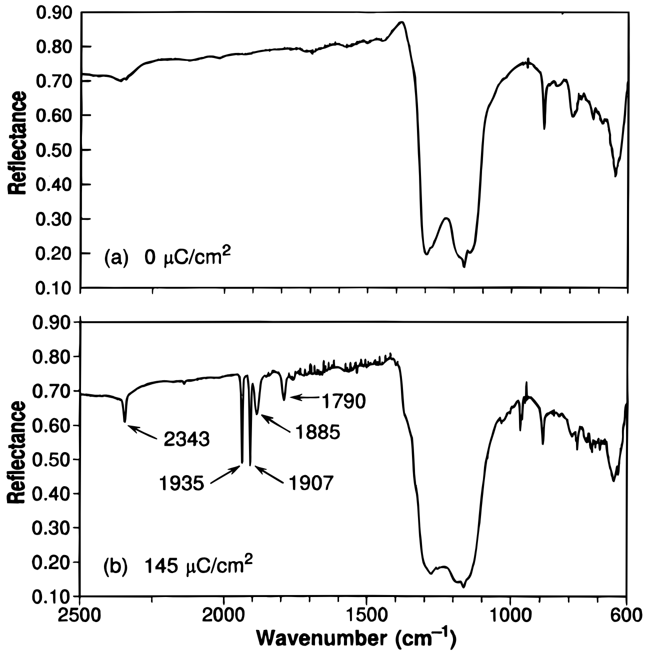

**Figure 2.** Specular reflection infrared spectrum of ≃4 *μ*m thick film of TFE−PFMVE on polished steel, recorded at $T = 20$ K under vacuum before (top) and after (bottom) exposure to a 25 kV electron beam: 0 and 145 *μ*C/cm$^2$.

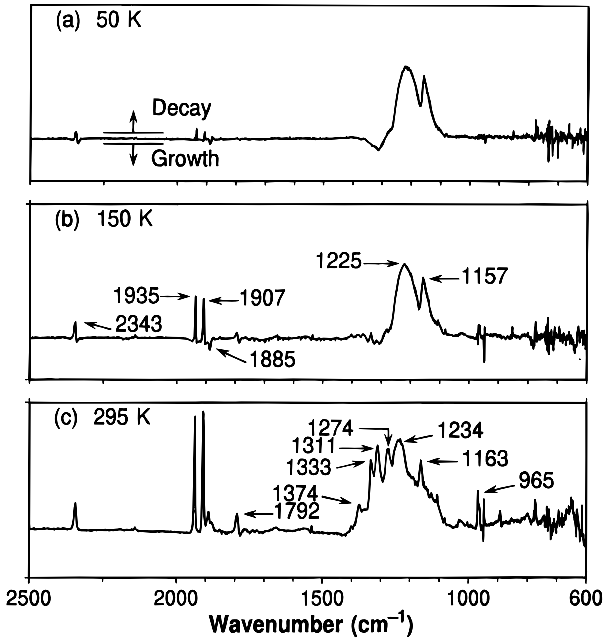

**Figure 3.** Specular reflection infrared spectra during warmup of irradiated TFE−PFMVE on polished steel after 145 $\mu$C/cm$^2$ exposure. The difference spectra are obtained by subtracting the infrared spectrum at the specified temperature (50, 150, and 295 K for a, b, and c, respectively) and the 20 K spectrum shown in Figure 2b.

polyperfluorinated ethers.[2−4] The possible origins for this absorption band include the C═C stretching vibration in perfluorinated alkene structures[11] of the type $-CF{=}CF_2$, ≃1790 cm$^{-1}$, and/or possibly the C═O stretching vibration[12−14] in perfluorinated ketones, e.g., $CF_3C({=}O)CF_3$, ≃1806 cm$^{-1}$, although these frequencies are slightly higher. The lack of resolution in the accompanying 1350−1000 cm$^{-1}$ region precludes any definitive assignment at this time. If the 1790 cm$^{-1}$ absorption originates from a $-CF{=}CF_2$ structural moiety, it would be attributed to a polymer chain end group since $-CF{=}CF-$ and $-CF{=}C<$ structures absorb at somewhat lower frequencies, near 1740 and 1680 cm$^{-1}$, respectively. Terminal $-CF{=}CF_2$ has been observed in the electron beam irradiation of poly(tetrafluoroethylene)[11] and hence is a likely product here also. Conversely, if the 1790 cm$^{-1}$ absorption is due to a C═O stretching vibration, the structure could possibly contain the $-CF_2COCF_2-$ structural moiety. This is unlikely, however, based upon the fact that the C═O stretching frequency for $CF_3C({=}O)CF_3$ occurs at slightly higher frequencies near 1806−1810 cm$^{-1}$.[12−14]

The subsequent warmup spectra are illustrated in Figure 3 and are quite informative. The series of spectra clearly illustrates the loss of the three carbonyl absorption bands in the 1900 cm$^{-1}$ range as the sample is warmed from the irradiation temperature of 20 K. At $T = 50$ K, Figure 3a, material(s) that give rise to infrared absorption in the 1400−1100 cm$^{-1}$ region could be either very low molecular weight volatiles that are pumped away by the vacuum system or simply scissioned polymer chains relaxing to a lower energy configuration. As the irradiation copolymer is gradually warmed up to 150 K, Figure 3b, the 1935 and 1908 cm$^{-1}$ bands ($COF_2$) begin to be pumped away by the vacuum. The 1885 cm$^{-1}$ absorption band persists during the sample warmup until a temperature of ≃230 K is reached, after which the vacuum system begins to pump some of this material away. The vapor pressure of the material giving rise to this absorption is therefore comparatively lower, consistent with an oligomer structure R−CFO. The 1790 cm$^{-1}$ structural moiety, tentatively assigned to terminal $-CF{=}CF_2$, also begins to be pumped away near 230 K. Above 230 K, many of the other bands in the 1400−1100 cm$^{-1}$ region are also pumped away; however, the lack of resolution in this region does not allow any definitive structural assignments. Hence, we have carried out additional irradiation experiments at room temperature and collected the gases, and these results are described in the next two sections.

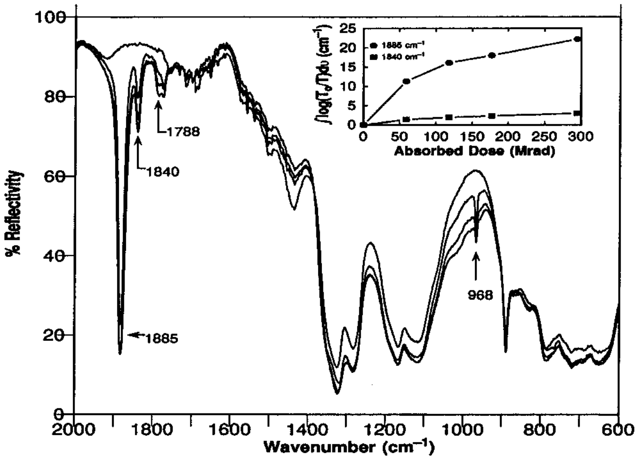

**Figure 4.** Specular reflection infrared spectrum of ≃20 $\mu$m thick film of TFE−PFMVE on polished steel, recorded at room temperature under nitrogen before and after exposure to a 175 kV electron beam: 0, 59, 118, and 177 Mrad. The inset figure shows the changes in the integrated absorbance of the 1885 cm$^{-1}$ band as a function of absorbed dose.

**Room Temperature IR Data.** In an effort to corroborate the results of the low-temperature irradiation and warmup data, films of TFE−PFVME were exposed to a 175 kV electron beam under $N_2$ (≃175 ppm $O_2$) at room temperature and the changes in the infrared spectrum are shown in Figure 4. As a function of electron beam irradiation, we observe the evolution of new bands at 1885, 1840, and 1788 cm$^{-1}$ that persist in the film. The observation and persistence of these bands in the TFE−PFVME solid film, shown in the inset in Figure 4, provide conclusive evidence that they must occur on the polymer chain ends after scissioning in the main chain, as a result of either an initial cleavage in the side chain and a subsequent $\beta$-scissioning reaction or a direct electron beam induced scissioning in the main chain followed by a subsequent rearrangement reaction. The absorption bands for $COF_2$ at 1935 and 1907 cm$^{-1}$ that were observed at 20 K (Figure 3) are not evident here in the bulk film at room temperature since $COF_2$ is a gas at room temperature and presumably diffuses out of the film. Interestingly, the new absorption band at 1840 cm$^{-1}$ was not observed during the low-temperature electron irradiation studies. The band center appears to be too high for the carbonyl stretching frequency in $-CF_2COCF_2-$ structures, which exhibit band centers near ≃1810 cm$^{-1}$, and too low for $CF_3[CF_2]_nCFO$ structures, which exhibit band centers near 1880 cm$^{-1}$. The structural moiety responsible for this absorption band remains unidentified at present.

A determination for the *G* value for the formation of R−CFO is possible from the infrared data provided in Figure 4. The methodology for determining the *G* value, i.e., the number of molecules formed or destroyed per 100 eV of absorbed energy, has been described.[3,4] The

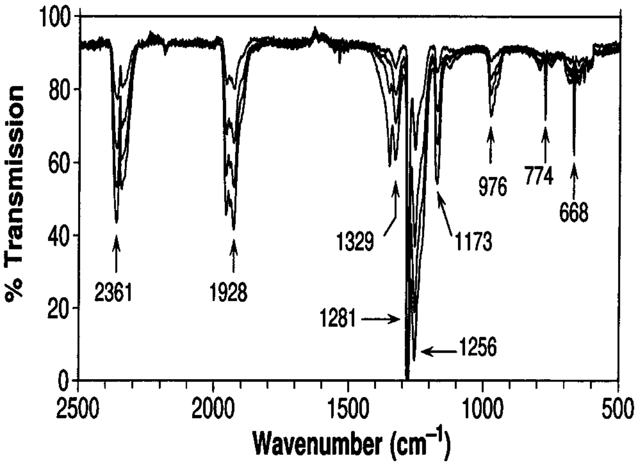

**Figure 5.** Gas-phase transmission infrared spectrum as a function of absorbed dose from the 175 kV electron beam irradiation of TFE−PFMVE polymer: 25, 50, 75, and 100 Mrad. The band intensities increase with increasing dose.

*G* value for evolution of the 1885 cm$^{-1}$ R−CFO group is 0.34.

**Room Temperature Gas−Phase IR Data.** To identify the effluents generated by the electron beam irradiation of TFE−PFMVE, gases were collected from room temperature irradiation of TFE−PFMVE films under an argon atmosphere using the 175 kV electron beam. The gas-phase spectrum as a function of absorbed dose is shown in Figure 5; $CO_2$, $COF_2$, $CF_4$, and $CF_3OCF_3$ are identified. $CO_2$ is observed at the characteristic 2361 and 668 cm$^{-1}$; $COF_2$ at 1957, 1928, 1256, 976, and 774 cm$^{-1}$; $CF_4$ at 1281 cm$^{-1}$. The latter two gases were identified by comparison with authentic gases which gave infrared absorption bands at identical frequencies. We note that when comparing infrared band centers between the gas phase (e.g., Figure 5) and the corresponding low-temperature solid state (e.g., Figure 2), there is a corresponding shift to higher frequencies; this effect has been observed previously.[15] The infrared absorption bands at 1329, 1256, and 1173 cm$^{-1}$ are assigned to $CF_3OCF_3$ based upon a comparison with authentic gas, to be discussed below. In Figure 6, some of the known gases are subtracted from the experimental gas-phase infrared spectrum to help identify any other entities that may be present. Subtraction of $COF_2$ and $CF_4$ yields four prominent bands at 1329, 1256, 1173, and 976 cm$^{-1}$, excluding the bands attributed to $CO_2$. Comparison with a gas-phase spectrum of $CF_3OCF_3$, Figure 6, bottom, results in an identical set of bands, and on this basis we have assigned these bands to $CF_3OCF_3$. No other products appear in sufficient quantity for identification. Both the 1885 and the 1790 cm$^{-1}$ bands observed at 20 K are absent in the room temperature gas-phase infrared spectrum. Since these bands could only be pumped away at higher temperatures, Figure 3, we conclude that the structural moieties giving rise to these absorption bands reside on a polymer chain.

A summary for the formation of product gases evolved from the electron beam irradiation of TFE−PFMVE as a function of absorbed dose is provided in Figure 7. From these data, the *G* values for evolution of $COF_2$, $CF_4$, $CO_2$, and $CF_3OCF_3$ are summarized in Table 1. The results in Table 1 indicate that among the gases identified, $CF_4$ is produced most efficiently from TFE−PFMVE, with a *G* value for $CF_4$ evolution of 0.93. The *G* values for evolution of $COF_2$, $CF_3OCF_3$, and $CO_2$ are 0.31, 0.14, and 0.06, respectively.

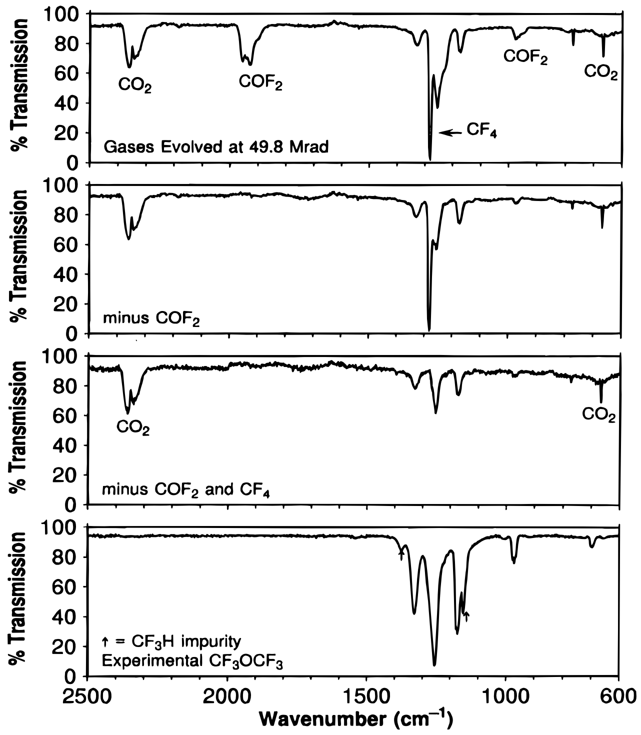

**Figure 6.** Gas-phase transmission infrared spectra of TFE−PFMVE after 50 Mrad and subtraction of $COF_2$ and $CF_4$ authentic gases. The bottom spectrum of authentic $CF_3OCF_3$ is presented for comparison.

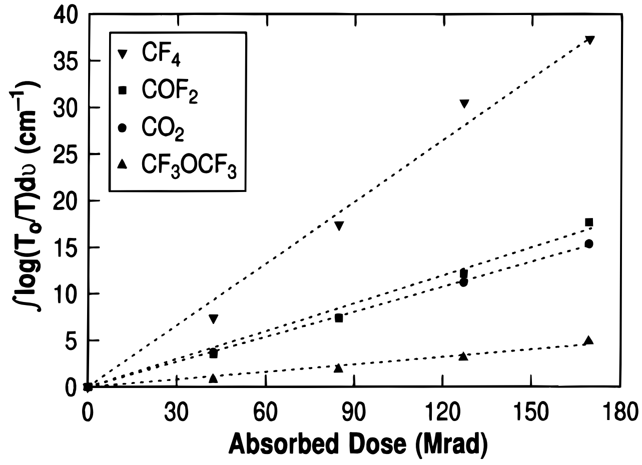

**Figure 7.** Changes in the integrated absorbance as a function of absorbed dose for $CF_4$, $COF_2$, $CO_2$, and $CF_3OCF_3$.

**Table 1. Gases Produced upon Electron Beam Irradiation of Tetrafluoroethylene/Perfluoromethyl Vinyl Ether Copolymer and Their *G* Values**

| gas | *G* value |
|---|---|
| $CF_4$ | 0.93 |
| $COF_2$ | 0.31 |
| $CF_3OCF_3$ | ≈0.14 |
| $CO_2$ | 0.055 |

**Room Temperature Weight Loss Measurements.** The weight loss in a TFE−PFMVE film as a function of absorbed dose at room temperature is presented in Figure 8. A least-squares fit to the experimental data points provides the slope from which a *G* value may be determined. The mole ratio of the two comonomer units $-CF_2CF_2-$ and $-CF[OCF_3]CF_2-$ is 2:1, respectively; thus an average monomer unit contains 122 g/mol. The *G* value for mass loss of an average *monomer unit* is, from Figure 9, equal to 1.43. Since the *G* values (IR)

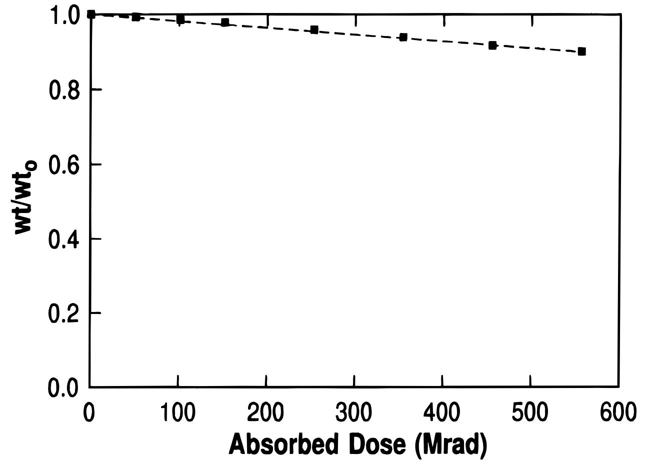

**Figure 8.** Normalized weight loss as a function of absorbed dose (Mrad) from the 175 kV electron beam irradiation of TFE−PFMVE polymer.

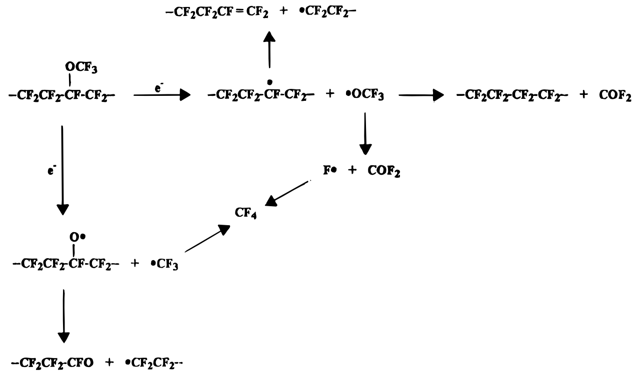

**Figure 9.** Possible electron beam induced decomposition of TFE−PFVME. Only the side chain scissioning reactions are considered here.

for formation of $CF_4$, $COF_2$, $CO_2$, and $CF_3OCF_3$ are 0.93, 0.31, 0.055, and $\approx$0.14, respectively , and sum also to 1.43, then on average a monomer unit lost is equal to the gases that are produced from TFE−PFMVE per 100 eV of absorbed energy.

## Discussion

When the TFE−PFVME copolymer is irradiated, the bulk material loses weight, gases are produced, and acid fluoride end groups are formed in the bulk. Mass loss measurements as a function of absorbed dose show that the material loses weight when exposures are performed under a blanket of nitrogen or within a vacuum chamber, showing that TFE−PFVME is a material that clearly undergoes scissioning. Based upon the oxygen content of the gas-phase products, side chain scissioning is apparently prevalent. The formation of acid fluoride groups in the bulk is indicative of some main chain scission.

Since TFE−PFVME contains both the $-CF_2CF_2-$ and $>CF-OCF_3$ structural moieties, significant insight into irradiation effects may be gathered by first considering the effects of irradiation on tetrafluoroethylene and perfluorinated ether polymers. Previous studies on the electron beam irradiation of poly(tetrafluoroethylene) reveal that perfluoroalkanes and perfluoroalkenes are produced in the absence of atmospheric oxygen.[11,16] The *G* value for main chain scission is reported to be 0.1−0.2;[17] $CF_4$, $C_2F_6$, and $C_3F_8$ are among the prominent products identified.[18,19] Previous studies on the electron beam irradiation of polyperfluorinated ethers indicate that perfluoroacid aldehydes and simple perfluoroalkanes are produced in the absence of atmospheric oxygen. The *G* value for main chain scission is reported to be 0.1−1.2, depending upon polymer structure,[3] and $COF_2$ and $CF_4$ are among the relevant products identified.[1−3] The *G* value for $COF_2$ evolution varies from 1 to 8 and for $CF_4$ evolution from 0.2 to 1.1, depending upon structure. The smallest *G* value ratio for $COF_2$ to $CF_4$ evolution is 1:0.7; thus $COF_2$ is always produced more efficiently.[3] In the TFE−PFVME copolymer investigated here, electron beam irradiation produces $CF_4$, $COF_2$, and $CF_3OCF_3$. The ratio of the *G* value for $COF_2$ to $CF_4$ evolution is 1:3 and favors $CF_4$ evolution instead of $COF_2$. Since $CF_4$ may be produced from the irradiation of the $-CF_2CF_2-$ backbone in poly(tetrafluoroethylene)[18,19] and from the perfluorinated ethers,[1−3] then $CF_4$ may be generated in TFE−PFVME from both the main chain and the side chain. The other three identified gas products, $COF_2$, $CF_3OCF_3$, and $CO_2$, all contain oxygen atoms, and thus scissioning necessarily involves the side chain, regardless of where the initial chain scissioning is induced.

The *G* value for formation of the R−CFO acid fluoride group in the bulk, 0.34, is also the lower limit of the *G* value for main chain scission. The assumption here is that the formation of a R−CFO end group results in a main chain scission. The *G* value represents a lower limit for the *G* value for main chain scission because we have neglected the formation of another end group at 1788 $cm^{-1}$ due to the terminal $R-CF=CF_2$. However, we note that the integrated absorbance of the 1788 $cm^{-1}$ absorption band is much smaller than the 1885 $cm^{-1}$ band. The magnitude of the *G* value for main chain scission, 0.34, is consistent with the reported $\approx$0.1 for poly(tetrafluoroethylene).[17] The higher *G* value for TFE−PFVME may be rationalized by side chain scissioning that leads to subsequent main chain scissions.

Based upon the infrared data, a summary of the possible electron beam induced scissioning reactions in TFE−PFVME is presented in Figure 9. Due to the high yield of $CF_4$, we consider first the cleavage of a $CF_3-O$ bond in the side chain to form the perfluoroalkoxy radical, $-CF_2CF_2CFOCF_2-$, and the perfluoromethyl radical, $CF_3^\bullet$. A subsequent main chain scission may occur from the cleavage of the $\beta$ C−C bond in the perfluoroalkoxy radical, a process with a relatively small activation energy; this reaction also produces an acid fluoride end group and provides a basis for the 1885 $cm^{-1}$ infrared absorption observed in Figure 3 and 5.

Next consider radiation-induced scission of the C−O bond in the side chain, resulting in the formation of the two radicals $-CF_2CF_2CFCF_2-$ and $^\bullet OCF_3$. The scission can explain the oxygen-containing volatiles, for example, disproportionation of the two radicals produces $-CF_2CF_2CF_2CF_2-$ and $COF_2$. This process accounts for the observed infrared absorption band at 1930 $cm^{-1}$, Figures 3 and 6. The various radical intermediates that are produced, e.g., $^\bullet OCF_3$ and $^\bullet CF_3$, may recombine to produce gases such as $CF_3OCF_3$. This process accounts for the observed infrared bands in Figure 6. Two primary radicals $-CF_2^\bullet$ on the ends of chains may disproportionate to produce $-CF=CF_2$ and $-CF_2CF_3$, where the former may account for the 1790 $cm^{-1}$ absorption band observed in Figures 2 and 4.

Logothetis[5] has observed gel formation in the same TFE−PFMVE copolymer after several Mrad; hence it is apparent that TFE−PFMVE undergoes both scissioning and cross-linking. An indication of the relative

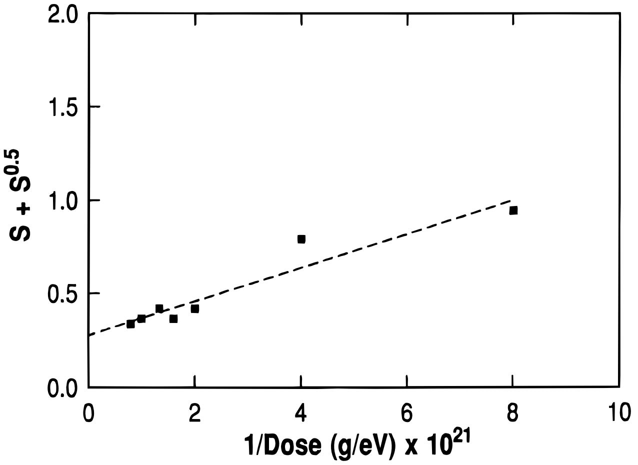

**Figure 10.** Plot of the soluble fraction, $S$, versus reciprocal dose. Original data taken from Figure 1 in ref 5.

efficiencies of both processes may be extracted by replotting Logothetis' Figure 1 data,[5] which we present in Figure 10. Extrapolation of the least-squares fit to 1/dose = 0 allows evaluation of the scissioning to cross-linking ratio, $G(\mathrm{s})/2G(\mathrm{x})$, which is equal to 0.28, assuming a random distribution. Extrapolation to complete solubility, $S + S^{0.5} = 2.0$, provides an estimate of the radiation dose to gel, 0.84 Mrad in this case. Since the infrared data we have presented provide a lower limit estimate for the $G$ value for main chain scission based upon the formation of acid fluoride end groups, $G(\mathrm{s}) \simeq 0.34$, then $G(\mathrm{x}) = 0.61$. Since $G(\mathrm{s})/2G(\mathrm{x}) = 0.28 < 2$, gelation is theoretically expected and observed experimentally. Thus, the TFE−PFVME copolymer is one that undergoes both cross-linking and scissioning processes. Since the scissioning process is dominated by loss of the pendant side groups, the "gelation" may have several origins. First, if the pendant $CF_3O$−groups are lost to irradiation, the TFE−PFVME copolymer may simply become more "Teflon-like". The only known solvent[20] for Teflon (poly(tetrafluoroethylene)) is perfluorokerosene at 350 °C; hence, if the copolymer becomes more Teflon-like as a result of the radiation-induced scissioning of the side groups, its solubility in perfluorinated solvents like Fluorinert FC-75, used by Logothetis in the gel experiments, undoubtedly decreases. Conversely, the oxygen-centered radicals that are generated by the irradiation of TFE−PFVME may provide cross-link sites to other chains. The fact that the mechanical property measurements of irradiated TFE−PFVME were compared to chemically cross-link control samples and provided similar results is indicative that cross-linking may have indeed occurred. Further work is required to understand the origins of the cross-linking in these materials.

## Concluding Remarks

We have characterized the electron beam induced scissioning reactions that take place in TFE−PFMVE copolymer, with the knowledge that the material may also cross-link.[5] Thus, when the TFE−PFVME copolymer is irradiated, the bulk material loses weight, gases are produced, and acid fluoride end groups are formed in the bulk. Based upon the oxygen-containing gas products that are formed, $COF_2$, $CF_4$, $CF_3OCF_3$, and $CO_2$, and their $G$ values, 0.31, 0.93, 0.14, and 0.055, respectively, side chain scissioning is apparently prevalent. The formation of acid fluoride end groups, as detected in the infrared spectrum, is indicative that main chain scission in the bulk has also occurred. The $G$ value for formation of −CFO acid fluoride groups in the bulk is 0.34, which is also a lower limit estimate for the $G$ value for main chain scission.

The volatile products that are produced from TFE−PFVME are similar to those produced from polyperfluorinated ethers. In essence, the facile nature of the radiation-induced decomposition of the side chain in the PFVME monomer unit renders the TFE−PFVME copolymer a material that undergoes significant side chain scission and some main chain scission. Decomposition reactions that are initiated in the side group account for all of the major changes in the infrared spectrum.

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