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Cross-Linking of PFA by Electron Beam Irradiation

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ABSTRACT: The effect of electron beam radiation on a perfluoroalkoxy (PFA) resin was examined using solid-state high-speed magic angle spinning ^{19}F NMR spectroscopy and FT-IR spectroscopy. Samples were prepared for analysis by subjecting them to electron beam radiation in the dose range 0.5−2.0 MGy at 633 K, which is above the crystalline melting temperature. The new structures were identified and include new saturated chain ends, short and long branches, unsaturated groups, and cross-links. The radiation chemical yield (G value) of new long branch points was greater than the G value of new chain ends, suggesting that cross-linking is the net radiolytic process. This conclusion was supported by an observed decrease in the crystallinity and an increase in the optical clarity of the polymer.

Introduction

An implication of the polarity and strength of the C−F bond is that, during synthesis of fully fluorinated polymers, F atom abstraction or disproportionation and branch formation are improbable. Poly(tetrafluoroethylene), PTFE, is therefore an inherently linear polymer, although fluoropolymers containing a small percentage of short branches have been prepared by incorporation of comonomers with pendant groups to form copolymers such as poly(tetrafluoroethylene-*co*-perfluoropropylene), FEP, and poly(tetrafluoroethylene-*co*-perfluoropropyl vinyl ether), PFA. While these copolymers are melt-processable, they essentially still have the properties of linear polymers. Producing fluoropolymers with cross-linked networks offers the possibility of improving the strength, dimensional stability, and resistance to solvents at elevated temperatures of these polymers.[1] We have previously shown that branched structures are formed when PFA is treated with γ-radiation at high temperature. However, it was not possible to show conclusively whether cross-linking occurred on radiolysis.

Thus, radiation processing offers a convenient pathway to formation of cross-linked networks in some fluoropolymers, and it has attracted much attention in the literature. One of the first fully fluorinated polymers to be cross-linked by high-temperature irradiation was FEP.[1,2] Bowers and Lovejoy observed an increase in the melt viscosity of FEP after it was irradiated under a nitrogen atmosphere at a temperature above the T_g of 353 K. They proposed that the changes observed were caused by an excess of cross-linking reactions over chain scission reactions. When FEP was irradiated above the crystalline melting temperature, the melt viscosity decreased, suggesting that the polymer was degrading. Bowers and Lovejoy also attempted to cross-link PTFE by subjecting it to irradiation above the T_g but below the melting temperature but found that the polymer only degraded. Forsythe et al.[3] cast doubt over the conclusions reported by Bowers and Lovejoy for the observations made when FEP was irradiated. Instead of cross-linking causing the observed increase in melt viscosity, Forsythe et al. suggested that perhaps an increase in crystallinity and presence of in-chain double bonds could lead to chain rigidity which would be responsible for the observations.[3]

Other workers have since reported the successful cross-linking of PTFE by irradiation above the crystalline melting point in the absence of oxygen. Using the NMR line width as a measure of the crystallinity of irradiated PTFE, Tutiya[4] noticed a correlation between the crystallinity and irradiation temperature. When PTFE was irradiated with γ-radiation below 573 K, the crystallinity increased with increasing temperature, while at 593 K the crystallinity decreased.[4] The same trends were also reported later, based on DSC measurements.[5] Increases in yield strength and modulus have also been observed when PTFE was irradiated at approximately 613 K.[6−8] More recently, with improvements in NMR sample spinning speeds, solid-state NMR spectroscopy has been used to characterize PTFE cross-linked by electron beam irradiation.[9−11]

No details of the experimental conditions necessary to cross-link PFA could be found in the literature. Sun et al. reported in 1993 that they had cross-linked PFA but did not disclose the conditions they used.[12] In a previous study,[13] in which we investigated the γ-radiolysis of PFA below its melting point, we showed that PFA undergoes net chain scission below 573 K. In this earlier study, the irradiation temperature was limited to an upper temperature of 573 K, which is just below the crystalline melting temperature.

In the present study the radiation chemistry of PFA above its melting point was investigated using spectroscopic methods following electron beam irradiation at 633 K, which is above the crystalline melting temperature.

Experimental Section

Electron Beam Irradiation. PFA pellets (DuPont, code TE 7132) were irradiated using an electron beam accelerator (ELV-2, Budker Institute of Nuclear Physics, Novosibirsk, Russia). The electron energy was 1.5 MeV with a beam current of 2 mA. A transport system was used with a conveyor speed of 0.6 m min^{-1}. The total irradiation dose was built up in steps with a dose of 50 kGy per step. The average dose rate was

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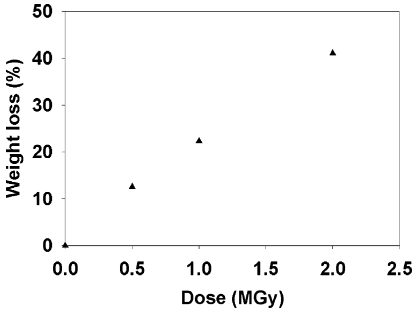


Figure 1. Weight loss (measured gravimetrically) of PFA samples irradiated at 633 K with electron beams.

14.7 kGy min^{-1}, and samples were irradiated to total doses of 0.5, 1, and 2 MGy.

Irradiation was performed by placing the PFA pellets in a vacuum vessel which was evacuated to a pressure of 4 × 10^{-2} Pa. The vessel was fitted with a thin metal foil window for electron beam penetration and contained an electric heating device. The vacuum vessel was mounted on the conveyor system of the irradiation facility and was passed under the electron beam. The irradiation experiments were carried out at 633 ± 2 K, which was measured using a resistance thermocouple in the sample holder. After irradiation the temperature was held at 633 ± 2 K for 20 min; then the vessel was filled with nitrogen gas to atmospheric pressure before cooling.

NMR Spectroscopy. Single-pulse NMR experiments were performed using a Bruker MSL 300 spectrometer with a Doty Scientific triple-resonance MAS probe operating at a ^{19}F resonance frequency of 282 MHz. Samples were spun at a maximum frequency of ≈20 kHz at the magic angle using a 2.9 mm o.d. rotor. The recycle time of 10 s was long enough to obtain quantitative integrated peak intensities. Spectra were acquired using a $\pi/2$ pulse duration of 3 μs, and in all cases, the width of the observation frequency was chosen to avoid peaks folding back in the spectra. The ^{19}F chemical shifts were reported relative to the CF_2 signal of PTFE at −122 ppm, which was externally referenced to $CFCl_3$. Peak areas were used when comparing the concentrations of different components in the spectra.

FT-IR Spectroscopy. FT-IR spectra of the nonvolatile component were recorded on a Bio-Rad FTS-155 spectrometer. Samples were prepared by pressing PFA pellets under 4 tons of pressure at room temperature. Intensities in the spectra were normalized to the CF_2 backbone overtone at 2365 cm^{-1}.

Crystallinity Measurements. Crystallinity measurements were carried out by differential scanning calorimetry (DSC) performed using a Perkin-Elmer DSC 7. All runs were performed on 10 ± 0.5 mg samples in a nitrogen atmosphere. The apparatus was calibrated using the onset of melting of indium (429.6 K) and zinc (692.47 K) and the heat of fusion of indium (28.45 J g^{-1}). The heat of fusion of the PFA samples was measured from the area under the melting endotherm which was converted to crystallinity based on a value of 82 J g^{-1} for the heat of fusion of a perfect crystal of PTFE.

Results and Discussion

Before irradiation the PFA used was semiopaque and had a crystallinity of 34 ± 3% as measured by DSC. After irradiation with electron beams in a vacuum at 633 K, the PFA changed in appearance and became progressively less opaque with increasing dose. Accompanying the change in appearance was a significant weight loss. At the highest dose examined (2 MGy) the weight loss was 41% (see Figure 1). These observations are evidence of dramatic chemical, structural, and morphological changes in the irradiated PFA.

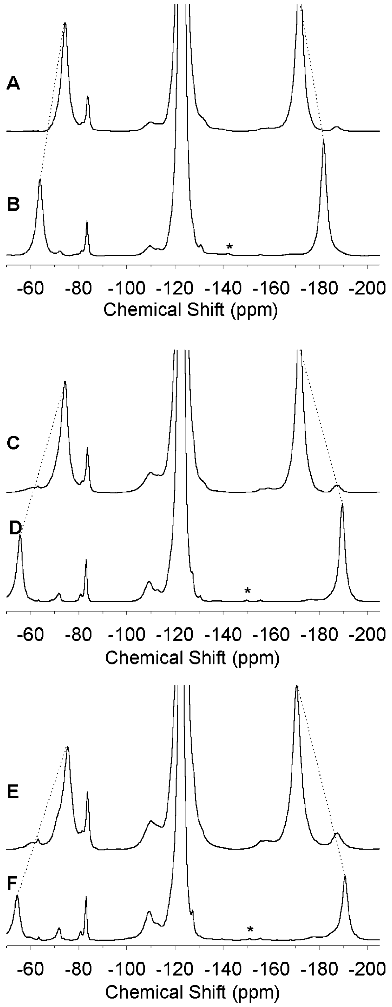
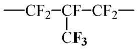
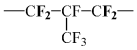
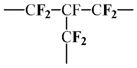
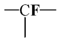


Figure 2. HS MAS ^{19}F NMR of PFA irradiated at 633 K in a vacuum: (A) 0.5 MGy,13.5 kHz; (B) 0.5 MGy, 17 kHz; (C) 1 MGy, 13.5 kHz; (D) 1 MGy, 19 kHz; (E) 2 MGy, 13.5 kHz; (F) 2 MGy, 19.5 kHz. * represents spinning sideband.

NMR Spectroscopy. To investigate the chemical changes in the irradiated PFA, high-speed MAS ^{19}F NMR spectroscopy was used. The NMR rotor was spun at a maximum spinning speed of approximately 20 kHz. At this speed the chemical shift anisotropy and dipole interactions were sufficiently averaged so that the ^{19}F line widths were narrow enough to identify individual peaks, but the spectra were partially obscured by spinning sidebands. At speeds between 17 and 19.5 kHz there were spinning sidebands overlapping with the $\rangle C\mathbf{F}-$ region (−180 to −190 ppm). To observe the full spectral range of interest, a second set of spectra were recorded using a slower spinning speed of 13.5 kHz to shift the spinning sidebands from the −180 to −190 ppm region.

Examination of the spectra in Figure 2A−F for PFA irradiated to 0.5, 1, and 2 MGy at 633 K reveals that chain scission and branching reactions are occurring simultaneously at this irradiation temperature. Chain scission is evident from the growth in the peaks at −83 and −127 ppm due to $-C\mathbf{F}_2C\mathbf{F}_3$ chain ends, while the peak at −187 ppm assigned to the fluorine atoms at branch points ($\rangle C\mathbf{F}-$) also increases in intensity with increasing dose. The movement of the spinning sidebands due to the CF_2 peak at −122 ppm is indicated by the dashed lines in Figure 2, and the asterisk on the peak at −150 ppm denotes the spinning sideband from the peak at −83 ppm.

Table 1. Assignments of New Peaks Observed in the ^{19}F NMR Spectra of Irradiated PFA at 633 K

Structure	Chemical shift (ppm)
$\sim\sim CF_2{-}C\mathbf{F_3}$	–83
$\sim\sim C\mathbf{F_2}{-}CF_3$	–127
 $-CF_2-\underset{\displaystyle C\mathbf{F_3}}{\underset{|}{CF}}-CF_2-$	–71 (crystalline), –68 (amorphous)
 $-C\mathbf{F_2}-\underset{\displaystyle CF_3}{\underset{|}{CF}}-C\mathbf{F_2}-$	–113
 $-C\mathbf{F_2}-\underset{\underset{|}{\displaystyle C\mathbf{F_2}}}{\underset{|}{CF}}-C\mathbf{F_2}-$	–109
 $-\underset{|}{C\mathbf{F}}-$	–187
$R_f{-}C\mathbf{F}{=}C\mathbf{F}{-}R_f$	–155
$C\mathbf{F_3}{-}CF{=}CF{-}$ or $(C\mathbf{F_3})_2{-}CF{-}$	–73

When PFA was irradiated below its melting temperature, the ^{19}F NMR spectra contained two new peaks due to CF_3 side chains in two different morphological environments.[13] In the spectra of PFA irradiated to 1 and 2 MGy at 633 K, the intensity of the peak at −68 ppm (assigned to CF_3 side chains in the crystalline regions) is negligible (Figure 2D,F). In the spectra of PFA irradiated to 0.5 MGy, this region of the spectra is partially obscured by a spinning sideband at both of the spinning speeds used in acquiring the spectra. The diminishing intensity of the peak at −68 ppm due to CF_3 side chains incorporated into the crystallites can be related back to the changing crystallinity of the samples after irradiation. (Of course, during the irradiation the samples are totally amorphous as they are in molten form.) Formation of long branches can hinder crystal formation and so lower the final overall crystallinity of the irradiated sample. It was shown that when PFA was irradiated at 633 K, the final overall crystallinity dropped significantly, and after a dose of 2 MGy the crystallinity was just 18%. This is almost half the crystallinity of the unirradiated polymer, so a much lower proportion CF_3 side chains would be incorporated into crystalline regions.

Less intense peaks in the spectra in Figure 2A−F not obscured by spinning sidebands include ones at −155 and −73 ppm. These peaks were also observed in similar intensity in the spectra of PFA irradiated with γ-radiation at 473 and 573 K[13] and can be assigned to either $C\mathbf{F_3}{-}CF{=}CF{-}$ or $(C\mathbf{F_3})_2{-}CF{-}$ for the peak at −73 ppm and to $-C\mathbf{F}{=}C\mathbf{F}-$ for the peak at −155 ppm.

The assignments for all of the peaks observed in the spectra of the PFA samples irradiated at 633 K are presented in Table 1.

FT-IR Spectroscopy. The FT-IR spectra of PFA following irradiation at 633 K and PTFE irradiated in the melt[14−17] contained many of the same bands. See Figure 3 for the peaks observed in the carbonyl and double-bond regions of the spectra of PFA after irradiation. The most prominent bands include internal and terminal double bonds (1785, 1730, and 1717 cm^{-1}), double bonds at branch points ($-CF{=}C\langle$) (1671 cm^{-1}) (only seen at 2 MGy), and carbonyl-containing end groups such as −COF and −COOH (1884, 1814, and 1775 cm^{-1}). A broad peak (not shown in Figure 3) associated with the −OH groups of the newly formed carboxylic acid end groups was also observed at 3100 and 3557 cm^{-1}. A list of the peak assignments is shown in Table 2. The oxygen-containing species were initially thought to originate from the cleavage of the ether group of the alkoxy side chain, since no oxygen would have been available as the irradiation was carried out in a vacuum. After irradiation, the samples were checked for residual radicals that may have reacted with oxygen in the air, but it was found that no radicals were present. This suggested that the oxygen-containing species must originate from the ether group of the side chain.

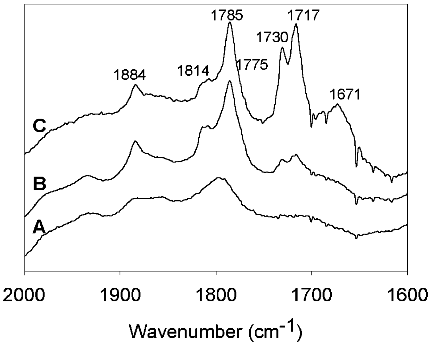


Figure 3. FTIR spectra of (A) untreated PFA, (B) PFA irradiated to 0.5 MGy at 633 K, and (C) PFA irradiated to 2 MGy at 633 K.

Table 2. Assignments of Bands in the FTIR Spectra of PFA Irradiated in Vacuum at 633 K

band (cm^{-1})	assignment	reference
1671	$-CF{=}C\langle$	14−18
1730, 1717	$-CF{=}CF-$	14−18
1785	$-CF{=}CF_2$	14−18
1814	−**CO**OH (free)	17−19
1884	−**CO**F	17−19
1775 (shoulder)	−**CO**OH (associated)	19, 20
3100	−CO**OH** (associated)	19
3557	−CO**OH** (free)	19

However, when PTFE was irradiated by Lappan and co-workers under almost identical conditions to those used here for PFA, −COF and −COOH end groups were also observed in the FT-IR spectra.[15,17] This was attributed to either trace amounts of oxygen remaining in the vacuum system or oxygen dissolved in the polymer which was not removed before radiolysis. So, if the −COF and −COOH groups can form in PTFE, which does not contain any oxygen, the oxygen in the new structures observed in the irradiated PFA may not arise exclusively from the oxygen of the ether group in the alkoxy side chain. A polymer containing labeled oxygen in the alkoxy groups may resolve this question.

***G* Values for Electron Beam Cross-Linking of PFA.** The proportion of cross-links in PTFE irradiated in the melt has been reported by Katoh et al. and also by Scheler and co-workers.[9−11] Unfortunately, the results cannot be directly compared as each group of workers have different definitions of what constitutes a cross-link. Scheler and co-workers define a cross-link as a long branch which meets with another main chain. This type of cross-link may be considered to be a "pseudo" H-type cross-link. A "real" H-type cross-link

Table 3. Comparison of the *G* Values for Formation of Functional Groups in Irradiated PFA (633 K) and PTFE (638 K)

property	*G* value PFA	*G* value PTFE[10]
PPVE	−6.0	n.a.
new chain ends	1.4	2.0
CF_3 side chains	0.4	1.2
long branch points	1.6	2.4
cross-links	0.2	0.4

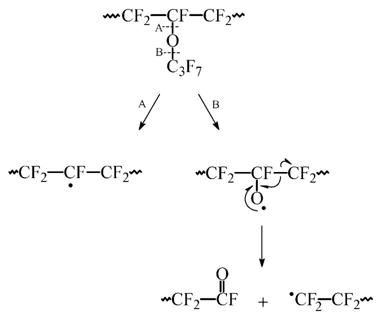
is formed when two main-chain radicals on adjacent molecules react to form a single-bond cross-link between the two chains.[21] H-type cross-links are generally observed in polyolefins but have a low probability of being formed in cross-linked PTFE and FEP. This is due to the steric hindrance encountered if the alkyl radicals were to combine.[22−24] The cross-links described by Scheler and co-workers are H-type in shape, but the cross-links are formed through many bonds ($-CF_2-CF_2-CF_2-$ type linkages) between the main chains. They calculated the proportion of cross-links as the difference between the number of long branch points and chain ends, and they stated that this was an estimate of the lower bound of cross-linking. At low dose, they reported that short and long branches were formed, while at high dose the long branches reacted with radicals formed on neighboring chains to form a cross-link between the two chains.[11]

Katoh et al. define a cross-link as any type of branch point or Y-type cross-link, perhaps erroneously including CF_3 side chains as cross-links. They reported the cross-link density as simply the number of tertiary CF groups as a fraction of the total number of CF, CF_2, and CF_3 groups. The *G* value of cross-linking was then calculated by converting the cross-link density to moles, expressing this as the number of cross-links per 16 aJ (100 eV) of energy deposited in the polymer. In this way they report a *G* value for cross-linking (*G*(X)) for each dose from 0 to 10 MGy. *G*(X) passed through a maximum at 2 MGy. Above this dose, the existing cross-links may be expected to hinder the chain mobility and so limit the formation of any subsequent cross-links.

Fuchs and Scheler[10] reported the relative content of cross-links, branches, and CF_3 side chains in irradiated PTFE over the dose range 0.5−3 MGy. While they did not report the relative content of the chain ends, it could be calculated from the difference between long branches and cross-links. The calculated *G* values for cross-linking, chain ends, and short and long branches are compared with the results obtained herein for PFA in Table 3.

The large negative *G* value for the PPVE groups indicated that the perfluoropropyl ether side chains were being cleaved very efficiently during irradiation of the PFA. The possible pathways to nonvolatile products from cleavage of the C−O−C bonds of the perfluoroalkoxy side chains are shown in Scheme 1. If the PPVE groups were cleaved according to the mechanism shown in pathway A, then a main chain radical and a small fragment would be formed. The latter would have been lost since the irradiation was performed under high vacuum. The alternative mechanism shown in pathway B results in an oxy radical being formed which would likely undergo rearrangement to form an acyl fluoride and a new chain end.[25,26] If the main pathway was pathway B, then the *G* value for new chain ends would be expected to be at least as large as the *G* value for loss of PPVE units.

Scheme 1. Possible Nonvolatile Radiation Products Arising from Cleavage of the C−O Bonds in the Alkoxy Group of the PVE Units in PFA



Since the *G* value for new chain ends (1.5) is much less than the *G* value for loss of PPVE groups (6.0), pathway A would appear to be more likely than pathway B for the loss of PPVE groups. In support of this, the *G* value for new chain ends in irradiated PFA (1.5) is not significantly different than for irradiated PTFE (2.0) which does not contain any alkoxy side chains.

The amount of branching, both long and short side chains, was less in PFA than in PTFE, as indicated by the higher *G* values for CF_3 side chains and long branch points for PTFE compared with PFA (see Table 3). It should be noted that in their measurement of CF_3 side chains Fuchs and Scheler[10] included structures such as $\rangle C{=}C(C\mathbf{F_3})-$ which were assigned to a number of small peaks in the region −55 to −65 ppm. In the spectra of PFA this region was obscured by spinning sidebands so it could not be measured. Interference from the spinning sidebands with other peaks was also problematic in the measurement of peak areas. The peaks at −71 and −187 ppm (Figure 2B,D,F) assigned to $C\mathbf{F_3}$ side chains and $\rangle C\mathbf{F}-$ groups, respectively, were partially obscured by spinning sidebands. This led to a certain degree of error in the measurements of the peak areas, making it difficult to compare the absolute *G* values of branching for PFA with PTFE. In addition to this, Fuchs and Scheler used an irradiation temperature 5 K higher than what was used for PFA. This temperature difference may also explain the differences in the amount of branching in the two polymers.

However, despite the small discrepancies between the experimental conditions and measurement of the peak areas used to derived the *G* values, it is clear that the *G* values for branching in electron beam irradiated PFA and PTFE are of the same order of magnitude.

The *G* value for cross-link formation in PFA reported in Table 3 was calculated by subtracting the number of chain ends from the number of long branch points. The value obtained, 0.2, is less than that of PTFE reported by Fuchs and Scheler, but it is still a positive value, indicating that cross-linking is the net process of radiolysis.

Conclusions

PFA has been cross-linked using electron beam irradiation at 633 K in a vacuum. This conclusion is based on the observation that the polymer lost most of its crystallinity based on the change in appearance from opaque to transparent after irradiation, and on NMR spectroscopy data showing an excess of branch points over chain ends, implying net cross-linking. The results complement those of our previous study using γ-radiolysis, proving that with the correct choice of conditions net cross-linking of PFA can be achieved.

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