Chem. Mater. **1996,** *8,* 2788−2791

Decomposition of Poly(perfluorinated ethers): Effect of End Groups on Main-Chain Degradation and Product Formation

J. Pacansky* and R. J. Waltman

IBM Almaden Research Center, 650 Harry Road, San Jose, California 95120-6099

Received May 10, 1996. Revised Manuscript Received July 15, 1996[⊗]

The decomposition of polyperfluorinated ether copolymers containing perfluoroethylene oxide, $-CF_2CF_2O-$, and perfluoromethylene oxide units, $-CF_2O-$, capped by different end groups, $-OCF_3$, $-CH_2OH$, and $-O(O{=}C)CH_3$, are investigated. Thus, the polymers are scissioned via an electron beam, and the subsequent chemistry is investigated. In all cases, the polymers lose mass, R−CFO on the ends of scissioned chains are produced, and volatile gases such as COF_2 are evolved. The *G* values for polymer decomposition are 0.2−0.8; for gas evolution are 6−7; and for R−CFO end groups are $\simeq$1.5. The end group $-CH_2OH$ has a significant effect on the chemistry after irradiation. The oligomeric R−CFO groups produced upon irradiation react with the $-CH_2OH$ end groups to produce ester and HF via alcoholysis. The aldehyde −CHO is also produced as a result of direct electron beam irradiation.

Introduction

Polyperfluorinated ethers are viscous liquids which are used in the magnetic recording industry as disk lubricants, as they provide the necessary tribological properties between disk and head, thereby protecting the magnetic media from wear and damage caused by direct head-to-medium contact. Consequently, much research has been devoted to the improvement of lubricant adhesion to the magnetic media surface.[1−3] One approach has been to tailor the polyperfluorinated ether end groups with more polar substituents containing functional groups as carbonyl $-C{=}O$ and hydroxy −OH, to improve bonding on the magnetic media.

From another perspective, chain degradation of the polyperfluorinated ethers has important consequences. For example, the heating of polyperfluorinated ethers in the presence of metals, metal oxides, and Lewis acids catalyze the chain degradation of polyperfluorinated ethers, leading to decreased molecular weights and small molecule products such as COF_2.[4−6] The mechanism which best fits the experimental findings is after a main-chain scission, some β-scissioning reactions occur that ultimately produce acid fluoride groups at the ends of broken chains. Similar products also result when the polyperfluorinated ethers are exposed to electron beams.[7−10] Thus, the electron beam is merely a convenient tool by which main-chain scissioning of the polyperfluorinated ethers is introduced, after which the subsequent chemistry of the liquid may be investigated.

In this report, we continue our studies on the degradation of poly(perfluoromethylene ethylene oxide) (PPFMEO). The materials under investigation differ in their structure primarily by the terminal groups, and their structures and associated acronyms are shown below: poly(perfluoromethylene ethylene oxide) (PPFMEO):

$$CF_3-O-(CF_2-O-)_x-(CF_2CF_2-O-)_y-CF_3$$

a PPFMEO copolymer with −OH end groups, poly(perfluoro methylene ethylene oxide), PPFMEO−OH:

$$HO-CH_2CF_2-O-(CF_2-O-)_x-(CF_2CF_2-O-)_y-CF_2CH_2-OH$$

and another PPFMEO copolymer with $-O(O{=})CCH_3$ ester end groups, poly(perfluoromethylene ethylene oxide) (PPFMEO−Ac):

$$CH_3C({=}O)-OCH_2CF_2O-(CF_2O)_x-(CF_2CF_2O)_y-CF_2CH_2O-(O{=})CCH_3$$

The *x* to *y* ratios for the structures illustrated above are provided in the Experimental Section. We present an analysis for the radiation-induced degradation of PPFMEO, PPFMEO−OH, and PPFMEO−Ac with particular emphasis on the effect of end groups. Thus, changes in the infrared spectra are reported as a function of absorbed dose, from which degradation products are identified, and the efficiencies (*G* values) by which they are produced determined.

Experimental Section

Materials. PPFMEO was obtained from Montedison USA, Inc., under the trademark Fomblin Fluids, Z-15 ($y/x = 0.7$, $M_n = 7200$, $M_w = 13\,400$, $\rho = 1.845$ g/cm^3). PPFMEO−OH and

---

[⊗] Abstract published in *Advance ACS Abstracts,* September 1, 1996.

(1) Ohtani, H.; Lin, L. J.; Seki, H. *Proc. Jpn. Int. Trib. Conf.* 1990.

(2) Saperstein, D. D.; Lin, L. J. *Langmuir* **1990**, *6*, 1522.

(3) Vurens, G. H.; Gudeman, C. S.; Lin, L. J.; Foster, J. S. *Langmuir* **1992**, *8*, 1165.

(4) Sianesi, D.; Zamboni, V.; Fontanelli, R.; Binaghi, M. *Wear* **1971**, *18,* 85.

(5) Chandler, W. L.; Lloyd, L. B.; Farrow, M. F.; Burnham, R. K.; Eyring, E. M. *Corrosion* **1980**, *36*, 152.

(6) Kasai, P. H. *Macromolecules* **1992**, *25*, 6791.

(7) Pacansky, J.; Waltman, R. J.; Wang, C. *J. Fluor. Chem.* **1986**, *32*, 283.

(8) Pacansky, J.; Waltman, R. J.; Maier, M. *J. Phys. Chem.* **1987**, *91,* 1225.

(9) Pacansky, J.; Waltman, R. J. *J. Phys. Chem.* **1991**, *95*, 1512.

(10) Pacansky, J.; Waltman, R. J. *Chem. Mater.* **1993**, *5*, 486.

S0897-4756(96)00274-8 CCC: $12.00

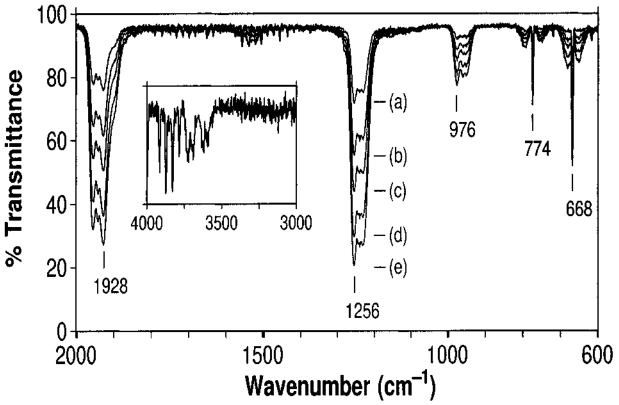

Figure 1. Gas evolution from the 175 kV electron beam irradiation of PPFMEO−OH at room temperature, 1 atm of argon: (a) 17.8; (b) 35.5; (c) 53.3; (d) 82.9; (e) 94.8 Mrad. Inset figure shows the gas-phase spectral region from 4000 to 3000 cm^{-1} after 83 Mrad.

PPFMEO−O(O=)CCH_3 were obtained from Austimont under the tradename ZDOL-2200 ($y/x = 0.7$, $M_w = 2200$, $\rho = 1.750$ g/cm^3) and ZDEAL-2200 ($y/x = 0.7$, $M_w = 2200$, $\rho = 1.770$ g/cm^3), respectively. $OFC-CF_2CF_2CF_2OCF(CF_3)CFO$ was obtained from 3M under the tradename L-9912.

Electron Beam Exposure. Electron beam exposures of the polyperfluoroether samples were achieved using a CB 150 electron processor (Energy Sciences, Inc., Woburn, Mass.). The samples were exposed to a 175 kV electron beam in an atmosphere of nitrogen. After corrections for the various windows and atmosphere between the electron beam gun and sample surface, the energy of the electron beam incident on the sample was 102 kV. A detailed description of the electron beam exposure tools and dosimetry has been given elsewhere.[10] 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, as described previously.[9] 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. Thin films of the polyperfluoroethers were spin-coated from Freon TF onto NaCl disks or Si wafers.

Results and Discussion

Gas Evolution. Gas evolution from the electron beam irradiation of PPFMEO, PPFMEO−OH, and PPFMEO−Ac were investigated. The liquids were separately exposed to the 175 kV electron beam at room temperature under 1 atm of nitrogen, and the evolved gases were collected. A gas-phase infrared spectrum for PPFMEO−OH irradiation as a function of absorbed dose in the liquid is shown in Figure 1 as an illustrative example. Product analyses reveal that carbonyl fluoride, COF_2, is the major stable gas product produced from the irradiation of all three liquids. COF_2 is identified by its characteristic carbonyl C=O stretching vibrations at 1956, 1928 cm^{-1}, and C−F stretches at 1256, 1232 cm^{-1}, as reported in previous works.[7−10] The absorption band at 668 cm^{-1} is identified as carbon dioxide. A comparison of the *G* values for formation of gas product molecules is summarized in Table 1. Here, the *G* value is defined as the number of molecules of gaseous products produced per 100 eV of absorbed energy. The methodology for calculating *G* values from infrared measurements has been outlined previously.[9,10] Briefly, a plot of the changes in the integrated absorbance ($\int \log(T_0/T)\, d\nu$) versus absorbed dose is related to changes in the number of molecules formed or destroyed per absorbed dose. The *G* value for formation of COF_2 from the electron beam irradiation of PPFMEO, PPFMEO−OH, and PPFMEO−Ac liquids are 7.7, 6.2, and 6.0, respectively. CF_4 was also produced in the irradiation of PPFMEO, with a *G* value of 0.35; however, it was not produced from PPFMEO−OH or PPFMEO−Ac. The CF_4 evolution in PPFMEO most probably arises from the CF_3- end groups that cap the polymer, in analogy to the previously observed[10] evolution of CF_4 from poly(perfluoropropylene oxide), $[-CF(CF_3)-CF_2-O-]$, containing CF_3- pendant groups. The CF_3- pendant group is absent in PPFMEO−OH and PPFMEO−Ac. Finally, infrared absorption bands characteristic of hydrogen fluoride[12] have also been detected in the gas phase from the electron beam exposure of PPFMEO−OH, as shown in the inset in Figure 1. In PPFMEO−OH, hydrogen fluoride is presumably generated from the alcoholysis of R−CFO end groups produced in the liquid upon irradiation, to be discussed below. We conclude from the infrared studies that the main-chain scission of the relatively inert polyperfluoroethers renders the physical and chemical properties of the altered materials considerably more reactive by the creation of perfluorinated aldehyde functional groups.

Table 1. *G* Values for the Formation of Gas Products (Data Based upon Three or More Measurements)

liquid	COF_2	CF_4	total
PPFMEO	7.7 ± 0.5	0.35 ± 0.07	8.1
PPFMEO−OH	6.2 ± 0.3		6.2
PPFMEO−Ac	6.0 ± 0.4		6.0

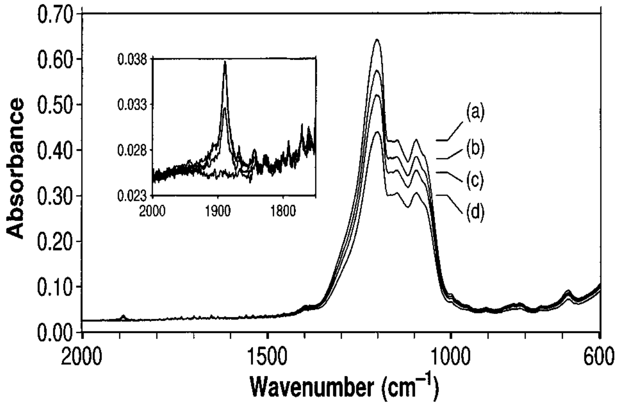

Figure 2. Absorbance infrared spectrum of 0.98 μm PPFMEO film as a function of absorbed dose at room temperature, 1 atm nitrogen: (a) 0; (b) 38.0; (c) 75.9; (d) 113.8 Mrad. The inset figure shows an expanded region of the carbonyl fluoride absorption region as a function of absorbed dose.

Mass Loss. When the polyperfluorinated ether liquids are exposed to a 175 kV electron beam at room temperature and under 1 atm of nitrogen, the major changes observed are mass loss and the formation of R−CFO acid fluoride group(s) in the liquid. Direct mass loss measurements have already been presented.[10] The mass loss and chemical changes may also be observed directly by monitoring the infrared spectrum as a function of absorbed dose (Figure 2) using PPFMEO as the illustrative example. As shown in Figure 2, there is a decrease in the integrated absorbance of the major

---

(11) Wilson, J. E. *Radiation Chemistry of Monomers, Polymers, and Plastics*; Marcel Dekker, Inc.: New York, 1974; p 223.

(12) (a) Atwood, M. R.; Vu, H.; Vodar, B. *Spectrochim. Acta* **1967**, *23A*, 553. (b) Bowers, M. T.; Kerley, G. I.; Flygare, W. H. *J. Chem. Phys.* **1966**, *45*, 3399.

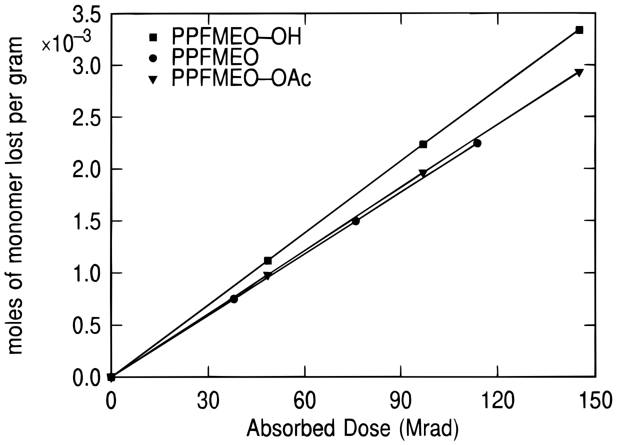

Figure 3. Number of molecules of monomers produced per unit weight of polyperfluoroether, as a function of absorbed dose. Data from infrared spectra of thin films.

Table 2. *G* Values for Monomer Formation and Polymer Decomposition[a]

		IR data		weight loss data	
liquid	*n*	monomer	polymer	monomer	polymer
PPFMEO	81	19.0 ± 5.4	0.23	22.8 ± 0.6	0.27
PPFMEO–OH	25	18.9 ± 3.5	0.76		
PPFMEO–Ac	25	19.5 ± 1.6	0.78		

[a] *n* is the average degree of polymerization. All data based upon three or more measurements.

Table 3. *G* Values for the Formation of R–CFO Oligomers in the Liquid[a]

liquid	thin-film IR	thick-film IR
PPFMEO	1.63 ± 0.08	1.5
PPFMEO–OH	2.01 ± 0.11	1.6
PPFMEO–Ac	1.56 ± 0.10	1.7

[a] All thin film data obtained by infrared analysis based upon three or more measurements.

absorption bands characteristic of PPFMEO, i.e., the 1400–1000 cm^{-1} region. There is also evolution of a band centered at 1885 cm^{-1}, the carbonyl absorption of an acid fluoride group which persists in the liquid. Similar changes are observed after the irradiation of PPFMEO–OH and PPFMEO–Ac. From the changes in the infrared spectra, the number of moles of monomers lost (or decomposed from the polymer) per unit weight of polymer as a function of absorbed dose is presented in Figure 3, for all three polymers. The monomer unit is defined from the polymer stoichiometry and, neglecting end groups, an average monomer unit contains 74 g/mol. The *G* values for monomers lost are on the order of ≃20 for PPFMEO, PPFMEO–OH, and PPFMEO–Ac (Table 2). These values compare favorably with the *G* values obtained directly from direct weight loss measurements.[10] By dividing the *G* value for monomers lost by the average number degree of polymerization, 81 for PPFMEO, and 25 for both PPFMEO–OH and PPFMEO–Ac, the *G* values for polymer decomposition are 0.23, 0.76, and 0.78 for PPFMEO, PPFMEO–OH, and PPFMEO–Ac, respectively. The *G* values are consistent with literature findings.[13,14] The disparity between the *G* values for PPFMEO, 0.23, and PPFMEO–OH and PPFMEO–Ac, 0.76 and 0.78, respectively, is attributable to the differences in the degree of polymerization, as reported previously.[8]

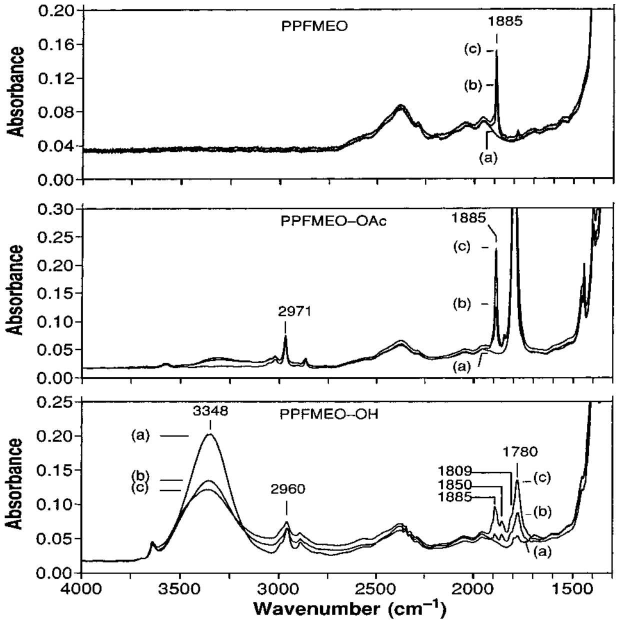

Figure 4. Changes in the infrared absorption spectrum of (top) PPFMEO, (middle) PPFMEO–Ac, and (bottom) PPFMEO–OH as a function of absorbed dose at room temperature, 1 atm N_2. The film thicknesses are 0.029 mm for all samples. PPFMEO: (a) 0; (b) 55.6; (c) 111.1 Mrad. PPFMEO–Ac: (a) 0; (b) 48.0; (c) 120.0 Mrad. PPFMEO–OH: (a) 0; (b) 55.8; (c) 148.8 Mrad.

The *G* value for the formation of the R–CFO end groups in the polymer bulk was determined from the infrared data as presented in Figure 2. The *G* values are summarized in Table 3. They are close to ≃1.6 for all of the polyperfluorinated ethers. If we assume that a single chain scission produces two R–CFO end groups, then the *G* value for main-chain scission is ≃0.8, consistent with the values presented in Table 2.

End Group Effects. The infrared spectra of 0.029 mm thick films of PPFMEO, PPFMEO–OH, and PPFMEO–Ac are shown as a function of absorbed dose in Figure 4. At these film thicknesses, the carbonyl fluoride absorption band at 1885 cm^{-1} is readily observed in all three liquids and is attributed to –CFO groups that have formed on the ends of fragmented chains; see also Figure 2. All of the electron beam exposures and infrared measurements were carried out in a N_2 blanket (1 atm) to prevent hydrolysis of the acid fluoride which would otherwise occur in ambient air. For example, when PPFMEO is exposed to air, the moisture in the air converts the 1885 cm^{-1} –CFO infrared band to the 1770 cm^{-1} –COOH carboxylic acid band. We note that the intense 1790 cm^{-1} absorption band in PPFMEO–Ac is attributed to the acetyl end group (Figure 4b). A comparison of the infrared spectra of all three liquids indicates a dramatic difference in products formed for PPFMEO–OH (Figure 4c). After 55 Mrad, additional absorption bands are observed at 1850, 1809, and 1780 cm^{-1}, which are *not* observed in PPFMEO and PPFMEO–Ac and hence must be associated with effects caused by the –CH_2OH end groups. The decrease in the 3348 cm^{-1} infrared band indicates that the end-group hydroxyl functionality is involved,

---

(13) Barnaba, P.; Cordischi, D.; Delle Site, A.; Mele, A. *J. Chem. Phys.* **1966**, *44*, 3672.

(14) Pacansky, J.; Waltman, R. J.; Pacansky, G. *Chem. Mater.* **1993**, *5*, 1526.

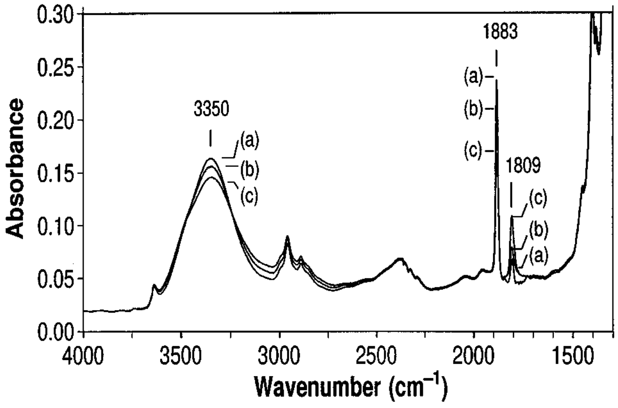

Figure 5. Changes in the infrared spectrum of a mixture of PPFMEO−OH and OFC−$CF_2CF_2CF_2OCF(CF_3)CFO$, as a function of time in a KBr cell: (a) 0; (b) 42; (c) 160 min. The reaction was monitored out at room temperature under 1 atm of N_2.

decreasing significantly as a function of absorbed dose. In an effort to obtain further insight on possible reaction pathways, an additional experiment was carried out. Hence, a nonirradiated, virgin sample of PPFMEO-OH was mixed with the oligomer OFC-$CF_2CF_2CF_2OCF(CF_3)CFO$, containing −CFO end groups, and allowed to react under 1 atm of nitrogen; the mixture was not exposed to an electron beam. The infrared spectrum of the mixture was monitored as a function of time (Figure 5). We observe that both the carbonyl fluoride absorption at 1885 cm^{-1} and the end-group hydroxyl band at 3350 cm^{-1} decrease as a function of time, concomitant with evolution of a new absorption band at 1809 cm^{-1}. The 1809 cm^{-1} absorption is attributed to the ester that is formed from alcoholysis of the two end groups. The 1809 cm^{-1} absorption band center is consistent for the $-CF_2-C(=O)-O-CH_2CF_2-$ carbonyl stretch which has been determined[15] to be centered at 1808 ± 6 cm^{-1}:

$$-CF_2CFO + HO-CH_2CF_2- \rightarrow -CF_2-C(=O)-O-CH_2CF_2- + HF$$

Figure 6 additionally reveals that the decrease in the R−CFO band appears to be kinetically correlated to the increase in the ester band.

In Figure 5, we also note a lack of evolution of the 1780 cm^{-1} infrared band that is prominent in the infrared spectrum of Figure 4c. The 1780 cm^{-1} band is characteristic of a C=O stretching vibration. Since atmospheric moisture is excluded here (see Figure 4a, for example), hydrolysis of the acid fluoride to a carboxylic acid is also excluded, whose C=O stretching frequency would otherwise occur at 1770 cm^{-1}.[7] Since Figure 5 unequivocally illustrates that the only possible reaction product of R−CFO and the alcohol end group is alcoholysis to an ester, the 1780 cm^{-1} band must then arise from the direct electron beam induced decomposition of the $-CH_2OH$ end group. This hypothesis is further supported by comparison of the O−H stretching region in Figures 4 and 5, which show that while alcoholysis results in a gradual decrease in the intensity of the O−H stretching absorption band when left to end-group reactions alone (Figure 5) radiolysis causes a much more efficient decay in the O−H band (Figure 4c). It is well established in the radiolysis of alcohols that a predominant product is aldehyde.[16−18] The mechanism involves an initial cleavage of a C−H bond α to the hydroxyl, followed by decomposition to the aldehyde. The R−CF_2−CHO function is known to have the C=O stretching vibration near 1780 cm^{-1}, approximately 40−60 cm^{-1} higher than alkyl aldehydes.[19]

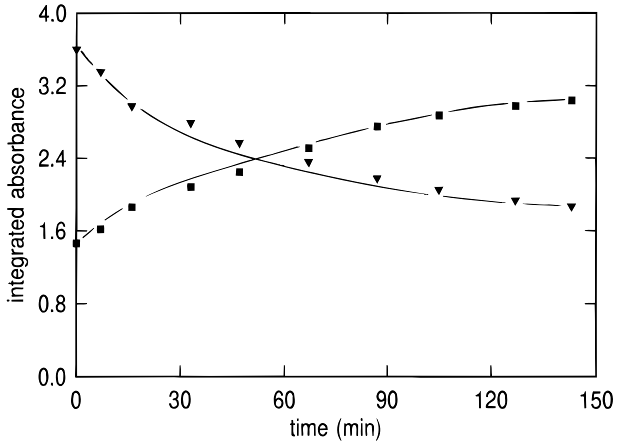

Figure 6. Summary plot of the changes in the infrared spectrum of PPFMEO−OH as a function of time, after exposure to 149 Mrad and left standing in a KBr cell at room temperature under nitrogen: (■) 1809 cm^{-1} ester; (▼) 1891 cm^{-1} acid fluoride.

Conclusions

The experimental studies on radiation-induced main-chain degradation of PPFMEO, PPFMEO−OH, and PPFMEO−Ac reveal that these materials undergo scissioning reactions causing mass loss and evolution of small gaseous molecules such as COF_2. Oligomeric R−CFO caused by broken chains are introduced in the bulk liquid, causing a compromise of its initial chemical and physical properties. Chain scissioning in PPFMEO−OH is additionally complicated by the $-CH_2OH$ end groups which react with the oligomeric R−CFO groups to produce ester and HF. The implication for PPFMEO−OH is, therefore, that while terminal −OH may provide favorable bonding to magnetic media, chain scission will produce HF even under inert atmospheric conditions, thereby compromising significantly the initial physical and chemical properties of the liquid.

CM960274E

---

[15] Rappaport, G.; Hauptschein, M.; O'Brien, J. F.; Filler, R. *J. Am. Chem. Soc.* **1953**, *75*, 2695.

[16] McDonnell, W. R.; Newton, A. S. *J. Am. Chem. Soc.* **1954**, *76*, 4651.

[17] Hayon, E.; Weiss, J. J. *J. Chem. Soc.* **1961**, 3962.

[18] Taub, I. A.; Dorfman, L. M. *J. Am. Chem. Soc.* **1962**, *84*, 4053.

[19] Weiblen, D. G. In *Fluorine Chemistry*; Simons, J. H., Ed.; Academic Press Inc.: New York, 1954; p 449.