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NMR Study of the Radiation-Induced Cross-Linking of Poly(tetrafluoroethylene-*co*-perfluoromethyl vinyl ether)

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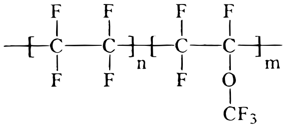
ABSTRACT: The γ-radiolysis of poly(tetrafluoroethylene-*co*-perfuoromethyl vinyl ether) (TFE/PMVE) was investigated using solid state ^{19}F and ^{13}C NMR spectroscopy. Chain scission products identified in the polymer were saturated chain ends $-CF_2CF_3$ ($G = 1.0$), methyl ether end groups $-CF_2OCF_3$ ($G = 0.9$), acid end groups $-CF_2COOH$ ($G = 0.5$), and a small amount of terminal unsaturation $-CF{=}CF_2$ ($G = 0.2$). A mechanism for the formation of these scission products was proposed and the G value for main chain scission, G(S), was determined to be 1.4. Cross-linking of TFE/PMVE was found to proceed via a Y-linking mechanism. The G value for cross-linking, G(X), was determined to be 0.9. A maximum of 0.2 mol % cross-links were formed under the experimental conditions.

Introduction

The radiolysis of poly(tetrafluoroethylene) (PTFE) has been extensively studied and it has been shown to degrade rapidly when irradiated in vacuum and air at room temperature.[1−3] This has been attributed to the limited chain mobility resulting from highly ordered, linear chains and the absence of branching.[4] Only recently has PTFE been shown to cross-link when irradiated in vacuum and with increased chain mobility above the T_m of 600 K.[5−8] The importance of chain mobility on the radiation chemistry of fluoropolymers was first investigated by Lovejoy et al.[9] for the radiolytic cross-linking of poly(tetrafluoroethylene-*co*-hexafluoropropylene) (FEP).

In order to increase the chain mobility of PTFE at room temperature, a copolymer possessing side chains may be introduced into the polymer to disrupt chain packing.[10] One such copolymer is poly(tetrafluoroethylene-*co*-perfluoromethyl vinyl ether) (TFE/PMVE) which contains approximately 30 mol % of the vinyl ether monomer. This amorphous perfluoroelastomer (Figure 1) is marketed by Du Pont Dow Elastomers L. L. C. under the trade name Kalrez. Since the high chemical stability of PTFE is derived from the strong carbon−fluorine bond, incorporation of the perfluorinated comonomer PMVE maintains the high chemical stability in the copolymer. Radiolysis of the elastomer above the glass transition temperature leads to an increased opportunity for chain radicals to recombine producing cross-links between the polymer chains. TFE/PMVE is usually cross-linked by chemical methods,[10−12] which utilize the incorporation of a small amount of a cure site monomer. However chemical cross-linking produces unwanted contaminants, restricting its use in applications such as in the semiconductor industry. It is therefore envisaged that radiation cross-linking could provide a much cleaner, cross-linked end product.[13]



$$-[CF_2-CF_2]_n-[CF_2-CF(OCF_3)]_m-$$

Figure 1. Structure of TFE/PMVE random copolymer.

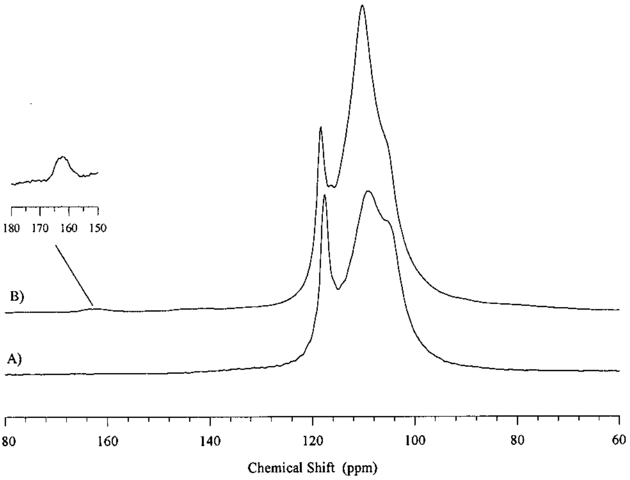


Figure 2. ^{13}C NMR spectra of TFE/PMVE (A) unirradiated and (B) γ-irradiated to 2000 kGy. A new absorbance was identified at 162.0 ppm and assigned to new carboxylic acid chain ends ($-CF_2COOH$)

In 1984, Uschold,[14] while attempting to graft vinyl monomers onto electron beam irradiated TFE/PMVE, found that the fluoroelastomer cross-linked, forming an insoluble network. Uschold found that the mechanical properties of irradiated TFE/PMVE were inferior when compared to the chemically cross-linked analogues, because of simultaneous scission reactions in the irradiated polymer. The radiation cross-linking of TFE/PMVE was also briefly studied by Luo et al.[15] and later by Sun et al.,[16] who looked exclusively at the sol/gel behavior. Pacansky et al.[17] identified and quantified

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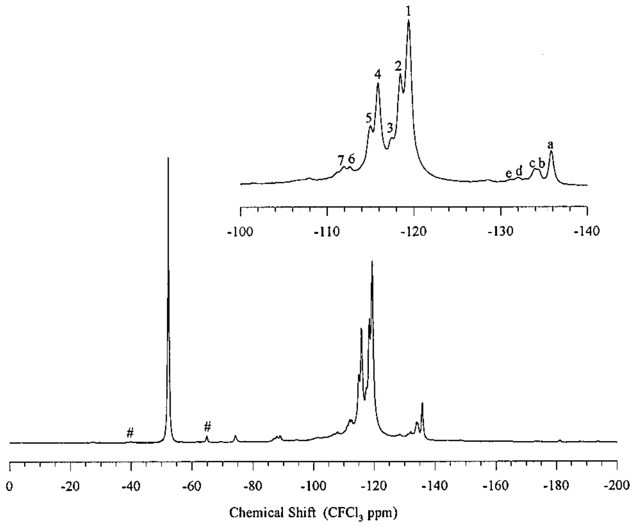

Figure 3. ^{19}F NMR spectrum of unirradiated TFE/PMVE. The spectrum was acquired at 420 K. Peaks marked # represent spinning side bands. Sequence distributions of the $-CF_2$ and $-CF$ resonances have been expanded and are given in Table 1.

the volatile products from electron beam irradiated TFE/PMVE to be CF_4, COF_2, CO_2, and CF_3OCF_3 with *G* values of 0.93, 0.31, 0.055, and 0.14 respectively, using GCMS, FTIR, and weight loss measurements. The *G* value for side chain scission and main chain scission was calculated to be 1.11 and 0.34, respectively. The *G* value is defined as the number of events or product formed for every 16 aJ (100 eV) of absorbed energy.[18] Logothetis[19] investigated the effect of radiation sensitizers randomly incorporated along the polymer chain on the radiation chemistry, but he found little difference in the cross-linking efficiency. Logothetis concluded from the high chemical resistance of the cross-linked elastomer that the cross-link was a carbon−carbon bond. In all previous investigations of the radiation chemistry of TFE/PMVE, the exact identity of the cross-link has remained unidentified.

Recently, Lyons[20] reviewed the radiation chemistry of fluoropolymers and showed that most research was solely focused on the physical properties of the cured material and little had been concluded about the radiolytic processes of fluoropolymers. This has mainly stemmed from their poor solubility, thereby limiting characterization by conventional techniques.

High-temperature, high-resolution NMR has successfully been used in highly accurate compositional analysis of fluoropolymers such as FEP.[21] Poliks[22] determined microstructural information of poly(tetrafluoroethylene-*co*-2,2-bis(trifluoromethyl)-4,5-difluoro-1,3-dioxole) (Teflon AF) using C−F CP-MAS. Tonelli et al.[23,24] obtained ^{13}C and ^{19}F chemical shifts and the microstructure of poly(vinylidene fluoride) (PVDF), poly(fluoromethylene) (PFM), poly(vinyl fluoride) (PVF), and poly(trifluoroethylene) (PTrFE). Hewes et al.[25] used ^{19}F and ^{13}C MAS NMR spectroscopy to follow the direct fluorination of ion exchange resins. Plasma-polymerized tetrafluoroethylene (PPTFE) was shown to consist of a highly branched cross-linked network using ^{19}F NMR.[26] The high-resolution ^{19}F magnetic resonance of solids has been reviewed by Harris and Jackson.[27]

In this study we have shown that the problems of investigating the radiolytic changes in insoluble fluo-

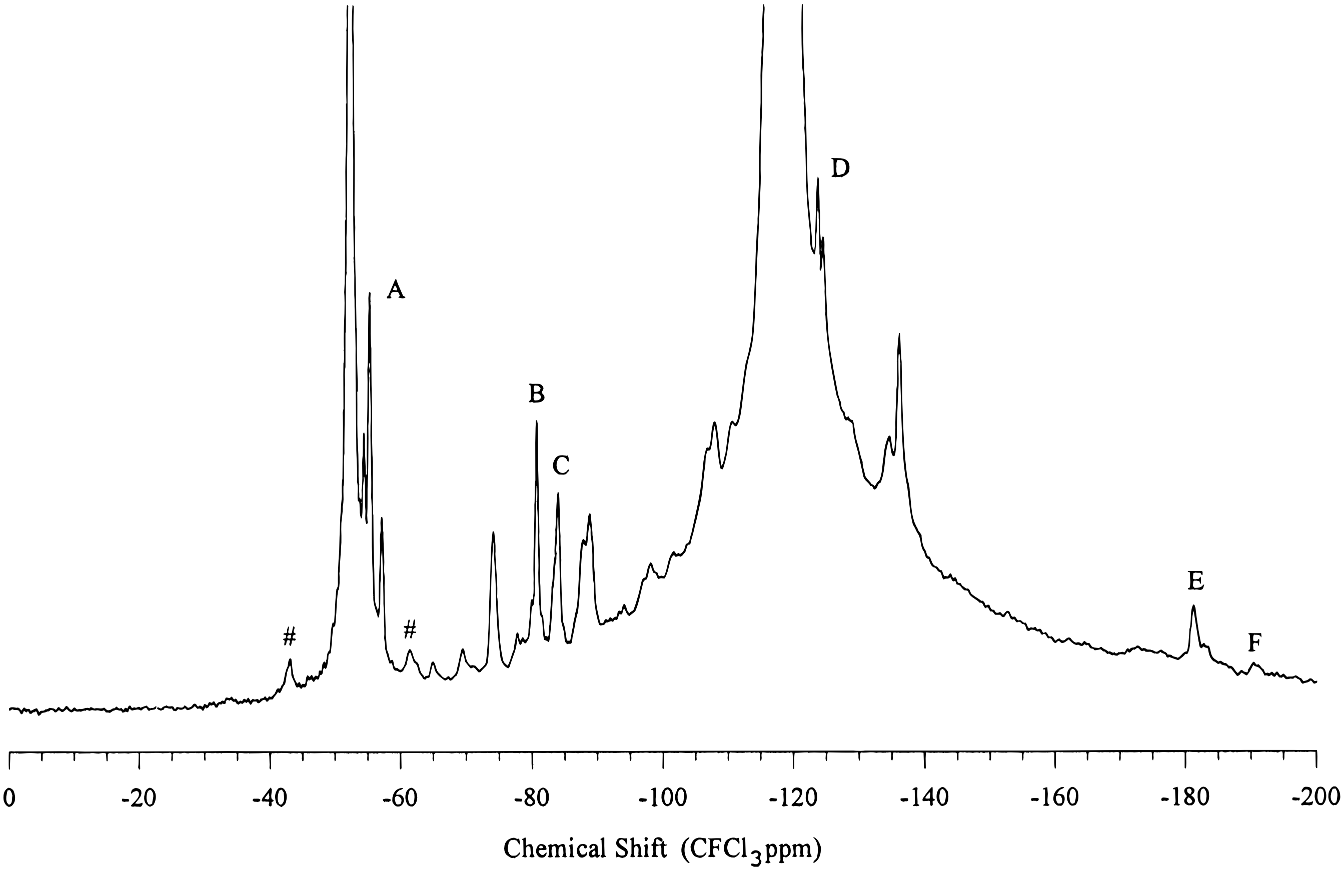

Figure 4. ^{19}F NMR spectrum of TFE/PMVE γ-irradiated to 4200 kGy. The spectrum was acquired at 420 K. New functionalities include (A) $-CF_2OCF_3{}^*$, (B) $-CF_2-CF_3{}^*$ (C) $-CF_2{}^*OCF_3$, (D) $-CF_2{}^*COOH$, (E) $-CF_2CF^*(-CF_2-)CF_2-$, and (F) $-CF^*{=}CF_2$. Peaks marked # represent spinning side bands.

Table 1. Sequence Distributions for the CF_2 and CF Resonances Observed in the ^{19}F NMR Spectra (Figure 3)[a]

Functionality	Assignment	Chemical Shift (ppm)
$-CF_2-\overset{OCF_3}{\overset{\vert}{CF^*}}-CF_2-$	$-CF_2-CF_2-\overset{\vert}{CF^*}-CF_2-CF_2-$	a) -135.9
	$-CF_2-CF_2-\overset{\vert}{CF^*}-CF_2-\overset{\vert}{CF}-$	b) -134.4
	$-\overset{\vert}{CF}-CF_2-\overset{\vert}{CF^*}-CF_2-\overset{\vert}{CF}-$	c) -134.0
$-CF_2-\overset{OCF_3}{\overset{\vert}{CF^*}}-\overset{\vert}{CF}-$	$-CF_2-CF_2-\overset{\vert}{CF^*}-\overset{\vert}{CF}-CF_2-$	d) -132.0
	$-\overset{\vert}{CF}-CF_2-\overset{\vert}{CF^*}-\overset{\vert}{CF}-CF_2-$	e) -131.1
$-CF_2-CF_2^*-CF_2-$	$-CF_2-CF_2-CF_2^*-CF_2-CF_2-$	1) -119.5
	$-CF_2-CF_2-CF_2^*-CF_2-\overset{\vert}{CF}-$	2) -118.5
	$-\overset{\vert}{CF}-CF_2-CF_2^*-CF_2-\overset{\vert}{CF}-$	3) -117.5
$-CF_2-CF_2^*-\overset{OCF_3}{\overset{\vert}{CF}}-$	$-CF_2-CF_2-CF_2^*-\overset{\vert}{CF}-CF_2-$	4) -116.0
	$-\overset{\vert}{CF}-CF_2-CF_2^*-\overset{\vert}{CF}-CF_2-$	5) -115.0
$-\overset{OCF_3}{\overset{\vert}{CF}}-CF_2^*-\overset{OCF_3}{\overset{\vert}{CF}}-$	$-CF_2-\overset{\vert}{CF}-CF_2^*-\overset{\vert}{CF}-CF_2-$	6) -112.0
	$-CF_2-\overset{\vert}{CF}-CF_2^*-\overset{\vert}{CF}-\overset{\vert}{CF}-$	7) -111.2

[a] Assignments were originally made by Lovchikov et al.[31]

Table 2. ^{19}F Chemical Shifts of New Structures Identified in the ^{19}F NMR Spectrum of TFE/PMVE γ-Irradiated to 4200 kGy, with Calculated *G* Values for the Formation of These Structures Also Shown

Chemical Shifts (ppm $CFCl_3$)	Assignment	Calculated G value (error ~20%)
-54.4 -55.3 -57.2	$-CF_2-O-CF_3^*$	0.9
-80.7	$-CF_2-CF_3^*$	1.0
-84.0	$-CF_2^*-O-CF_3$	0.8
-123.7 -124.6	$-CF_2^*-COOH$	0.5
-181.3	$-CF_2-\underset{\underset{\vert}{CF_2}}{\underset{\vert}{CF^*}}-CF_2-$	0.9
-190.9	$-CF^*=CF_2$	0.2

ropolymers may be overcome using solid state ^{13}C CP MAS, high-power ^{19}F decoupling, solid state NMR, and solid state ^{19}F NMR at elevated temperatures, as well as using the two-dimensional technique, COSY. The perfluoroelastomer TFE/PMVE was fully characterized, and the new radiolytic functionalities identified and quantified using these spectroscopic techniques.

Experimental Section

Materials. The TFE/PMVE used in this study was synthesized by Du Pont Dow Elastomers L. L. C. in an emulsion polymerization continuous reactor with a free radical initiator.[10] The emulsion was coagulated using $MgSO_4$, which upon hydrolysis gave Mg^{2+}/carboxylate ionomers.[10,28] The TFE/PMVE used in this study was free of additives. The estimated molecular weight is in excess of 100 000. The fluoroelastomer was completely amorphous and had a glass transition temperature of 3 °C when unirradiated and was in the form of a crumb.

Radiolysis of TFE/PMVE. TFE/PMVE samples were γ-irradiated as received in glass tubes at a reduced pressure of 10^{-4} Torr. The samples were irradiated at the Japan Atomic Energy Research Institute (Takasaki Branch) using a γ pond facility. The irradiations were carried out at a dose rate of 20 kGy h^{-1}. The samples reached a temperature of approximately 40 °C during irradiation due to the high dose rate. Calculations of the absorbed dose were made from the total irradiation time, and the average dose rate was measured from radical yields from a commercial alanine dosimeter, *Aminogray*. TFE/PMVE samples were irradiated at various doses up to 4200 kGy. The irradiated samples were opened to the atmosphere and then placed in a vacuum oven at 100 °C overnight to remove any volatiles such as hydrogen fluoride from the polymer matrix.

NMR Method. The sensitivity of dilute spins such as ^{13}C to the NMR technique in solids, has been shown to greatly improve with the advent of magic-angle spinning (MAS) in conjunction with cross-polarization (CP)[29] and high-power decoupling.[30] In fluoropolymers there is an abundant ^{19}F dipolar reservoir (^{19}F spin $^{1}/_{2}$) which is exploited in the CP experiment. The $^{19}F/^{13}C$ cross polarisation is achieved through the transfer of magnetisation from the ^{19}F reservoir to the ^{13}C through direct dipole−dipole coupling.

The NMR spectra were obtained on a Bruker MSL200 spectrometer operating at a ^{13}C frequency of 50.29 MHz and 188.15 MHz for the ^{19}F frequency. Samples were spun at the magic angle with a frequency of 3 kHz in a DOTY Scientific 7 mm CP MAS probe with the Vespel rotor having a low ^{19}F background signal. ^{13}C spectra were obtained employing CP MAS and high-power decoupling. The CP contact time was 0.6 ms with a recycle delay time of 2.0 s. The ^{13}C chemical shift was determined using adamantane as an external reference. At least 5000 scans were acquired for each ^{13}C spectrum.

^{19}F spectra were obtained using a $\pi/2$ pulse-decay of 5 μs with a 2 s recycle delay period between pulses at a temperature of 420 K. Sufficiently long delay times were used to ensure quantitative integrated peak intensities. Trifluoroacetic acid was used as an external standard and chemical shifts were reported relative to trichlorofluoromethane.

The COSY spectrum was acquired using a COSY 90 pulse sequence. The spectral sweep width in ω_2 was 62500 Hz, and the increment in t_1 equal to 16 μs. A total of 1024 points were collected in t_1.

Sol/Gel Analysis. The sol/gel determinations were performed on molded samples of approximately 1.5 mm thickness with a length of 10 mm and width of 5 mm. Samples were preweighed and placed in stainless steel mesh bags. These were then placed in a Soxhlet apparatus from which freon FC-77 (a mixture of perfluorinated octanes) vapors could condense, thus immersing the sample. The freon solvent was allowed to drain and refill the Soxhlet apparatus at regular 10 min intervals during a 48 h period. The samples were dried in a vacuum oven at 80 °C and weighed to constant weight. The gel content was determined from the ratio of the weight of the dried extract to the original weight.

Results

Characterization of Unirradiated TFE/PMVE.

^{13}C NMR. Three peaks were identified in the ^{13}C NMR spectrum of TFE/PMVE (Figure 2A); two were ascribed to the $-OCF_3$ at 117.6 ppm, $-CF_2-$ centered at 109.1 ppm, and a small peak on the higher field side of the CF_2 shoulder was assigned to $-CF-$ 105.7 ppm. The

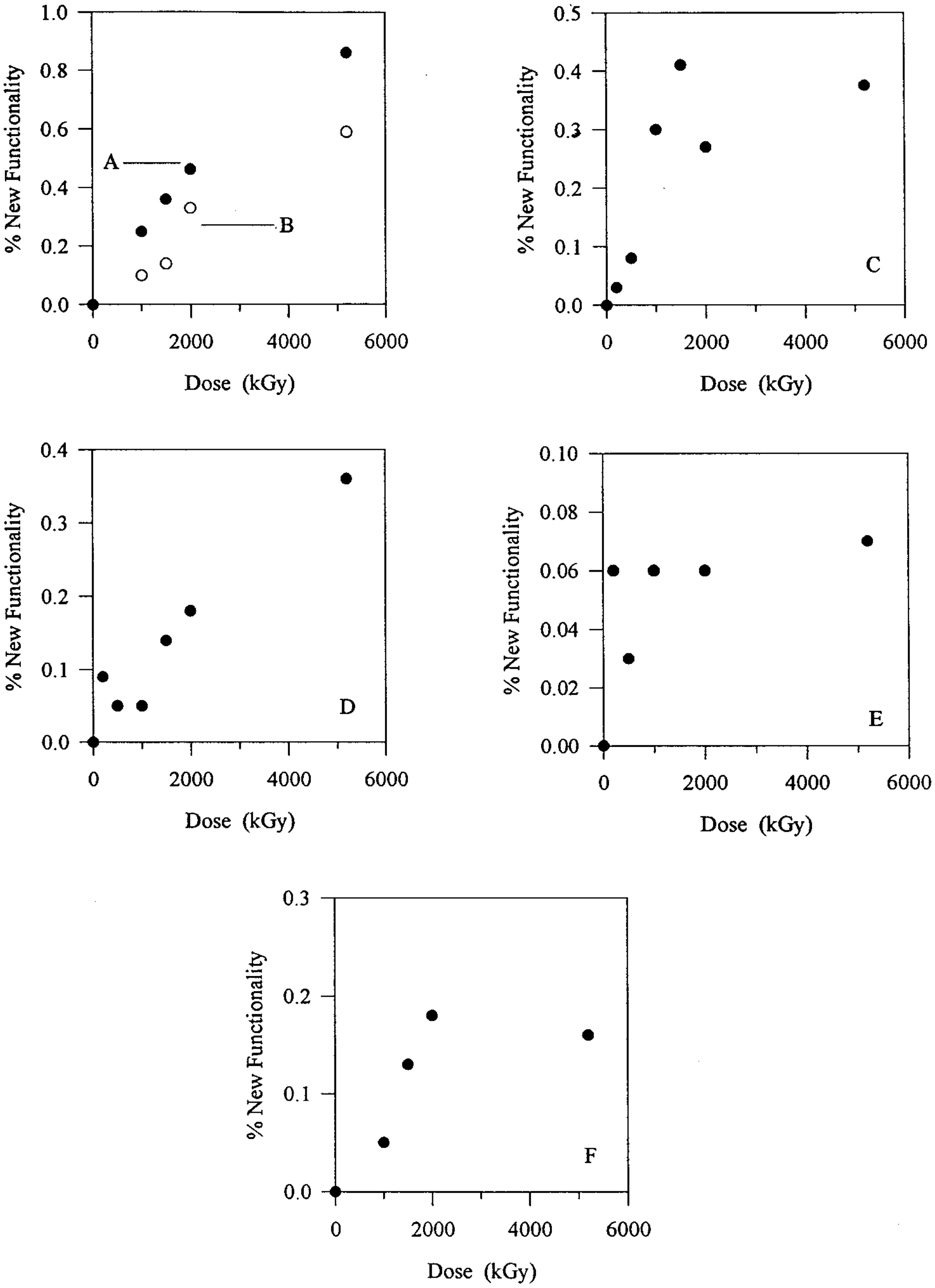

Figure 5. Mol % of the new functionality as a function of dose of γ-irradiated TFE/PMVE. Measurements taken from ^{19}F NMR at 420 K. New functionalities identified include (A) $-CF_2OCF_3^*$, (B) $-CF_2^*OCF_3$, (C) $-CF_2CF_3^*$, (D) $-CF_2^*COOH$, (E) $-CF^*{=}CF_2$, and (F) $-CF_2CF^*(-CF_2-)CF_2-$.

sequence distribution of the $-CF_2-$ resonances were unresolved.

^{19}F NMR. The ^{19}F spectrum of unirradiated TFE/PMVE is shown in Figure 3. The three major fluorine resonances were assigned: $-OCF_3$, -52.4 ppm, $-CF_2-$, -110 to -120 ppm; $-CF-$, -130 to -136 ppm. The integrated area of the peaks confirmed a 2:1 ratio of the TFE to the PMVE comonomer. The CF_2 and CF resonances showed splitting due to sequence distributions. Assignments for these splittings were made by Lovchikov et al.[31] and are shown in Figure 4 and Table 1. Small absorbances at -74.2 and -181.1 ppm were attributed to a hexafluoropropylene impurity. The small absorbance at -88.9 ppm was attributed to an unidentified impurity. The ^{19}F chemical shift is predominantly influenced by the paramagnetic term of the screening constant, which in turn is affected by the degree of ionic character of the bond; i.e., as the ionic character of the bond increases, the shielding and thus the chemical shift will decrease.[32] Electronegative atoms, such as oxygen attached as an ether bond, cause an approximately 70 ppm decrease in the chemical shift from the $-CF_2-$ resonances. The effect of attached oxygen and fluorine atoms on the chemical shifts has been investigated and empirical additivity rules developed.[32,33]

Characterization of Irradiated TFE/PMVE. ^{13}C NMR. Figure 2B shows the ^{13}C spectrum of TFE/PMVE irradiated to a dose of 2000 kGy. A broad absorbance was observed at 162.0 ppm and assigned to carboxylic acid chain ends $-CF_2COOH$.

^{19}F NMR. Figure 4 shows the spectrum of TFE/PMVE irradiated to a dose of 4200 kGy. New absorbances with their assignments are given in Table 2. Line widths in the irradiated copolymer broadened due to limited motional averaging in the highly cross-linked

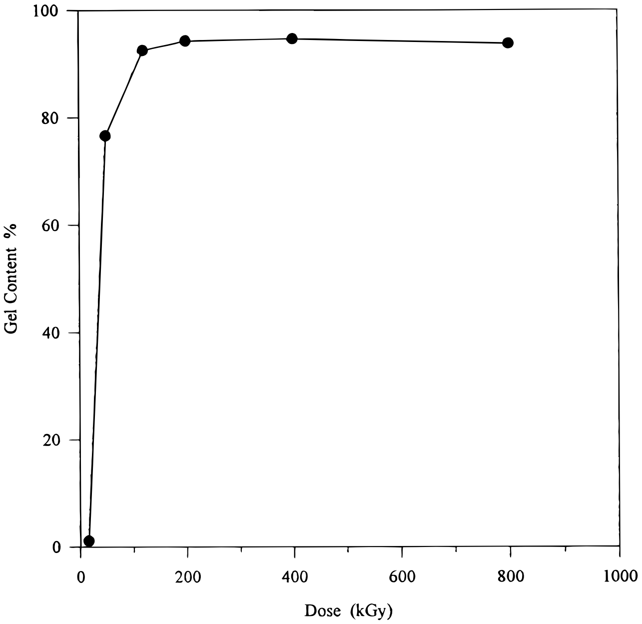

Figure 6. Percent gel formation as a function of irradiation dose for TFE/PMVE. Samples were γ-irradiated in vacuum at room temperature and extracted using a freon solvent.

network. The integrated areas of the new functionalities were determined and the mol percent change plotted as a function of absorbed dose (Figure 5). The *G* values were determined from the initial slopes of these plots and are given in Table 2.

Sol/Gel Behavior. TFE/PMVE readily formed a cross-linked network upon exposure to γ-radiation giving 90−95% gelation after a dose of 100 kGy (**Figure 6**). The gel dose was determined to be 15.8 kGy using the cross-linking/molecular weight relationship developed by Saito, which assumes a *Y*-linking cross-linking process.[34]

COSY: ^{19}F correlation spectroscopy (COSY) confirmed the assignments of the new chain scission products. Figure 7 clearly shows coupling of the CF_2 (−84.0 ppm) and CF_3 (−54.4, −55.3, −57.2 ppm) in the chain end, $-CF_2OCF_3$.

Discussion

The ease with which TFE/PMVE cross-links upon radiolysis has been attributed to the high chain mobility at room temperature which promotes radical recombinations that lead to the formation of cross-links.[14,19] The percent gelation of 90−95% agreed with values obtained by Logothetis,[19] who used electron beam irradiation in air and in vacuum.

It is believed that the formation of scission products as well as the cross-links upon ionizing radiolysis occurs via the formation of free radical intermediates. Many electron spin resonance studies have been conducted on irradiated fluoropolymers especially in the cases of PTFE[35−40] and FEP,[41−44] which have shown that both the C−C and C−F bond are susceptible to homolytic scissions.

Scission Products of TFE/PMVE. The formation of carboxylic acid end groups was confirmed in both the ^{13}C and ^{19}F NMR spectra (Figures 2B and 4D). Logothetis[19] identified carboxylic acid end groups upon irradiation using transmission FTIR, and Packansky et al.[17] similarly showed formation of acid groups to occur through the hydrolysis of an acyl fluoride from moisture in the atmosphere. Similar results were observed in the

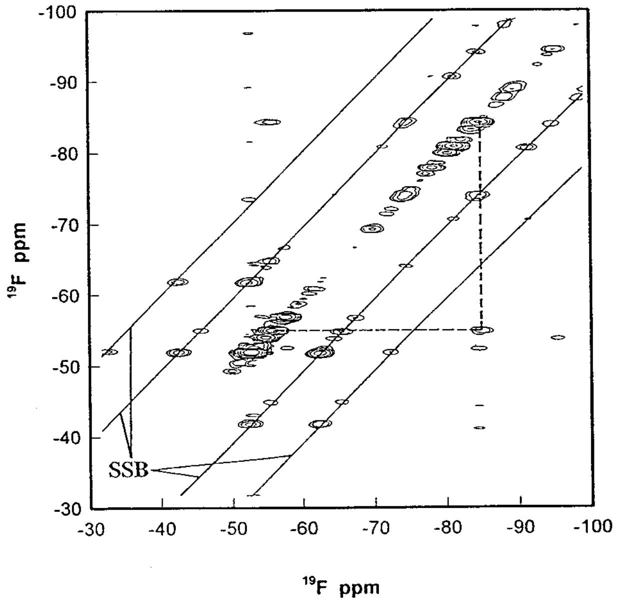

Figure 7. ^{19}F COSY spectrum for TFE/PMVE γ-irradiated to a dose of 4200 kGy. Lines have been drawn through the spinning side bands (SSB). The dotted lines show coupling between the CF_3 and CF_2 of the methyl ether chain end, $-CF_2$-OCF_3. The spectrum was acquired at 420 K.

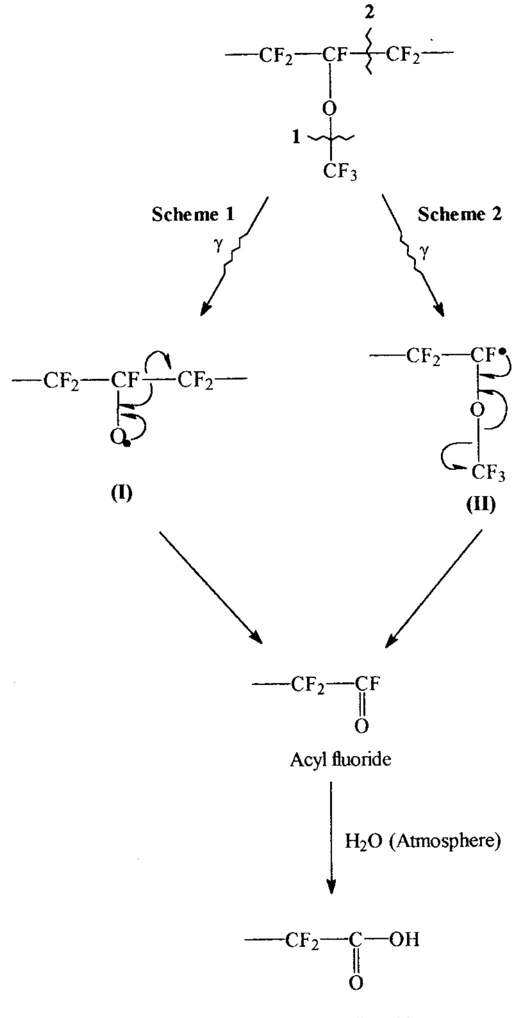

Figure 8. Proposed mechanism for the formation of carboxylic acid end groups of γ-irradiated TFE/PMVE. The acid end groups were identified using ^{13}C and ^{19}F NMR.

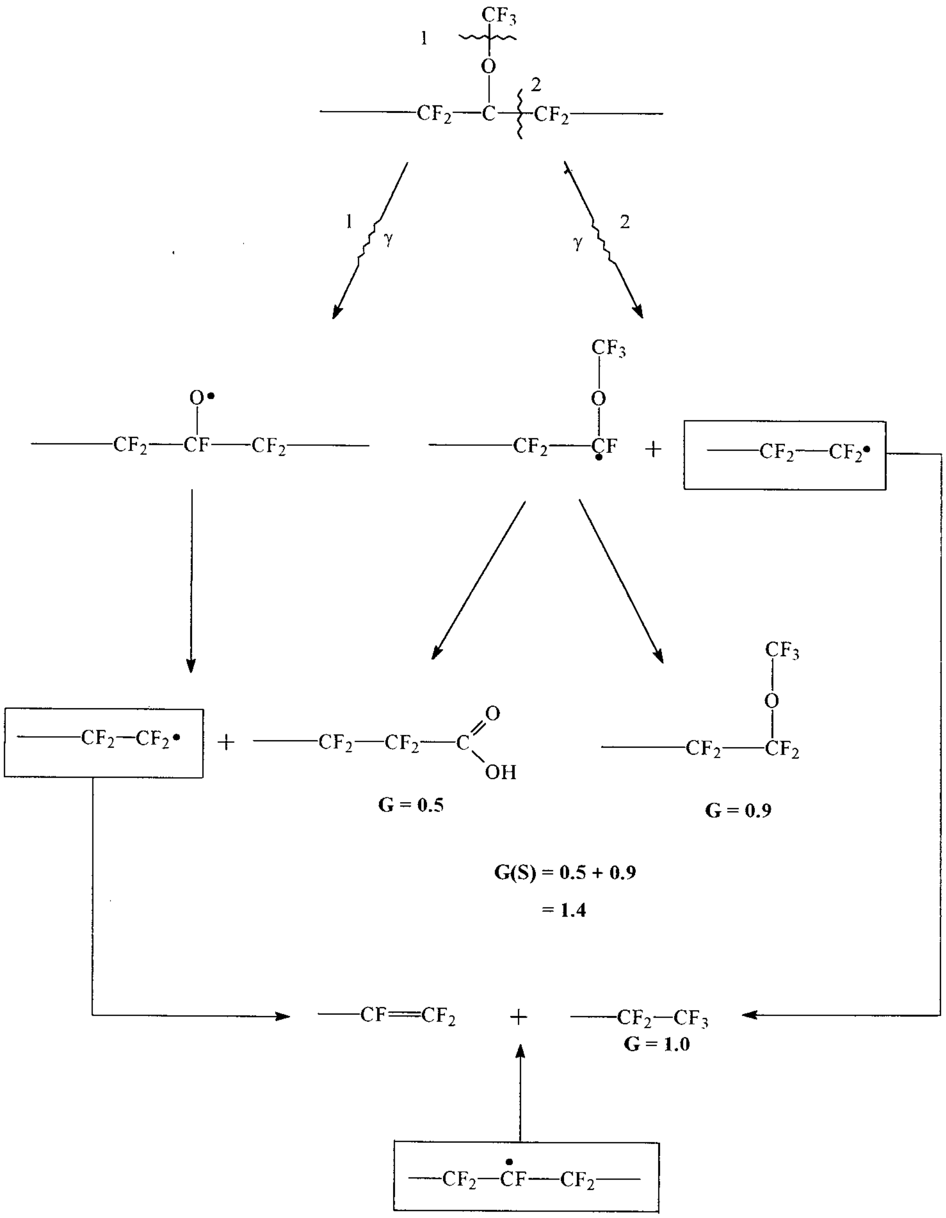

Figure 9. Proposed mechanism for the formation of scission products. The G value for main chain scission, $G(\mathrm{S}) = 1.4$, was determined from the amounts of $-\mathrm{CF_2COOH}$ ($G = 0.5$), and $-\mathrm{CF_2OCF_3}$ ($G = 0.9$).

radiolysis of PTFE by Fisher et al.[45] Figure 8 shows two possible mechanisms leading to the generation of the acid end groups. Scheme 1 shows homolytic scission of the ether bond to give both an oxygen-centered radical and a $^{\bullet}\mathrm{CF_3}$ radical. The latter would most likely recombine with a fluorine radical to produce $\mathrm{CF_4}$ which was found to be a major volatile radiolytic product of TFE/PMVE ($G(\mathrm{CF_4}) = 0.93$).[17] A β-scission would follow producing a chain end radical and an acyl fluoride chain end, the latter readily hydrolysing upon exposure to moisture in the atmosphere. Alternatively, scheme 2 shows initial main chain scission followed by loss of a $^{\bullet}\mathrm{CF_3}$ radical to produce the acyl fluoride. Additional evidence for radical **II** was determined indirectly by the identification of $-\mathrm{CF_2OCF_3}$ chain ends in the ^{19}F NMR spectrum (Figure 4A,C). This chain end product would be produced by the recombination of radical **II** with a fluorine radical.

The absorbance at −80.7 ppm in the ^{19}F spectrum (Figure 4B) was assigned to saturated chain ends, $-\mathrm{CF_2}$-$\mathrm{CF_3}$ ($G = 1.0$). The formation of these new chain ends would most likely proceed by the reaction of a $-\mathrm{CF_2}^{\bullet}$ chain end radical with a fluorine radical (Figure 9).[3,46]

A small amount of terminal unsaturation was observed in the ^{19}F NMR spectrum of the irradiated copolymer ($G = 0.2$) (−190.8 ppm Figure 4F). Terminal unsaturation has been observed in irradiated fluoropolymers such as PTFE[2,45-47] and TFE/PMVE.[17] The formation of terminal double bonds may result from irradiation of "in-chain" radicals, $-\mathrm{CF_2{}^{\bullet}CFCF_2}-$ (Figure 9). Another possible mechanism is decarboxylation of the carboxylate/Mg^{2+} end groups. Radiolysis of these salt end groups could result in the formation of terminal double bonds. Lyons[20] proposed that the highly reactive fluorine radical, formed from an initial scission of a C−F bond, could attack a C−C bond along the main chain of PTFE, giving a saturated chain end and a terminal double bond. The low concentration of terminal double bonds was attributed to their high sensitivity towards radiation.

The proposed mechanism for the formation of the $-\mathrm{CF_2OCF_3}$ chain ends is outlined in Figure 9. Main chain scission of the bond adjacent to the ether linkage would produce a $-\mathrm{CF_2{}^{\bullet}CFOCF_3}$ radical (Figure 9). It therefore appears that there are two competing reactions for this radical: (1) loss of the fluoromethyl group to form the acyl fluoride (which gives carboxylic acid end groups on hydrolysis) ($G = 0.5$) (Figure 8) or (2) recombination with a fluorine radical giving $-CF_2OCF_3$ ($G = 0.9$) (Figure 9). A comparison of the G values of the two competing reactions suggests that the latter reaction was more favorable.

The yield of main chain scission, $G(S) = 1.4$, was calculated from the addition of the G-values for the formation of new chain ends ($G(COOH) = 0.5$ and $G(-CF_2OCF_3) = 0.9$). The formation of these new end groups must originate from scission of the main chain. Pacansky[17] identified acyl fluoride functionalities as the only new chain ends using FTIR and calculated a G value of 0.34 for its formation. A lower limit for $G(S)$ was therefore determined to be 0.34. However it is believed that the reaction leading to the formation of $-CF_2OCF_3$ would be an additional source of main chain scission and must be taken into consideration in the calculation of $G(S)$.

Cross-Linking of TFE/PMVE. Lovejoy et al.[9] investigated the radiation cross-linking of FEP on exposure to high energy electrons, X-rays, and UV light above the glass transition temperature. The cross-linking of FEP was explained with reference to steric hindrance, radical reactivity, and chain mobility of the possible radical recombination reactions. Using molecular models and model compounds, they concluded that there must be at least two carbon units between branch points and that the major cross-linking reaction would proceed via a *Y*-linking mechanism. More recently, Zhong et al.[48] used X-ray photoelectron spectroscopy to identify the cross-link of FEP and concluded a predominant *Y*-linking process. Tabata et al.[49] also concluded that the radiation cross-linking of PTFE at temperatures above the melt was due to *Y*-linking. This conclusion was based on the work by Tsuda et al.[50] who showed that it was theoretically difficult to produce a H-type cross-link via the recombination of alkyl radicals.

Upon radiolysis of TFE/PMVE, a new absorbance appeared in the ^{19}F NMR spectra at −181.3 ppm (Figure 4E), which was attributed to a tertiary fluorine at the branching site on the main chain. It was therefore apparent that *Y*-linking was responsible for the cross-linking of the fluoropolymer. *Y*-linking would proceed via the radical recombination of a chain end radical ($-CF_2CF_2^{\bullet}$) with a radical within the polymer chain ($-CF_2^{\bullet}CFCF_2-$). Following the peak in Figure 4E we observe the concentration of branches to increase almost linearly up to a dose of 2000 kGy (Figure 5F). A G value of 0.9 was therefore calculated for the cross-linking of TFE/PMVE in this dose range. At doses higher than 2000 kGy, the yield of cross-links did not increase which was attributed to the limited polymer chain mobility in the cross-linked network, inhibiting radical recombination reactions. The limited chain mobility was also consistent with an observed increase in the glass transition temperature. The glass transition temperature of TFE/PMVE increased from 3 to 25 °C after a dose of 2000 kGy indicating the polymer had reduced chain mobility at the irradiation temperature of 40 °C. Therefore the maximum yield of cross-links when irradiated under our conditions, was approximately 0.2 mol %.

Conclusions

Solid state ^{13}C and ^{19}F NMR provides a useful means of studying the radiation chemistry of fluorinated systems. The identification of the chain ends, $-CF_2COOH$ and $-CF_2OCF_3$, in relatively large amounts suggests that the PMVE is the focus of the radiation scission reactions in the polymer. ESR studies of γ-irradiated TFE/PMVE with differing comonomer compositions also indicated the susceptibility of PMVE to undergo scission reactions.[51] The ability of TFE/PMVE to cross-link when irradiated at room temperature was attributed to the high polymer chain mobility of the elastomer at room temperature allowing *Y*-linking radical recombination reactions to occur freely. At doses higher than 2000 kGy, the concentration of *Y*-links remained constant, which was attributed to a decrease in polymer chain mobility in the cross-linked network.

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