Journal of Fluorine Chemistry, 32 (1986) 283–297

Received: December 28, 1985; accepted March 12, 1986

IRRADIATION OF POLY(PERFLUOROPROPYLENE OXIDE) BY A 175 KV ELECTRON BEAM: THE FORMATION AND HYDROLYSIS OF ACID FLUORIDE GROUPS

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SUMMARY

Poly(perfluoropropylene oxide), $-(CF(CF_3)CF_2O)_n-$, was exposed to a 175kV electron beam while under a blanket of N_2 at atmospheric pressure. The electron beam induced chemistry was spectroscopically analyzed using infrared techniques. The IR analysis revealed that acid fluoride groups were formed by the electron beam exposure which rapidly hydrolyzed to form a carboxylic acid and HF. Viscosity studies on the irradiated material show that the net effect of the electron beam exposure is to initially reduce the viscosity; when the irradiated material is exposed to air the viscosity increases as a function of the time in contact with the atmosphere. These latter viscosity changes are attributed to the hydrolysis reaction.

INTRODUCTION

Due to their exceptional chemical and physical stability, polyperfluoroethers are used extensively in industry as lubricants [1], dielectric fluids [2], diffusion pump oils [3] and, due to their high O_2 solubility [4], as blood substitutes [5]. While these materials have desirable chemical and physical properties, they are nevertheless relatively sensitive to high energy electron beams, x-rays and gamma radiation [6]. This sensitivity, coupled with their chemical inertness, presents a number of technological problems in areas requiring the use of high energy radiation as, for example, in the curing of coatings, and in radiation induced polymerizations. Most of the problems generally arise from materials analysis requiring high energy radiation and, in particular, the analysis of chemical products as a result of thermal or radiation degradation. This latter point is a direct result of the extreme insolubility of the materials which renders routine chemical analysis a difficult task.

0022-1139/86/$3.50

In this report, the high energy (175 kV) electron beam chemistry of poly(perfluoropropylene oxide), hereafter called PPFPO, is studied. We discuss several aspects of the electron beam chemistry at this point because of the technological importance of the results. We show that acid fluoride groups are introduced at ends of fragmented PPFPO polymer chains making it possible to chemically modify the otherwise relatively chemically inert material. In addition, studies are presented that show electron beam irradiated PPFPO is hygroscopic (in comparison to the virgin polymer) and that the hydrolysis reaction has a large effect on viscosity.

EXPERIMENTAL

PPFPO was obtained from Montedison USA Inc. (1114 Avenue of the Americas, New York, NY 10036). PPFPO has the trade name Fomblin YR and has a viscosimetric average molecular weight of 6,000 - 7,000 and a kinematic viscosity of 1,000 to 2,000 centistokes. More recently, Cantow *et al.* [7] have characterized the dynamic viscosity of PPFPO and have related it to its weight average molecular weight M_w. An average polydispersity index $M_w/M_n = 1.38$ was also found [7], thereby establishing a relationship between dynamic viscosity and M_n, the number average molecular weight. Accordingly, the dynamic viscosity at 25°C of PPFPO was measured utilizing a Ferranti-Shirley Cone Plate Viscometer; the calibration standards against which the viscosity was determined were 51.02 and 1783 centipoise (cp) standards obtained from Cannon Instruments. The viscosity of PPFPO was found to be 1675 cp, corresponding to a $M_n = 5{,}020$.

The equipment used for the electron beam exposures was a CB 150 Electrocurtain Processor (Energy Sciences Inc., Woburn, Mass.) that permits the exposure of samples in the presence of air or an inert atmosphere such as N_2. The major components of the Electrocurtain are a shielded conveyor which transports samples through the processor, and an electron beam gun which is capable of operating at accelerating voltages between 150 to 175kV. The filament in the gun is shaped in the form of a cylindrical rod, thus, when electrons are extracted from the gun a planar-like beam is formed perpendicular to the direction of the sample. A brief schematic of the apparatus is shown in Figure 1.

Samples of the liquid poly(perfluoropropylene oxide) PPFPO for chemical analysis were prepared for irradiation using the sample tray shown in Figure 2. A well of 3 mil depth (1 mil ~ 25μm) and of an area equal to 161 cm^2 was machined into a stainless steel block. Several milliliters of the sample were placed on the tray to flood the well, and the sample thickness was brought to 3 mils by pulling a straight-edge across the sides of the well. After the sample was exposed to the 175kV electron beam it was collected and stored in capped bottles for analysis. During the sample preparation, and exposure,

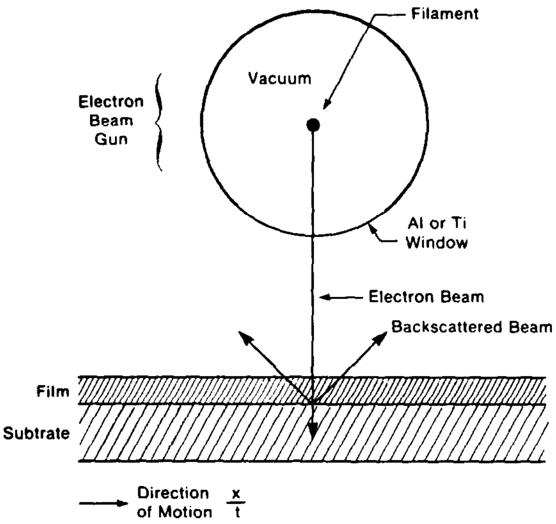

Fig. 1. A schematic showing the major components of an electron beam exposure tool. The electron beam gun emits electrons sequentially into an inert atmosphere and then into a film that is coated on a substrate moving in the x direction.

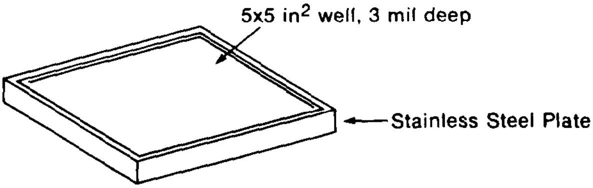

Fig. 2. The apparatus used to expose liquid PPFPO to a known thickness. The tray was machined to the proper depth. The trough-like nature allows one to pull a straight edge over the top to attain the correct film thickness.

experience showed that it was very important to keep the samples in an atmosphere as free as possible from water vapor, consequently samples were prepared and stored under a blanket of dry N_2 as much as possible.

The sample thickness, 3 mils (75μm), was chosen to irradiate the largest quantity of sample as possible without exceeding the Grün range R_G, for energy deposition. These parameters and the usual geometry employed in the exposure of a thin film are illustrated in Figure 3. A beam of electrons with energy E_o and current I, travelling in the z direction, is incident normally on a film with thickness z = t. The maximum depth to which energy is dissipated by the electron beam is given by the Grün range [8]:

$$R_G = (0.049/\rho)\ E_o^{1.75} \tag{1}$$

where E_o is the incident electron beam energy in kV, ρ is the density in gm/cm^3 and R_G is the Grün range for the electron beam in microns (μm). The rate of energy dissipation is obtained from:

$$\frac{dE}{dz} = (-E_o/R_G)\Lambda(f) \tag{2}$$

where Λ(f) is the depth dose function [9]:

$$\Lambda(f) = 0.6 + 6.21f - 12.4f^2 + 5.69f^3 \tag{3}$$

and $f = z/R_G$. The energy of the beam at a depth in the film, z, is readily found by integrating Equation (2) as given below:

$$E(z) = E_o - \int_0^z \left(\frac{dE}{dz}\right)dz \tag{4}$$

The depth dose function dE(z)/dz, which relates the rate of energy dissipation as a function of penetration z in the direction perpendicular to the film, is of primary importance. This is illustrated in Figure 3 along with E(z), the beam energy at a depth z, for an incident beam voltage of 175kV. The value for each of the parameters at z = 75μm is indicated in the figure, and relates the energy dissipation and beam energy in a plane normal to the z-axis at a depth of 75μm.

In a separate set of experiments the infrared spectrum of PPFPO was recorded as a function of absorbed dose. For these, thin films of PPFPO (~1-3μm) were spin coated onto Si substrates and the IR spectra were obtained using a Perkin-Elmer 621 IR spectrometer. The thickness of the PPFPO films were controlled from Figure 4, which shows a plot of the optical density of the characteristic IR bands in PPFPO as a function of film thickness. The optical constants for PPFPO, such as the complex refractive index, molar absorbtion coefficient, etc., were given in a previous report [10].

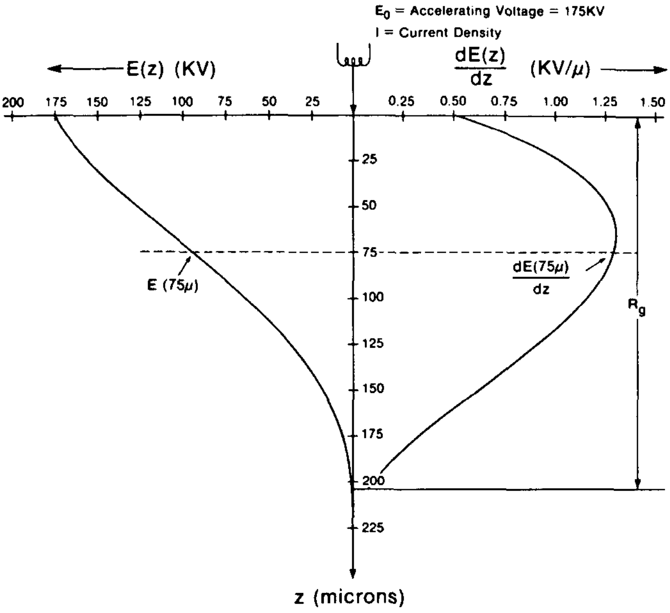

Fig. 3. The depth dose curve for the penetration depth for energy dissipation, R_G, the rate of energy dissipation, dE/dz, and the beam energy at a particular depth in the film, E(z).

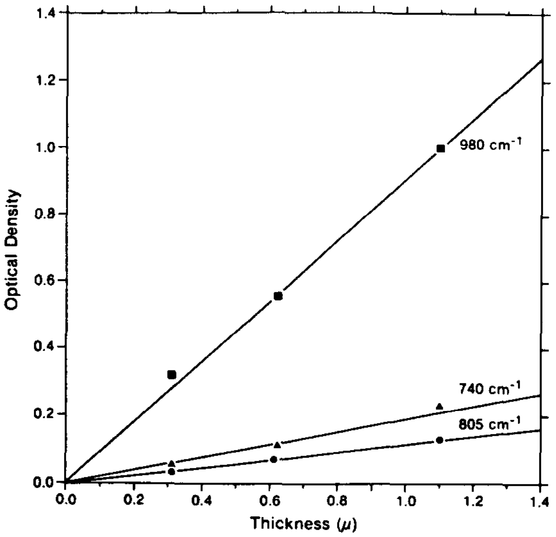

Fig. 4. A plot for the optical density versus thickness for several infrared absorptions in PPFPO.

The Si substrates were obtained from General Diode Corp., Framington, Mass., and were polished on both sides and tapered (8 - 12 mils) in order to eliminate interference fringes. Spectra were always recorded using an identical wafer in the reference beam of the spectrometer. Exposure of the bare silicon substrates to the 175kV electron beam for doses of up to 1000 Mrad showed no new infrared absorptions.

The silicon substrates were useful for chemical treatment of the irradiated samples. Using the silicon as a substrate permitted the samples to be treated to water vapor, aqueous NaOH, and NH_4OH by submerging the silicon substrate containing the irradiated poly(perfluoropropylene oxide) in each reagent. The infrared spectrum could thus be recorded before and after the treatment to follow the chemical change exhibited by the PPFPO.

Dosimetry

The absorbed dose was measured using the aminotriphenyl methane dye-doped nylon plastic films that give rise to an absorption at 510nm when exposed to high energy radiation. The films, obtained from Far West Technology, Inc. [11], have a thickness of 50μm. The absorption at 510 and 600nm has been studied and calibrated against absorbed dose by McLaughlin [12] and Humpherys [13]. The absorbed dose was found by running a dye containing film in tandem with the sample tray. The holder used for the actinometric film, shown in Figure 5, consists of a 7μm Al foil placed over the film to protect it from oxidation when under the electron beam, and a bulk steel substrate underneath the film to obtain the contribution to the absorbed dose from backscattered electrons. Accordingly, the actinometric film was exposed to the 175kV electron beam under conditions identical to PPFPO, *i.e.*, the same line speed, voltage and current was

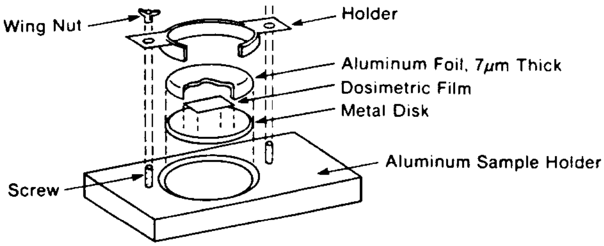

Fig. 5. The sample holder used to electron beam irradiate films of PPFPO, and to perform dosimetry.

used. The exposures performed in this manner could only exhibit changes that were a manifestation of the dose received by electrons backscattered from the steel substrate. The backscattering coefficient of a substrate as defined by Darlington [14] is:

$$\eta = \frac{\textit{number of backscattered electrons}}{\textit{total number of incident electrons}} \tag{5}$$

The optical density at 510nm was recorded on a Perkin-Elmer UV-visible spectrophotometer. These data are summarized in Figure 6. Curve (b) indicates the change in the optical density at 510nm of the actinometric film as a function of absorbed dose when placed upon a metallic substrate with a low backscattering coefficent, *i.e.* Be whereby η_{Be}=0.042, thus yielding a color-dose calibration plot. However, for a thin film (defined as ~10-15% of R_g) backscattering of electrons from the metal substrate, in this case steel, underneath the actinometric film is significant since η_{steel}=0.265, and will contribute to the absorbed dose. This is illustrated by the (experimental) curve (a), which may be translated along the dose axis by a factor of $(1 + \eta_{steel} - \eta_{Be})$ to coincide with curve (b). Thus, the absorbed dose received by a thin film on any metallic substrate may be corrected for by their respective backscattering coefficient.

In order to determine the absorbed dose by PPFPO, a further correction which accounts for the differences in polymer film density and elemental composition must be

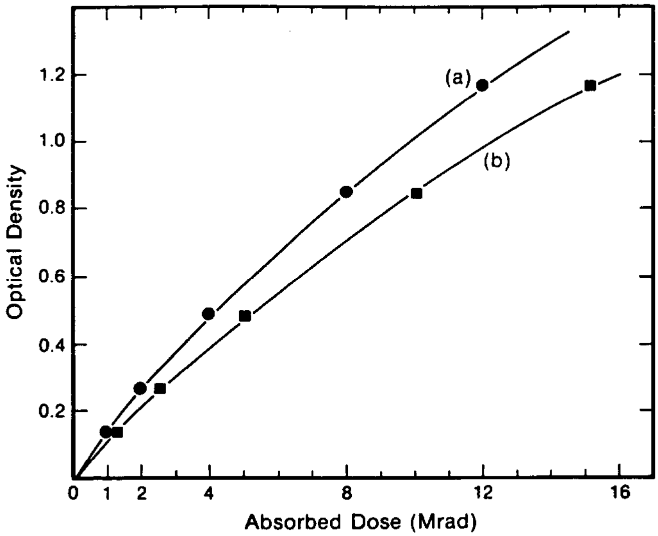

Fig. 6. A plot for the optical density of the dosimetric film as a function of absorbed dose: (a) for a steel substrate used in the experiment, and (b) for a Be substrate with a small backscattering coefficient.

invoked [15]. The absorbed dose by PPFPO, D_s, is determined by multiplying the absorbed dose obtained from the dosimeter, D_d, by the stopping power of the sample integrated over the PPFPO film thickness h_s, and dividing by the stopping power of the dosimetric film integrated over its thickness h_d. This is given by:

$$D_s = D_d \frac{\rho_d h_d}{\rho_s h_s} \left\{ \frac{\int_0^{h_s} (dE/dS)_s \, dS_s}{\int_0^{h_d} (dE/dS)_d \, dS_d} \right\} \tag{6}$$

where $(dE/dS)_s$ and $(dE/dS)_d$ are the stopping powers for PPFPO and the dosimetric film, respectively, and ρ_s and ρ_d are the densities for PPFPO and the dosimetric film, respectively. Equation 6 then allows evaluation of the true absorbed dose of PPFPO utilizing the actinometric film to calibrate the dose.

RESULTS AND DISCUSSION

Radiation Induced Damage in PPFPO.

The IR spectrum of a thin film (~0.35μm) of PPFPO spin coated onto a Si wafer is shown in Figure 7. Due to the perfluorinated nature of the material no major absorptions appear at frequencies higher than ~ 1400 cm^{-1}; as shown below this facilitates the identity of the radiation induced products. The infrared spectrum of PPFPO contains several characteristic spectral features; the absorptions for the CF_3 and CF_2 stretching modes at ~ 1300 cm^{-1}; the bands for the C-O-C ether stretching motions at ~ 1100 cm^{-1}, and the relatively narrow, isolated feature at 980 cm^{-1} associated with the perfluormethyl group.

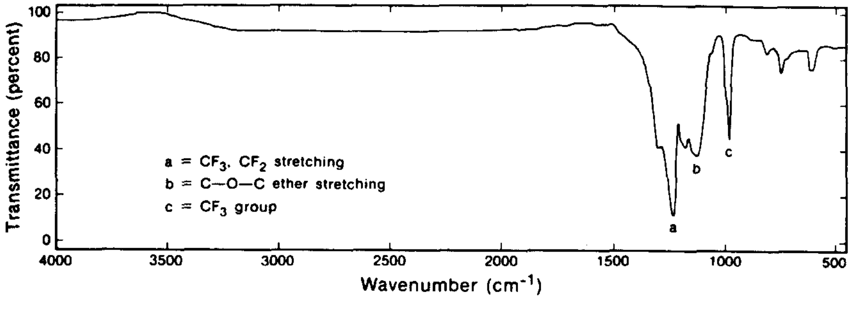

Fig. 7. The infrared spectrum of PPFPO coated on a silicon wafer; thickness = ~0.35μm.

Thin films of PPFPO, whose infrared spectra were identical to the one displayed in Figure 7, were exposed to a 175 kV electron beam; however, since the only spectral change that was observed was a band with ~ 5 per cent transmittance at 1885 cm^{-1}, thick films were taken for analysis. The infrared spectrum of a thick film (~3.5μm) of PPFPO coated on a silicon substrate is shown in Figure 8. This spectrum thus serves as a baseline from which new spectral features will be observed. In Figure 9 we show a series of infrared spectra obtained by overlaying thick film PPFPO spectra after exposure to a 175 kV electron beam (dose rate = 20.3 Mrad/sec) to doses = 40, 92, 277 and 462 Mrad. To the best of our ability to detect changes in the infrared using standard dispersive spectrometers the only radiation induced band observed is the one centered at 1885 cm^{-1}. This band and the dose required to form the new material responsible for its absorption is shown in Figure 9.

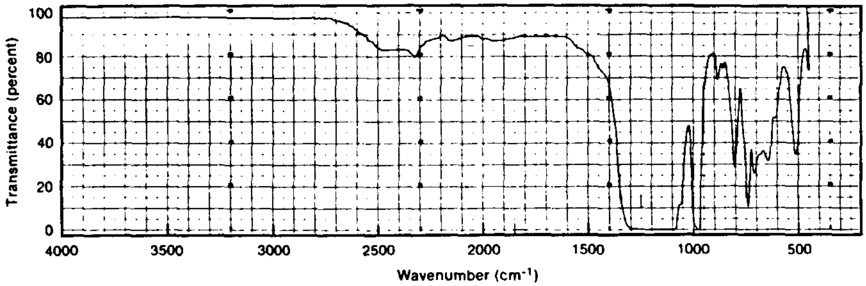

Fig. 8. The infrared spectrum of a thick film of PPFPO coated on a silicon wafer; thickness = ~3.5μm.

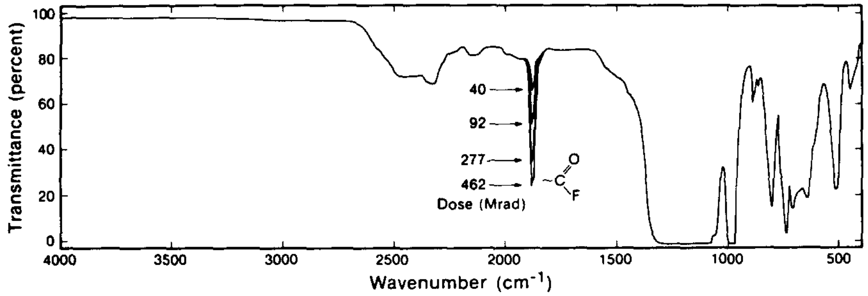

Fig. 9. The infrared spectrum of PPFPO after electron beam irradiation. The only significant change is the new band at 1885 cm^{-1}. The absorbed dose required to increase the absorption of the 1885 cm^{-1} feature is indicated in the Figure.

The radiation induced band centered at 1885 cm^{-1} is identified as a carbonyl absorbtion of an acid fluoride group on the basis of the following evidence: acid fluoride groups characteristically occur at this frequency [16,17] and the electron beam exposure of poly(tetrafluoroethylene) produces similar absorptions also assigned to acid fluoride groups but produced by way of a subsequent oxidation step [18]. The acid fluoride groups produced during the electron beam exposures of PPFPO reported herein are not formed via an oxidation step. In order to investigate this aspect, irradiations were conducted using samples which were repeatedly degassed in a vacuum system and backflushed with high purity nitrogen; these exposures were performed under a blanket of nitrogen and gave the same dose dependence and IR spectral features regardless of dose rate or of conditions of exposure.

In order to unequivocally assign the 1885 cm^{-1} band to the acid fluoride group, thin films of PPFPO on Si were separately treated to steam, aqueous NaOH and NH_3 vapor from a NH_4OH solution. When an acid fluoride group is exposed to water vapor or immersed in water, it undergoes hydrolysis to the carboxylic acid whose characteristic

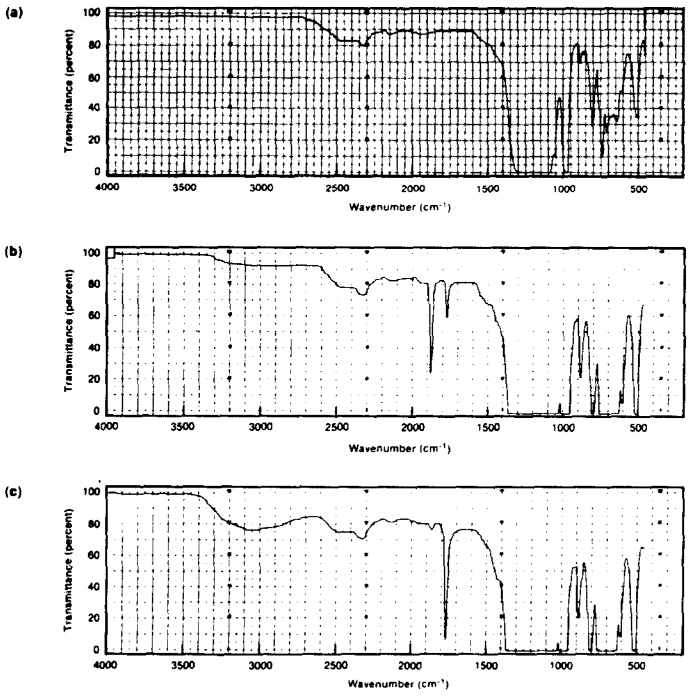

Fig. 10. a) the infrared spectrum of PPFPO before irradiation; b) the infrared spectrum recorded after receiving an absorbed dose equal to 280 megarads and exposure to moist air for a brief period; and c) the infrared spectrum recorded after receiving an absorbed dose = 280 megarads and exposed to steam for three hours.

absorption appears at 1770 cm^{-1} for perfluorinated carboxylic acids. Figure 10 contains several spectra demonstrating the conversion of the radiation induced acid fluoride groups to carboxylic acid groups. Figure 10a is the spectrum of PPFPO before irradiation while Figure 10b is the spectrum after receiving a 280 megarad dose and partial hydrolysis by exposure to moist air. Note that the acid fluoride absorption is still present and an absorption due to a carboxylic acid appears. The characteristic absorption for the latter is accompanied by the broad absorption for the acid -OH groups which appears at higher frequencies. The last spectrum, Figure 10c, is the spectrum recorded after an irradiated sample (280 megarads) was brought into contact with steam for three hours. In this case the acid fluoride groups have been completely hydrolyzed to carboxylic acid. The PPFPO films containing the hydrolyzed or non-hydrolyzed acid fluoride groups were then immersed into an aqueous solution of NaOH; the IR spectrum recorded after treatment with aqueous NaOH, shown in Figure 11a, contains two important features. The first is the carboxylic acid band due to partial hydrolysis of the acid fluoride at 1770 cm.$^{-1}$. The second is the broad band in the region of 1600 cm^{-1} due to a carboxylate anion; the latter is formed by an acid-base reaction. Again, these results are consistent with an acid fluoride precursor. Finally, when electron beam exposed PPFPO is brought into contact

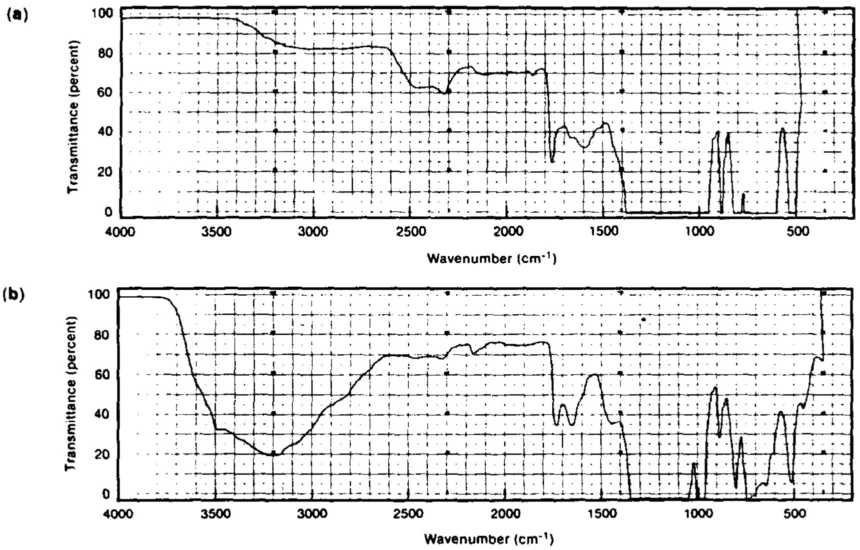

Fig. 11. a) The infrared spectrum recorded after PPFPO was irradiated to a dose = 280 megarads, and subsequently exposed to water vapor and then immersed in an aqueous NaOH solution; b) the infrared spectrum of PPFPO recorded after exposure to a 280 megarad dose and allowed to set over a solution of aqueous NH_4OH for eight hours.

with NH_3 vapor from an aqueous solution of NH_4OH, new bands at 1440 and 3150 - 3250 cm^{-1} appear, which may be attributed to ammonium ion absorption. The corresponding carboxylate anion appears at ~ 1650 cm.$^{-1}$ Thus, it is evident from the chemistry of the exposed PPFPO film that the acid fluoride group is indeed the primary species formed upon electron beam exposure; the plot for the relative absorbance of the 1885 cm^{-1} band versus absorbed dose shown in Figure 12, appears to be linear and hence supports this contention.

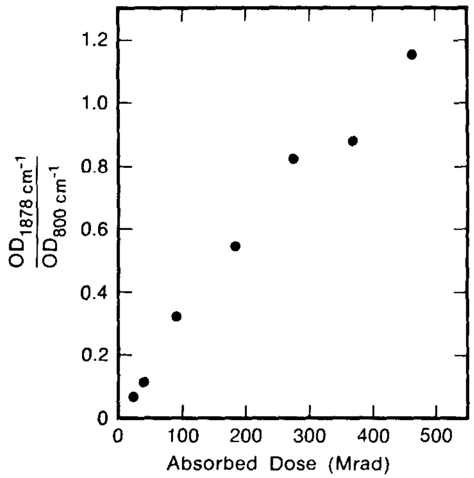

Fig. 12. The optical density of the 1878 cm^{-1} band relative to the 800 cm^{-1} as a function of absorbed dose (Mrad).

The hydrolysis of an acid fluoride must also produce HF. Hydrogen fluoride is of course a very corrosive material and, because of this, we tried to detect its formation after hydrolysis, but were unsuccessful.

As mentioned in the Introduction PPFPO is used extensively in industry. One important application is as a lubricant where changes in chemical and physical properties may affect the performance of a device. Since it has been reported that a product of the thermal degradation of PPFPO is also an acid fluoride terminated polymer chain a study was performed on the viscosity changes occurring after introduction of -CFO groups by electron beam exposure. These studies are not only important technologically but are also important for molecular weight measurements. PPFPO was exposed to a 175 kV electron beam under a blanket of dry nitrogen. The viscosity of the irradiated liquid was then measured under anhydrous conditions to obtain a value for PPFPO with acid fluoride.

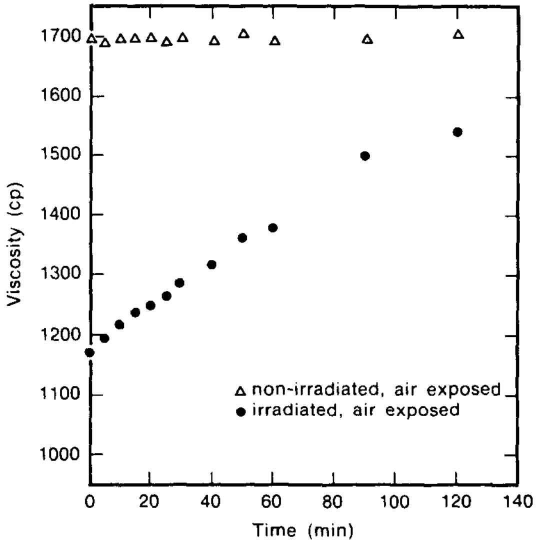

Fig. 13. A plot of the viscosity of irradiated and non-irradiated PPFPO as a function of time in air (T = 25°C). The irradiated PPFPO received a dose = 245 megrads. The irradiation was performed under dry conditions to prevent hydrolysis of the acid fluoride.

Subsequently, this sample was allowed to set under ambient conditions to permit diffusion of water vapor from air and to the acid fluoride groups within the PPFPO. The viscosity of a control was also measured; this sample was merely unirradiated PPFPO. The results of the viscosity versus time measurements are shown in Figure 13. The viscosity of the unirradiated PPFPO shown at the top of Figure 13 remains constant; the fluctuations that are observed are believed to be due to experimental reproducibility. The change in the viscosity of PPFPO when irradiated by the 175 kV electron beam, shown at the bottom of Figure 13, reveal that the viscosity of PPFPO decreases as a function of increasing absorbed dose, as indicated by the point at t = 0, ie., before being brought in contact with water vapor in air. As summarized in Figure 13 the viscosity of the irradiated PPFPO dramatically increases as a function of time in air, and tends to approach the viscosity of the unirradiated material. The initial change in viscosity for the irradiated material at t = 0, is attributed to a lowering of molecular weight by radiation induced main chain scission; the subsequent increase in the viscosity is the result of the hydrolysis of the acid fluoride to carboxylic acid groups, and hence is a reflection of the hygroscopic nature of the electron beam irradiated material. The carboxylic acid groups thus formed associate to produce hydrogen bonded chains of PPFPO. This was supported by studying the disappearance of acid fluoride groups via IR spectrometry. Films of PPFPO coated on Si disks were exposed to 280 megarads under anhydrous conditions. The hydrolysis of the acid fluoride groups was followed by recording the decay in absorbance of the 1885 cm^{-1} band as a function of time in air. These results summarized in Figure 14 show that there is a considerable decrease in the number of acid fluoride groups during the time of the viscosity measurements.

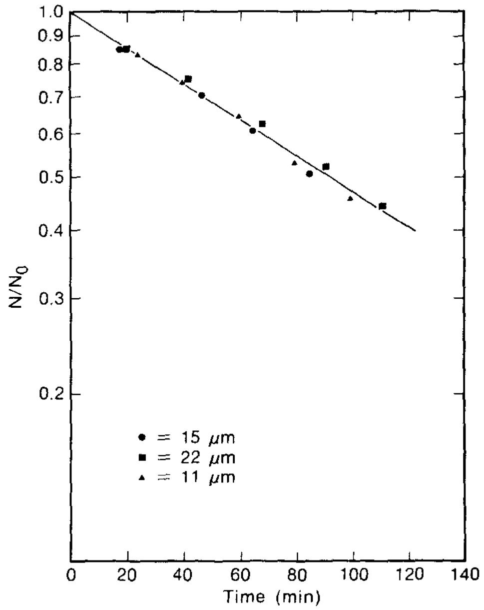

Fig. 14. A semilog plot of the optical density of the acid fluoride absorbtion normalized to its absorption before exposure to the water vapor in air. Note that within the range of film thickness studied the fraction of acid fluoride groups surviving hydrolysis appears to be independent of film thickness.

CONCLUSION

When poly(perfluoroether) is exposed to an electron beam, its viscosity decreases as a function of increasing absorbed dose, due to decreasing molecular weight. IR spectrometry of the exposed PPFPO reveal that the acid fluoride group is the primary species formed. This is confirmed by treating the acid fluoride group to water vapor, aqueous NaOH and NH_4OH. Their subsequent IR spectra reveal the formation of carboxylic acid, carboxylate and ammonium ions, respectively, consistent with an acid fluoride precursor. This result has important technological consequences in so far that a functional group may be introduced at the ends of a poly(perfluoroethers) chain, and hence facilitate further chemical modifications of a relatively inert material.

Viscosity measurements show that the molecular weight of PPFPO decreases and when acid fluoride groups are present the viscosity is a function of the extent of the hydrolysis reaction. Thus, the viscosity not only depends upon the concentration of the acid fluoride groups originally present but also upon humidity and time in air.

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