

# Some Effects of Ionizing Radiation on Tetrafluoroethylene Copolymers

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## Synopsis

The effect of high energy electron radiation on TFE copolymers of perfluoro(methyl vinyl ether) (PMVE) and perfluoro-3,6-dioxa-4-methyl-7-octene sulfonyl fluoride (PSEPVE) was studied. The PMVE copolymers were found to crosslink when irradiated as either a gum or as a compounded elastomer. Attempts to graft vinyl monomers to the PMVE copolymers were unsuccessful. In contrast, grafts to PSEPVE copolymers were easily made by exposing irradiated samples to TFE or mixtures of TFE and methyl perfluoro-3,6-dioxa-4-methyl-7-octenoate.

## INTRODUCTION

The sensitivity of fluoropolymers to ionizing radiation is well known and has been studied for some time.<sup>1,2</sup> Investigators found that polytetrafluoroethylene (PTFE) rapidly degrades when subjected to even mild doses of radiation. Numerous studies<sup>3</sup> have shown that PTFE undergoes a variety of reactions leading to chain scission and the formation of primary and secondary radical species. Under appropriate conditions some radicals are stable and have been used to graft vinyl monomers such as TFE<sup>4</sup> or acrylic acid<sup>7</sup> to PTFE substrates. Other perfluorinated polymers like polyhexafluoropropylene and polytetrafluoroethylene oxide are similar to PTFE in that they degrade<sup>2</sup> when irradiated. In contrast, copolymers of TFE and hexafluoropropylene are notable exceptions in that irradiation caused mild crosslinking.

We have studied the effects of electron radiation on two perfluorinated TFE copolymers and have found examples which predominantly crosslink and which predominantly cleave to yield stable radical species. Copolymers of TFE and perfluoro(methyl vinyl ether),  $\text{CF}_2=\text{CFOCF}_3$ , (PMVE) were observed to crosslink, while copolymers of TFE and perfluoro-3,6-dioxa-4-methyl-7-octene sulfonyl fluoride,  $\text{CF}_2=\text{CFOCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$ , (PSEPVE) were observed to yield stable radicals. Fluoromonomers were grafted to the radicals generated in the PSEPVE copolymers, and the morphology of the resulting composites was investigated.

## EXPERIMENTAL

**Materials.** The PMVE and PSEPVE copolymers used in this work were commercial intermediates available from the DuPont Co. The PMVE copolymer contained about 30 mol % of the ether monomer. The composition of the PSEPVE copolymers is given in the text.

Methyl perfluoro-3,6-dioxa-4-methyl-7-octenoate (EVE) was prepared by literature methods<sup>8</sup> and was kindly supplied by D. C. England.

Literature methods<sup>9</sup> were used to prepare 2,2,4,4-tetrakis(trifluoromethyl)-1,3-dithietane (TTD). This solvent was purified by fractional freezing at 15°C. The liquid phase, accounting for about 20% of the material, was discarded. The crystals were melted and distilled at 104–5°C. THIS SOLVENT IS KNOWN TO BE HIGHLY TOXIC AND SHOULD ONLY BE USED WITH EXTREME CARE AND EXCELLENT VENTILATION.

Perfluoro(ethylene divinyl ether) (DVE) was prepared as described elsewhere.<sup>10</sup>

**Polymer Irradiation.** Samples to be irradiated were placed in heavy polyethylene bags fitted with nitrogen inlet and outlet tubes. The samples were purged with nitrogen for 1 h and the bag sealed. The sealed bag was placed in a second nitrogen flushed bag and transported to a 3-meV Van de Graaff accelerator. The inner bag containing the sample was passed under the electron beam at 1 mamp for sufficient time to give the dose indicated in the text. Dosimetry is described in the literature.<sup>11,7</sup> The sample was then returned to the second nitrogen flushed bag for transportation back to the laboratory.

**Grafting Experiments.** The irradiated sample was removed from the polyethylene bag in a nitrogen-filled glove bag and placed in a pressure bottle. The bottle was sealed, attached to a Parr hydrogenator charged with TFE, and pressurized to 50–60 psig with TFE. Progress of the TFE grafting reaction could be followed by observing a pressure drop in the apparatus.

In experiments where mixtures of TFE and EVE were grafted to PSEPVE copolymer substrates, the irradiated substrate was immersed in EVE previously charged to the bottle. The bottle was then transferred to the Parr apparatus and pressurized with TFE.

The amount of material grafted to the substrate was determined from the initial weight of the sample before irradiation and its final weight after the grafting reaction. Samples treated with TFE–EVE mixtures were dried in a vacuum oven at 120°C after grafting to remove any unconverted EVE before weighing.

**Crosslinking Experiments.** Irradiations were conducted as described above. Compounded samples were prepared on a two-roll rubber mill by adding 10 parts SAF carbon black, 4 parts micronized magnesium oxide, and 0.5 parts dicyclohexyl-18-crown-6 to 100 parts polymer. The compounded stock was molded into "O"-rings about 1 in. in diameter and 0.1 in. thick. Samples containing DVE were prepared by placing weighed "O"-rings in a vial with a small amount of DVE. The DVE was rapidly absorbed by the ring, and several days were allowed to pass before irradiating the sample to hopefully establish an equilibrium distribution of DVE in the ring. After irradiation the rings were heated in a vacuum oven at 120°C to remove any unreacted DVE. The final weight of the ring was then used to determine the amount of DVE remaining in the ring.

**Analytical Techniques.** Solvent swell measurements were made by immersing samples completely in TTD in capped vials. The percent swell was calculated from the initial and swollen sample weights after blotting excess solvent from the sample. 24 h were allowed for equilibration of the samples. No significant weight changes were detected for samples equilibrated longer periods of time.

Equivalent weight (EW) for the PSEPVE copolymers is defined as the weight of polymer required to neutralize one 1 g-eq of sodium hydroxide. EWs reported in this work were determined by the following procedure.

The sample in sulfonyl fluoride form was hydrolyzed in a mixture containing 15 parts by weight potassium hydroxide, 35 parts by volume dimethyl sulfoxide, and 50 parts by volume water for 2 h at 90°C. The hydrolyzed film was washed neutral to test paper with water and treated with three portions of 10% sulfuric acid for 30 min each. The sample, now in the sulfonic acid form, was washed free of excess acid with copious amounts of distilled water. The pH of the wash water was monitored with a glass electrode to insure all excess acid was removed. The sample was then placed in 10% sodium chloride containing standard sodium hydroxide and stirred for 30 min. The excess hydroxide was back titrated with standard acid. The sample was washed free of sodium chloride with distilled water and dried to constant weight. The EW was calculated from the titration data and the dry sample weight. Replicate samples showed the precision of these determinations to be  $\pm 2\%$  of the mean value. Accuracy is believed comparable.

Tensile measurements were made on die cut strips 5 in.  $\times$  0.25 in. from a film of PMVE copolymer 0.05 in. thick. Measurements were made on an Instron instrument at an elongation rate of 20 in./min. Compression set measurements were made on "O"-rings compressed to 75% of their original thickness and heated to 204°C for 70 h. The percent of the compression retained by the sample was then determined.

## RESULTS AND DISCUSSION

### Crosslinking PMVE Copolymers

Our original intent was to graft new monomers onto the amorphous TFE-PMVE backbone. Several attempts to accomplish this with techniques used to prepare the graft polymers described below failed. We discovered, however, that these polymers crosslinked during irradiation. To study this effect a number of samples were given different doses of radiation, and solvent swells were determined in 2,2,4,4-tetrakis(trifluoromethyl)-1,3-dithietane (TTD). The results are summarized in Figure 1.

TTD is normally a good solvent for amorphous PMVE copolymers. Samples irradiated with 0.5 or 1 Mrad were at least partially insoluble in TTD and yielded highly swollen irregularly shaped gel particles. Samples exposed to 2 Mrad doses were single pieces which retained their original shape, but they imbibed large quantities of solvent and swelled 2000%. Thereafter, swelling decreased rapidly with radiation doses up to 40 Mrad.

The tensile properties of the irradiated samples are presented in Figure 2. The modulus of the samples gradually increased with dose. Little effect was observed on the tensile strength or on the elongation at break until a dose of 10 Mrad was reached. Thereafter, sharp decreases in these properties were noted.

The uniform increase in tensile modulus and the uniform decrease in solvent swell would be expected if polymer networks formed during irradiation with crosslink density dependent on dose. The loss of tensile strength and elongation

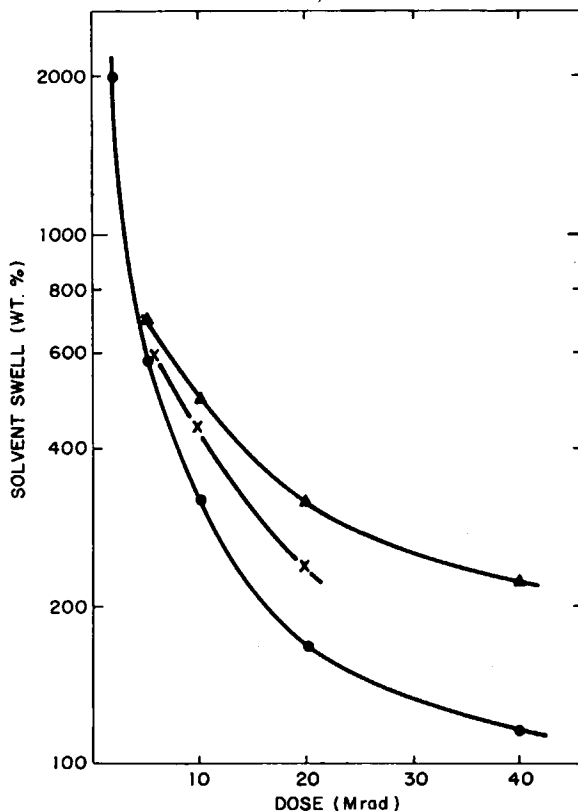


Fig. 1. Solvent swelling of irradiated PMVE copolymers: (●) gum elastomer; (▲) "O" ring compound; (x) "O" ring compound + DVE.

at the higher doses may indicate the formation of networks with relatively high crosslink densities. Similar patterns are observed for tensile properties of irradiated polyvinyl fluoride,<sup>12</sup> a polymer known to crosslink under similar conditions.

The effects of radiation on PMVE copolymers containing carbon black and magnesium oxide was also investigated. These ingredients are commonly found in rubber articles and would likely be required if any practical use was made of radiation crosslinking. Additionally, a small amount of dicyclohexyl-18-crown-6 was added as a processing aid during the milling operation. The rubber compound was molded into "O"-rings and irradiated.

Solvent swell measurements for these samples are included in Figure 1. In these cases, small corrections to the swell measurements were made to account for the carbon black and magnesium oxide content of the sample. The results clearly show the occurrence of crosslinking. For a given dose a somewhat higher swell, and, presumably, a lower crosslink density, was observed for the "O"-ring compound relative to the uncompounded elastomer. The mechanical properties of the crosslinked compound were investigated by compression set measurements on "O"-ring specimens. We found that samples irradiated with less than 20 Mrad exhibited 100% set, i.e., no recovery after stress on the specimen was released.

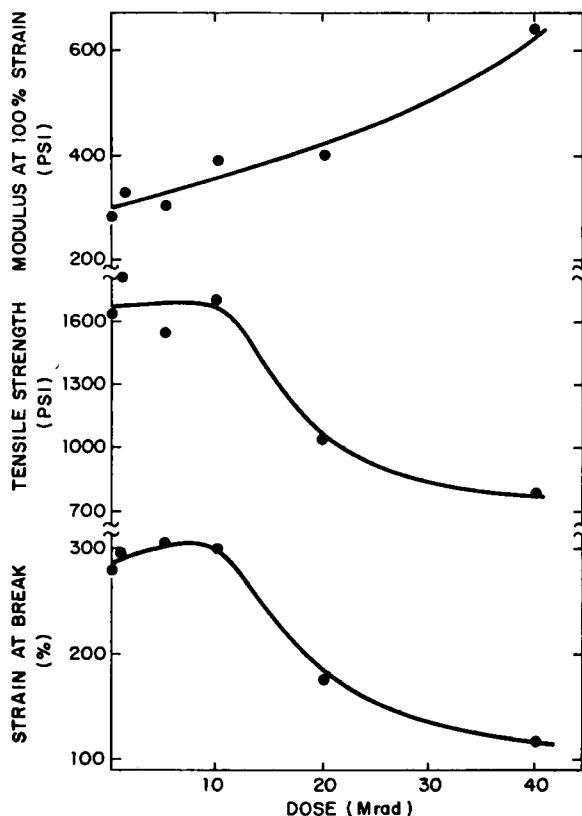


Fig. 2. Tensile properties of irradiated PMVE copolymers.

Samples irradiated with doses of 20 Mrad or more crumbled during the test.

To see if crosslinking efficiency could be improved so that better networks were formed at lower radiation doses, "O"-rings were doped with perfluoro(ethylene divinyl ether) (DVE). We have shown that DVE is an easily polymerizable monomer which will produce gelled copolymers under free radical conditions. The results in Figure 1 show lower swells at a given dose when DVE was present and indicate that the crosslinking process was somewhat more efficient. Unfortunately, compression set measurements on these samples were equivalent to those obtained without DVE. Sets of 100% were observed for samples irradiated with less than 20 Mrad, and crumbled samples were observed at doses of 20 Mrad or higher.

These poor mechanical properties indicate that chain scission in addition to crosslinking must be an important process occurring during irradiation. The simultaneous appearance of these two processes is a common occurrence and must lead to a network structure far different from that obtained by chemically crosslinking the PMVE copolymer. Networks formed by chemical crosslinks have good mechanical properties<sup>13</sup> and show lower compression sets than observed in this work. If radiation crosslinking was simply the formation of bonds between polymer chains, then mechanical properties similar to the chemically crosslinked polymers would be observed.

TABLE I  
TFE Grafts to PSEPVE Copolymers

Experiment	EW <sup>a</sup>	Mol % TFE	Dose (Mrad)	% TFE grafted	Atmosphere
A	1100	86.6	0.5	6.8	N <sub>2</sub>
B	1100	86.6	5.0	13.6	N <sub>2</sub>
C	1200	88.3	0.5	11.1	N <sub>2</sub>
D	1400	90.5	0.02	4.8	N <sub>2</sub>
E	1400	90.5	0.1	8.9	N <sub>2</sub>
F	734	75.7	5.0	4.0	N <sub>2</sub>
G	1100	86.6	2.0	0	air
H	1100	86.6	5.0	0	air
I	1100	86.6	10.0	0	air

<sup>a</sup> EW is the amount of polymer (g) required to neutralize 1 g-eq of NaOH.

### Grafting to PSEPVE Copolymers

In contrast to the PMVE copolymers, the PSEPVE copolymers were easily grafted with TFE after irradiation in a nitrogen atmosphere. No grafting was observed when samples were irradiated in air. The data in Table I illustrate these results for PSEPVE copolymers of different compositions.

We observe two features of the grafting process from these data. First, for a given polymer the amount of TFE grafted increases with the radiation dose. This point is established by comparing experiments A with B and D with E. Restaino and Reed<sup>14</sup> have found that the amount of vinyl acetate grafted to PTFE is proportional to the square root of the dose. Although we do not have sufficient data to permit a similar quantitative analysis for our case, the approximate doubling of the grafted amount of TFE as doses increase by factors of 5 or 10 suggests that a similar relationship exists here.

Second, experiments A and C or B and F show that the amount of TFE grafted for a given dose is also dependent on the TFE concentration in the irradiated copolymer. Even minor differences in polymer composition, as in experiments A and C, appear to have a significant effect. Thus, grafting is believed to occur predominantly on the TFE segments of the PSEPVE copolymer.

Examination of these grafted samples by differential scanning calorimetry (DSC) discloses the presence of a melting point at 325°C characteristic of PTFE. The area under the endotherm increased with the amount of grafted TFE, but the position of the endotherm is invariant.

TABLE II  
Effect of Radiation on Equivalent Weight and Solvent Swell

Experiment	Dose (Mrad)	EW
A	0	1109
B	2	1106
C	5	1087
D	10	1121

TABLE III  
TFE-EVE Grafts to PSEPVE<sup>a</sup> Copolymer

Experiment	Dose (Mrad)	% TFE/EVE Grafted	Composite EW	TFE/EVE EW (est)
A	5.0	12.1	1182	1700
B	5.0	16.0	1284	1980

<sup>a</sup> PSEPVE substrate was a film with EW = 1109.

At the higher radiation doses a faint odor of sulfur dioxide was sometimes noted in the sample bags, indicating that some radiolysis of the sulfonyl fluoride group in the polymer occurred. No other attempt to characterize the volatile radiolysis products was made, but equivalent weights and solvent swells for the polymers were checked. These data are reported in Table II. The equivalent weight measurements determined by titration are precise to within  $\pm 2\%$  and show no significant change when samples of PSEPVE copolymer are irradiated with doses up to 10 Mrad. These results are in substantial agreement with Balko and Chaklos,<sup>11</sup> who only observed significant changes in EW when doses exceeded 10 Mrad.

We examined the TFE grafted samples by scanning electron microscopy (SEM). No features were observed until the films were hydrolyzed and converted from the sulfonyl fluoride to the sulfonate form. This is most likely because the hydrolysis mixture washed low molecular weight PSEPVE copolymer, formed during irradiation,<sup>11</sup> from the film surface. SEM then revealed details as shown in Figure 3. At the lowest magnification the largest regions of PTFE, 4–8  $\mu\text{m}$  in diameter, are observed. These appear as rather angular clusters of many PTFE particles arranged in rows. The rows correspond to the direction of extrusion for the film and were not observed in melt pressed films treated in a similar manner. Higher magnification also shows the presence of numerous smaller granules of PTFE spread more or less uniformly over the surface. The smallest of these granules are about 0.1  $\mu\text{m}$  in diameter and are smoother and more spherical in appearance than the larger ones.

By exposing irradiated PSEPVE copolymer films to mixtures of TFE and methyl perfluoro-3,6-dioxo-4-methyl-7-octeneoate (EVE) we were able to prepare TFE-EVE copolymer grafts. Data for these materials are presented in Table III.

The infrared spectrum of the grafted film clearly shows the presence of the ester by the appearance of a band at 1780  $\text{cm}^{-1}$ . Upon hydrolysis of the film, the carbonyl band shifts to 1690  $\text{cm}^{-1}$ . These spectroscopic data are in precise agreement with those obtained on the monomer and its sodium salt. The measured equivalent weights of the composite grafted samples and the known equivalent weight of the substrate PSEPVE copolymer permitted the equivalent weight of the TFE-EVE grafts to be estimated. These estimates are included in Table III.

Information about the morphology of the grafted samples was obtained by SEM. When the hydrolyzed films were fractured in liquid nitrogen and viewed on edge, a layered structure was clearly evident as shown for sample A in Figure 4. The thickness of the top layer was 0.0006 in. and that of the bottom layer 0.0047 in. Assuming the densities of the carboxylate and sulfonate copolymers

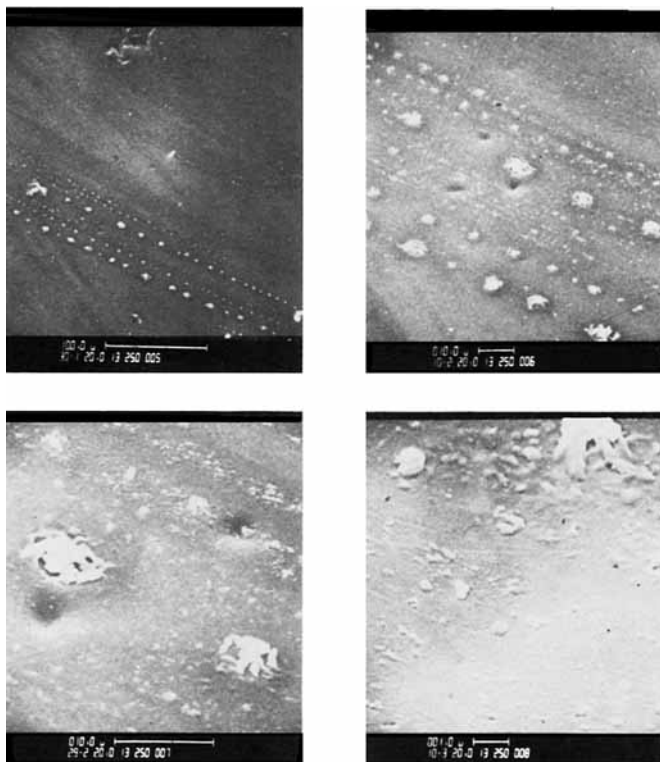


Fig. 3. TFE grafts on hydrolyzed PSEPVE copolymer. Large clusters of TFE particles are observed to coincide with the extrusion direction of the film. Small particles in the lower photographs appear more evenly distributed.

are nearly equal, the carboxylate layer accounts for 11.4% of the sample. This is in good agreement with the 12.1% reported for the graft in Table III and suggests that the TFE-EVE graft polymer formed a layer of uniform thickness. Adhesion between the layers was excellent, with no evidence of delamination occurring during hydrolysis of the sample. This may be due to some interpenetration between the layers. Close examination of the interface between the layers suggests the presence of a third layer which could be an overlapping boundary of the PSEPVE copolymer on one side and the TFE-EVE graft on the other. This is especially evident in the lower left photograph in Figure 4.

### CONCLUSION

The predominance of crosslinking during irradiation of PMVE copolymers is an unusual result for a perfluorinated material. The occurrence of crosslinking in hydrogen containing fluoropolymers, on the other hand, is commonly observed. This is often attributed to the formation of many double bonds in the polymer by loss of hydrogen fluoride<sup>2,15</sup> presenting sites for facile crosslinking. Presumably, the absence of such mechanisms in perfluorinated polymers provides chain scission with a kinetic advantage over crosslinking. This may account for the general dominance of chain scission in perfluorinated polymers. Crosslinking



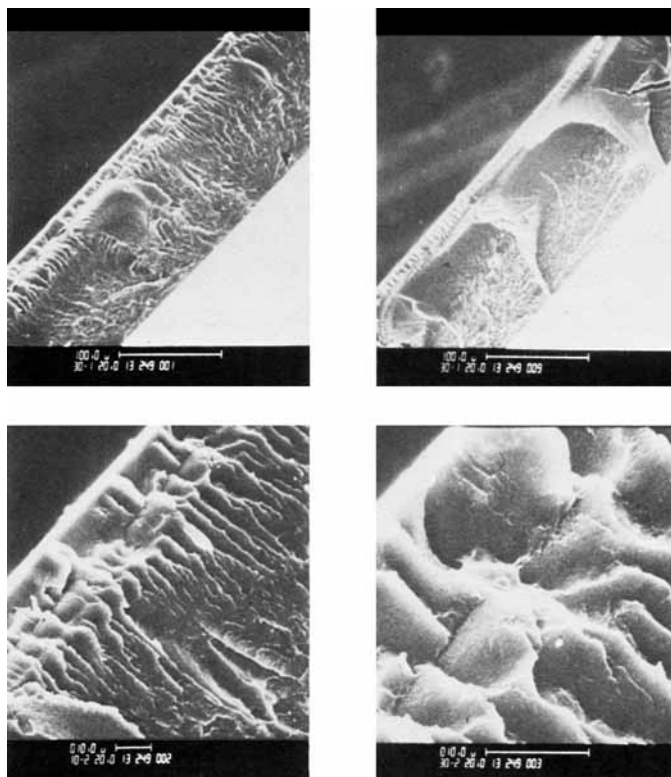


Fig. 4. Photomicrograph of hydrolyzed PSEPVE copolymer film with TFE-EVE graft (refer to Table III, experiment A). Film is viewed on edge. Note the thin TFE-EVE graft layer on the upper film surface. The lower photographs are magnifications of a portion of the area shown in the top left photograph.

in such cases will rely on radical coupling reactions. Evidence for the presence of terminal vinyl groups produced during irradiation has been obtained recently,<sup>6</sup> but no evidence for internal olefins was found. Since unsaturation appears limited to end groups, crosslinking by radical addition to these species will likely be a small factor. For these reactions to occur, it is necessary for the reactive species to have sufficient mobility to come in contact with each other. In crystalline materials like PTFE, this will be a relatively slow process because many of the radicals are imbedded in the crystalline matrix. The rubbery nature of the PMVE copolymers, however, should provide greater mobility to radical sites produced in those materials, and, thus, provide an enhanced opportunity for the radical recombination processes.

The PSEPVE copolymers contain large enough quantities of TFE to be slightly crystalline. The observed dependence of grafting on the TFE content of the polymer is consistent with the idea that the long-lived radicals necessary for grafting are imbedded in the crystalline portions of the polymer. The polymer crystallinity also increases with the TFE content. This would be expected to yield higher concentrations of stable radicals and account for the increased ease of grafting with polymer of higher TFE content. The failure of TFE to graft to samples irradiated in air demonstrates the absence of radicals in these cases.

Evidently the radicals, which must have been initially produced, reacted with oxygen to yield new stable species which did not initiate grafting. The literature<sup>3,5,6</sup> indicates that these new species could be acid fluorides, peroxides, or hydroperoxides. The two latter possibilities, if present, should be capable of initiating grafting at higher temperatures than the ambient conditions used in this work. It would be interesting to try and demonstrate this experimentally. The presence of sulfur dioxide as a radiolysis product indicates that radicals are produced in the rubbery part of the polymer. The role of these radicals in the chemistry occurring during irradiation remains to be determined.

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