Low Dose γ-Irradiation of Some Fluoropolymers: Effect of Polymer Chemical Structure

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SYNOPSIS

The effect of low dose (1–20 Mrad) γ-irradiation on five fluoropolymers (PVF, PVDF, ETFE, FEP, PFA), differing in fluorine content and chain structure, was studied. The radiation effect, reflected by changes in thermal and mechanical properties, as well as NaOH etched surface morphology, was investigated. The main chain structure was found to predominate the irradiated polymers' behavior. The tensile strength of PVF and its resistance to etching increased with radiation dose, while its degree of crystallinity and melting temperature decreased. These changes were correlated with network formation by irradiation and by the incorporation of crosslinked segments into the crystalline phase during recrystallization. Solvent extraction of PVDF (no solvents were found for the other fluoropolymers) revealed increased gel formation with increasing dose. The degree of crystallinity and the tensile strength dependence on radiation dose for PVDF and ETFE reflected the competition between crosslinking and chain scission events. FEP and PFA undergo predominantly chain scission accompanied by reduction of their mechanical properties. PFA even exhibited an increase in both its melting temperature and degree of crystallinity, stemming from a massive degradation process forming shorter chains. Chemical mechanisms are discussed in an attempt to correlate the irradiation effects with the polymers' chain structure.

INTRODUCTION

Radiation induced changes in polymeric materials continue to draw attention for practical reasons. For production, utilizing radiation chemistry alters the chemical and physical structures in order to improve some physical properties; for applications, the search is made for polymers that are not destructively affected by radiation. Polymers exposed to ionizing irradiation, even at low doses, often undergo structural changes accompanied by molecular crosslinking and chain scission (degradation) reactions.[1–4] The general effect of the radiation on polymers is determined by the ratio of crosslinking to chain scission events. This ratio depends on parameters such as chemical structure, physical state, radicals stability and mobility, irradiation rate, and irradiation atmosphere.

Polymers have often been classified according to their tendency to crosslink or to degrade upon exposure to ionizing irradiation.[5,6] However, some caution should be practiced, since this tendency may depend on external conditions, such as temperature and atmosphere.[7] Nevertheless, studying such classifications suggests certain principal chemical structural differences between the two polymer groups[8] and/or correlation between heats of polymerization and radiation effects.[9]

The present work focuses on the effects of radiation on various fluoropolymers. In the literature are reports on the response of fluoropolymers to irradiation sources, which sometimes do not draw satisfactory conclusions due to the diversity of the radiation sources and conditions, to contradicting results, and to the lack of experimental details and inconsistency in data interpretation.

Poly(tetrafluoroethylene), PTFE, predominantly undergoes degradation when irradiated[10–16] resulting in a marked decrease in melt viscosity and ultimate mechanical properties, as well as an increase in the

degree of crystallinity and crystal disorder[13–15,17]; the resulting density changes largely depend on the amount of void formation.[15,17] A marked effect of the irradiation environment, such as air, oxygen, nitrogen, or vacuum, was found; the presence of oxygen increases the degradation rate and level. Duraud et al.[18] and Straus and Wall,[19] however, reported that PTFE undergoes crosslinking mainly upon irradiation. Various copolymers of tetrafluoroethylene, TFE, were also investigated, for example, poly(TFE-co-hexafluoropropylene), FEP, has been reported to undergo both crosslinking and chain scission reactions,[10,12,17,20–22] while the respective hompolymers undergo only scission.[10,17] Interestingly, poly(TFE-co-perfluoro methyl vinyl ether), TFE-co-PMVE, is crosslinked,[10,17] probably due to its rubbery state at ambient irradiation temperature, which enables radical mobility. On the other hand, in poly(TFE-co-perfluoro-3,6-dioxa-4-methyl-7-octene sulfonyl fluoride), stable radicals are formed, which enable either further grafting reactions or degradation.[10,23] A series of pure fluorocarbon copolymers were found[12] either to form some crosslinks or mainly to degrade, depending on the effects of steric hindrances coupled with the various reaction kinetics. All of the copolymers were reported to degrade if irradiated in the presence of oxygen or chlorine. A few additional fluoropolymers were studied as to their structural and property changes upon exposure to ionizing radiation. Poly(chlorotrifluoro ethylene), PCTrFE, degrades[17] as does PTFE. However, PTrFE,[19] poly(CTrFE-co-ethylene),[19,24] poly(vinyl fluoride), PVF,[15,25] and poly(vinylidene fluoride), PVDF,[15,25–28] undergo various degrees of crosslinking accompanied by different levels of degradation. It should be mentioned that according to Sands and Perdirtz,[26] poly(vinylidene chloride) degrades.

These literature reports suggest that the dominating reactions, induced by high energy radiation of fluoropolymers, strongly depend on the chemical structure and hydrogen content in the chain backbone. It seems that the presence of the hydrogen atoms enables the formation of unsaturated bonds, which then participate in intermolecular crosslinking, a process accompanied by hydrogen and HF formation,[12,29] while other structural groups create radicals of different structures, mobility, and stability. The purpose of the present work is to study systematically the effect of a common ionizing radiation source under vacuum on a series of five fluoropolymers at room temperature. This study has been undertaken to shed more light on the effects of chain structure and H/F ratio on the radiation induced changes.
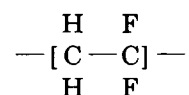
EXPERIMENTAL

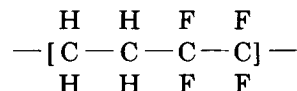Five different fluoropolymers were used in the present study as follows:
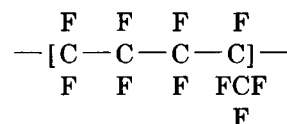
1. Poly(vinyl fluoride), (PVF, Tedlar, duPont, oriented)

$$-[\overset{\displaystyle H}{\underset{\displaystyle H}{C}} - \overset{\displaystyle F}{\underset{\displaystyle H}{C}}]-$$
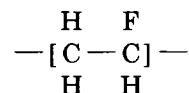
2. Poly(vinylidene fluoride), (PVDF, Kynar, Penwalt)

$$-[\overset{\displaystyle H}{\underset{\displaystyle H}{C}} - \overset{\displaystyle F}{\underset{\displaystyle F}{C}}]-$$

3. Poly(ethylene-co-tetrafluoroethylene), (ETFE, Tefzel, duPont)

$$-[\overset{\displaystyle H}{\underset{\displaystyle H}{C}} - \overset{\displaystyle H}{\underset{\displaystyle H}{C}} - \overset{\displaystyle F}{\underset{\displaystyle F}{C}} - \overset{\displaystyle F}{\underset{\displaystyle F}{C}}]-$$

4. Poly(tetrafluoroethylene-co-hexafluoropropylene), (FEP, Teflon FEP, duPont)

$$-[\overset{\displaystyle F}{\underset{\displaystyle F}{C}} - \overset{\displaystyle F}{\underset{\displaystyle F}{C}} - \overset{\displaystyle F}{\underset{\displaystyle F}{C}} - \overset{\displaystyle F}{\underset{\displaystyle FCF}{\underset{\displaystyle F}{C}}}]-$$

5. Poly(tetrafluoroethylene-co-perfluorovinyl-ether), (PFA, Teflon PFA, duPont)

$$-[\overset{\displaystyle F}{\underset{\displaystyle F}{C}} - \overset{\displaystyle F}{\underset{\displaystyle F}{C}} - \overset{\displaystyle F}{\underset{\displaystyle \underset{\displaystyle R_f}{FCF}}{\underset{\displaystyle O}{C}}} - \overset{\displaystyle F}{\underset{\displaystyle F}{C}} - \overset{\displaystyle F}{\underset{\displaystyle F}{C}}]-$$
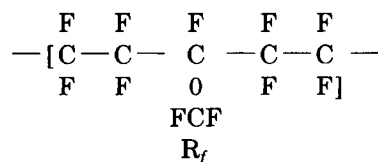
$$R_f = C_n F_{m+1}$$

All polymers were in a sheet form, 3–10 mil thick, and were studied "as received."

Samples were vacuum packed in sealed bags of a nylon/polyethylene laminate and then γ-irradiated, using a C_6^{60} source, at a rate of 0.064 Mrad/h up to doses of 20 Mrad. Treated samples were kept UV protected in a desicator until tested and characterized.

Gel content in the irradiated PVDF films was determined by extraction in N,N-dimethylacetamide (DMA) at 160°C for 24 h. The gel content in the other polymers was not determined for lack of appropriate solvents. For the same reason, the swelling ratio of only PVDF was determined, using DMA.

Thermal analysis was applied to all samples to study the effect of γ-irradiation on the melting and crystallization temperatures and on the heat of fusion (degree of crystallinity) of the various fluoropolymers. A Mettler differential calorimeter (DSC-TA3000) was used at either heating or cooling rates of 10°C/min. Samples, $\sim$ 10 mg, were heated from 35°C to a temperature of about 30°C above melting (first run). Samples were then cooled at a controlled rate back to 35°C and were reheated (second run). The peak melting, T_m, and crystallization, T_c, temperatures will be reported as well as the heats of fusion, ΔH_f, and crystallization, ΔH_c, as calculated from the endo- and exotherms area, respectively.

The surface morphology of some films was studied by a two stage replicating technique using a cellulose acetate film, Pd/Au shadowing and C deposition. To enhance the observed morphology, the films were etched with NaOH (20% aqua sol). A Joel 100CX STEM was used to analyze the surface replicas.

Tensile properties were determined using a Zwick 1445 universal testing machine operated at 5 cm/min. Film strips, 100 × 15 mm, were tested at room temperature and the characteristic tensile modulus, ultimate strength and strain (average of 3–5 tests), were calculated from the stress–strain curves.

RESULTS AND DISCUSSION

Thermal Analysis

In the thermal analysis of polymers irradiated in the solid state, it is important to include both first and second DSC runs. The first run represents a polymer crystallized from the melt and then irradiated in the solid state, while the second run represents the a polymer crystallized from a melt of previously irradiated chains. Thus, structural changes induced by irradiation of the solid polymer affect the first run data, while the effect of irradiation on the chains' crystallization process, and the final crystallinity, is manifested in the second run.[30] It should be mentioned that the difference between the two DSC runs is also due to the different thermal history of the analyzed samples (manufacturing conditions vs. controlled cooling in the instrument). Representative examples of both effects are depicted

in Figure 1. For the unirradiated samples, the differences between the first and second runs are solely due to thermal history effects. In the irradiated samples, the difference is a result of a coupled effect: thermal history as well as irradiation. It should be mentioned that all irradiated samples exhibit a single melting endotherm.

Irradiation doses of up to 20 Mrad do not affect the melting temperature of PVF, as seen in the first run thermograms (Fig. 2b). Thus, no significant changes occur in the crystalline degree of order and all the irradiation induced alterations in the amorphous phase are such that they do not affect T_m. However, PVF, crystallized from the irradiated melts, exhibits melting temperatures that gradually decrease with increasing irradiation dose (ΔT of 5°C at 20 Mrad). The crystals formed from these irradiated melts are smaller and less perfect than the unirradiated counterparts, due to the presence of crosslinks and branches in the irradiated melts. In
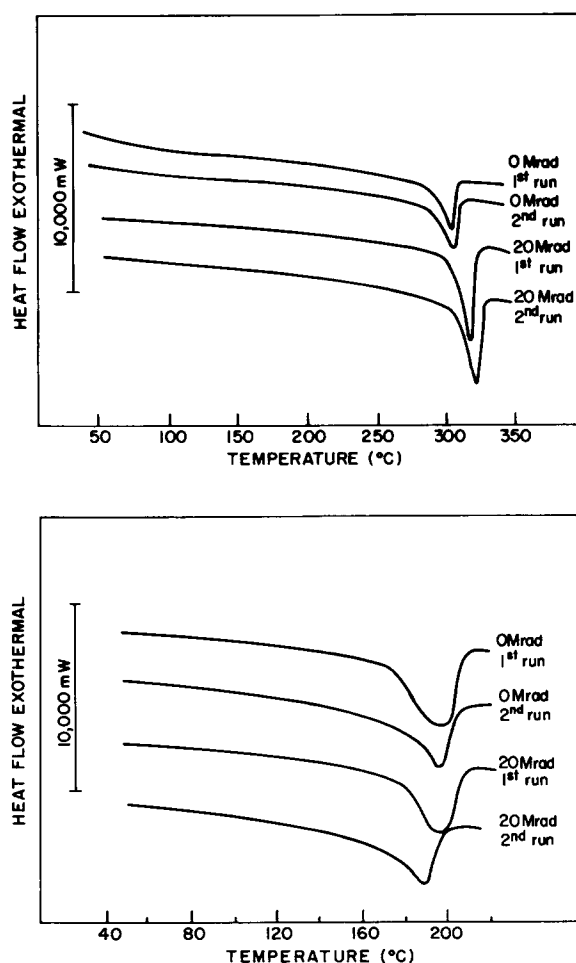
Figure 1   The effect of γ-irradiation on the DSC thermograms of (a) PVF and (b) PFA.
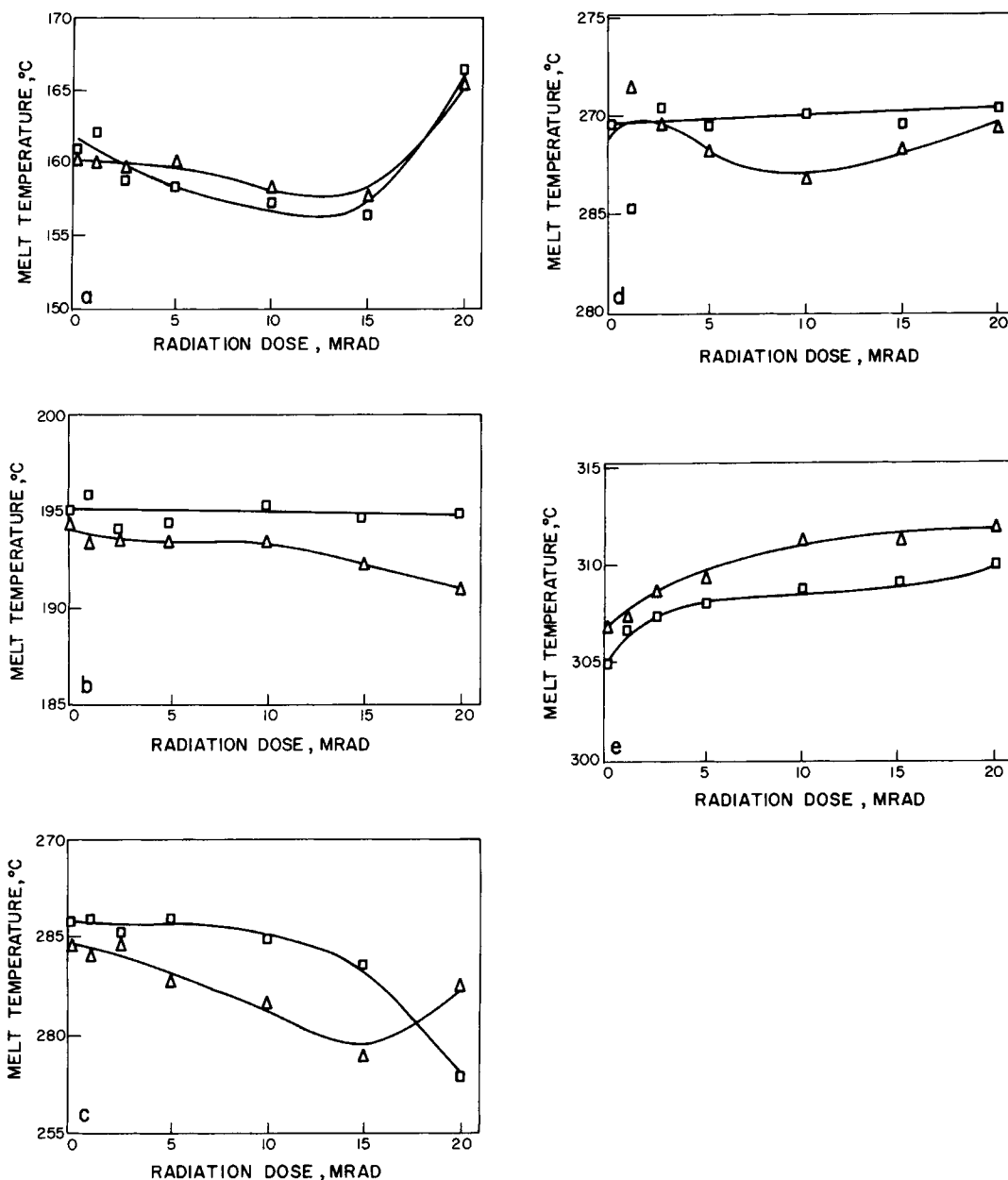
Figure 2   The effect of γ-irradiation on the melting temperature of (a) PVDF, (b) PVF, (c) ETFE, (d) FEP, and (e) PFA.

the case of PVDF (Fig. 2a), the melting temperatures of the irradiated polymer (1st run), as well as those of the recrystallized irradiated polymer (2nd run), decrease with increasing the dose up to 15 Mrad. Samples irradiated at 20 Mrad exhibit T_m values higher than those of the original sample. The decreasing T_m measured during the first run may be due to the irradiation induced radicals that undergo, during the heating cycle in the DSC, crosslinking reactions, resulting in larger defect content in the

crystals. Mukherjee et al.[31] have reported similar behavior for irradiated polypropylene. Often, however, irradiated polymers, exhibit increasing first run T_m with increasing dose. The increase in T_m observed in the 20 Mrad irradiated PVDF was not observed in the corresponding extracted gel (free of sol); instead, in the latter, T_m was the lowest among the studied samples.[28] It should be mentioned that the T_m of the gel fraction is lower than that of the whole irradiated polymer; the difference increases with

dose. Such a sol effect was also reported for poly-ethylene,[32] becoming stronger with increasing gel content (increasing irradiation dose), actually, with increasing branching and lower molecular weight chains content in the sol fraction. ETFE exhibits changes in T_m similar to those described above for PVDF. In the first run, the degree of crystallinity of PVF slightly increases with irradiation dose (1st run in Fig. 3A–a) while that measured in the second run gradually decreases with dose. Such a behavior is suggested to indicate that crosslinking is the preferred radiation induced process. The slight crystallinity increase may be due to some chain scission of, for example, tie molecules, which then crystallize at ambient temperature (about 45°C above T_g). The observed decrease in crystallinity (up to 30%) is
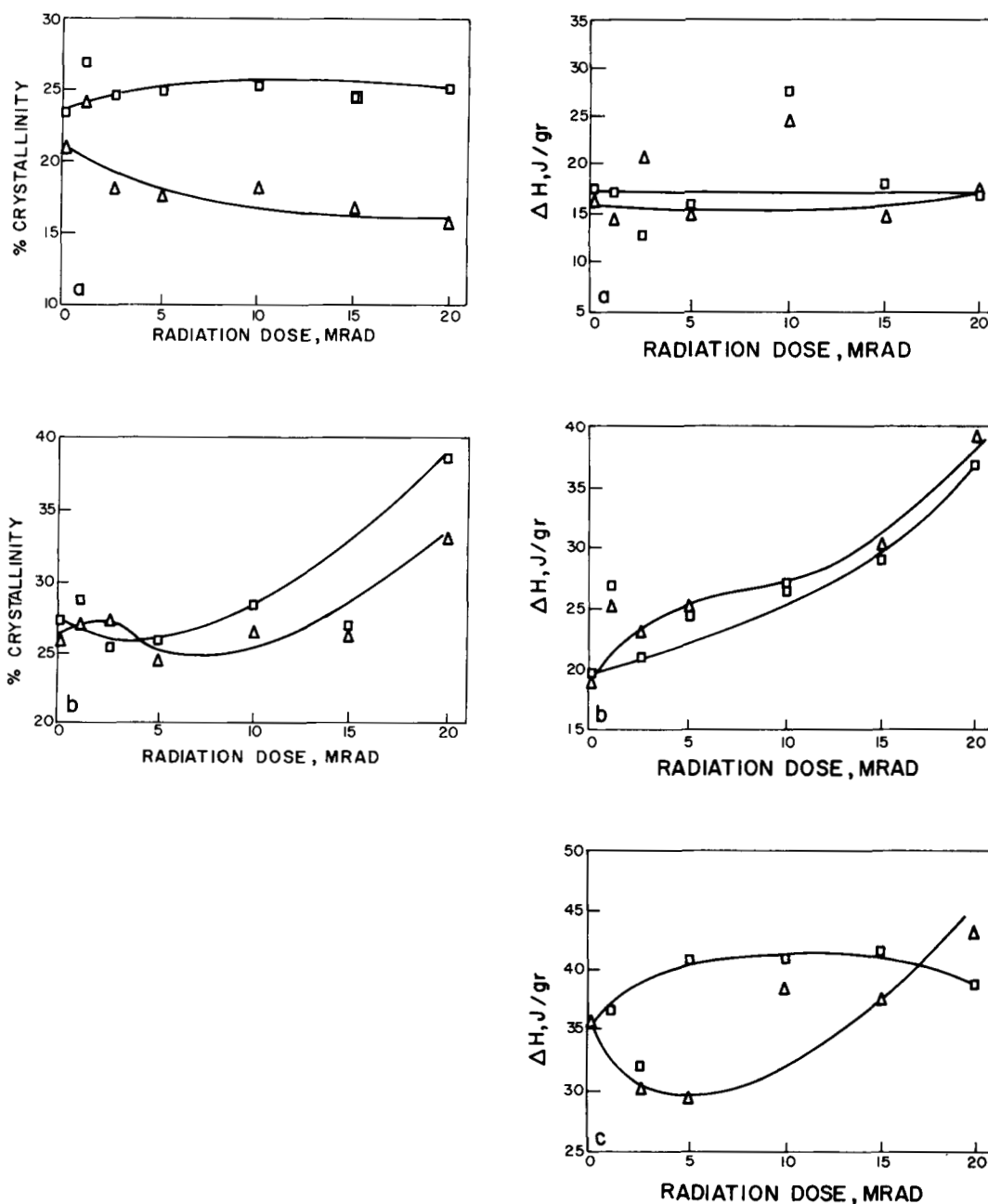

Figure 3 (A) The effect of γ-irradiation on the degree of crystallinity of (a) PVF and (b) PVDF. **B:** The effect of γ-irradiation on the heat of fusion of (a) FEP, (b) PFA, and (c) ETFE.

mainly due to crystallization from the partially crosslinked melt (some decrease in crystallinity was also observed in the 2nd DSC run of the unirradiated PVF, probably due to some orientation loss in the original film). The extraneous increased crystallinity in samples irradiated by a dose of 1 Mrad should be noted; similar behavior has also been reported by Timmerman and Greyson.[15] This behavior could stem from initial chain scission of stressed tie molecules. PVDF also exhibits peculiar behavior at low irradiation doses (Fig. 3 A, b), however, the general trend is toward increasing crystallinity, first and second runs, with dose. Based on solubility measurements,[28] PVDF undergoes upon irradiation both crosslinking and chain scission (3 scission events/ 5 crosslinking events.[28] The increasing second run crystallinity with dose, especially the high value at 20 Mrad, suggests that the sol and not the gel fraction predominates the crystallization process. The degree of crystallinity of the extracted gel was previously[28] found not to depend on the irradiation dose. Thus, the effect of the sol fraction on the crystallinity in irradiated PVDF increases with dose, actually decreasing with its content. This increasing degree of crystallinity with irradiation dose may also be due to a varying ratio of degraded chains to branched ones in the sol fraction, resulting from further irradiation and not just due to the changing sol content. Similar behavior has been reported for chemically crosslinked LDPE.[32] The degree of crystallinity in irradiated ETFE (Fig. 3B–c) first increases with dose, up to 5 Mrad, and then levels off, indicating transfer of chains from the amorphous to the crystalline phase due to chain scission. The second run crystallinity, however, decreases at the lower doses, up to 5 Mrad, and then increases attaining values higher than those of the original polymer. At the same time, the second run T_m gradually decreases with dose and only at 20 Mrad T_m almost increases back to the value of the original polymer (Fig. 2c). The melting temperature of FEP is not affected by radiation of up to 20 Mrad and its second run T_m is only slightly changed (Fig. 2d). It may stem from a low degree of crystallinity to begin with and thus most irradiation induced changes occur in the amorphous phase. PFA exhibits a different behavior; both first and second run T_m (Fig. 2e) increase with dose, the second one more significantly. This indicates that PFA undergoes mainly chain scission and the lower molecular weight polymer chains crystallize into more ordered crystals and are thus more thermally stable.

The irradiation induced changes in the heats of

fusion of the various polymers, and the differences between the values measured during the first and second DSC runs, are informative in regard to the radiation chemistry of these polymers. The degree of crystallinity in PVF (ΔH_f = 162.9 J/g[33]) becomes just slightly higher than that of the original polymer. Interestingly, the changes observed in the degree of crystallinity during the second runs in ETFE and PVDF (Fig. 3 B,c and Fig. 3A,b) are quite similar, suggesting similarity in their response to ionizing irradiation. Actually, they should be expected to behave similarly due to their chemical structure (identical H/F ratio). Since no solvent was found for ETFE, data on its crosslinking are still lacking, however, comparison with PVDF shows that ETFE does undergo crosslinking. The degree of crystallinity of FEP does not seem to be significantly affected by radiation (Fig. 3 B–a). The degree could stem from, as stated above, either balanced effects or low degree of crystallinity in this polymer (ΔH_f = 16 J/ g). PFA exhibits a different behavior (Fig. 3 B–b); its first and second run crystallinities sharply increase with dose, almost doubling its value in the 20 Mrad sample. This by itself indicates that irradiation results in a massive chain scission.

Additional information on the effect of radiation on the semicrystalline fluoropolymers is obtained by studying their crystallization upon cooling the irradiated samples from the melt. It should be mentioned that for all studied polymers, a single crystallization exotherm was observed, thus the sol and gel fractions either cocrystallize or at least crystallize within the same temperature range. The crystallization temperatures, as well as the degree of cooling of PVDF and PVF (Fig. 4 a,b), are not significantly affected by radiation. However, it has been recently reported[28] that the crystallization temperature of the PVDF gel fraction markedly decreases with dose or the resulting crosslink density. Thus, the observed crystallization temperatures are strongly affected by the presence of the sol fraction, probably so in most crosslinked polymers. The crystallization temperature of ETFE (Fig. 4 c) significantly decreases with dose (10°C at 20 Mrad), which suggests crosslinking to occur predominantly. On the other hand, both irradiated FEP and PFA exhibit increasing crystallization temperatures (Fig. 4 d,e), up to 2 and 9°C in the studied dose range. These observations are interpreted as a result of a chain scission effect.

It has been clearly shown that the thermal behavior of irradiated fluoropolymers is affected by the original chain structure. Coupling the thermal behavior of these polymers with their mechanical
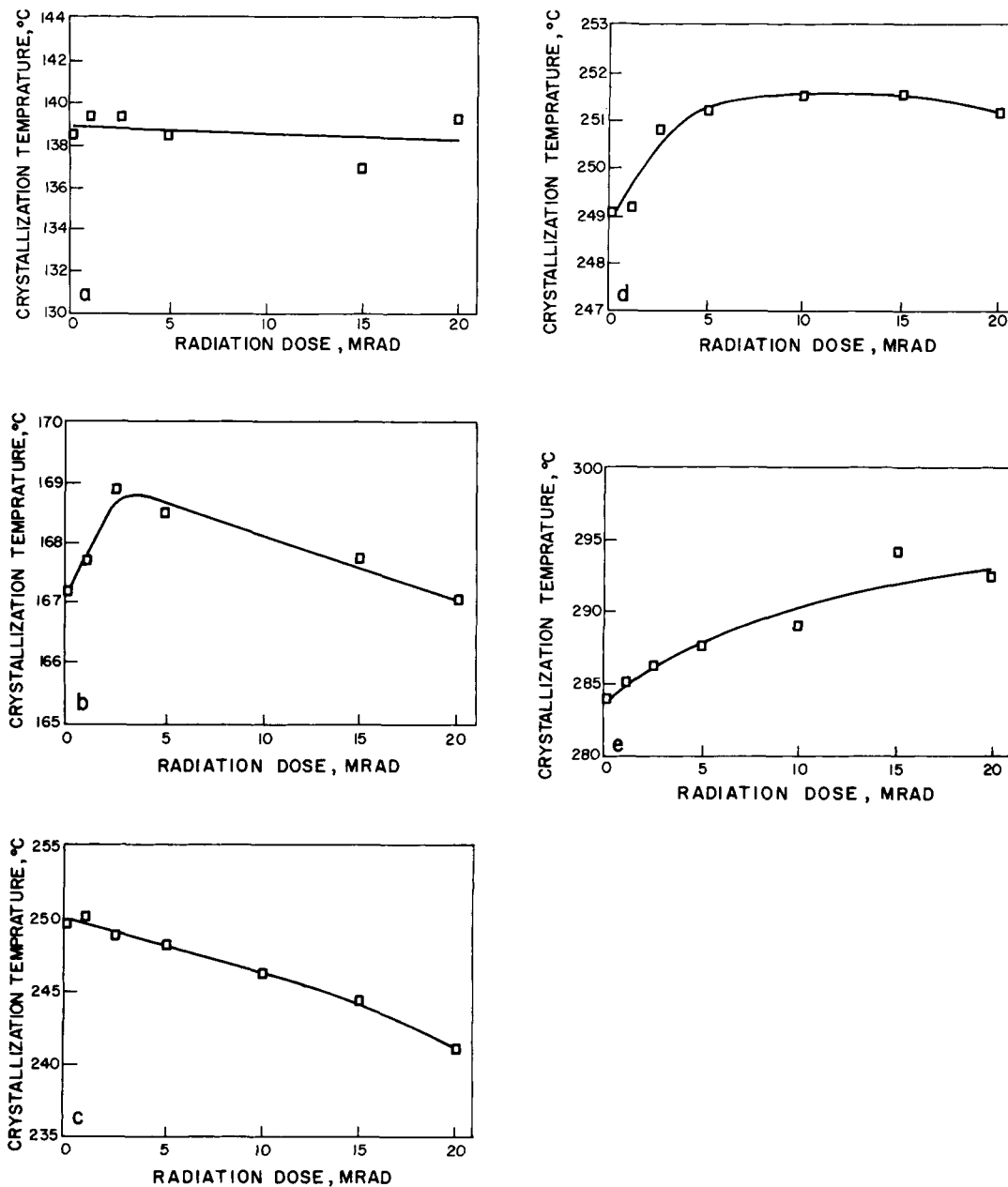
Figure 4   The crystallization temperature, as affected by γ-irradiation, of (a) PVDF, (b) PVF, (c) ETFE, (d) FEP, and (e) PFA.

behavior, described below, shows more conclusively the dependence of the radiation effects on the chains structure.

MECHANICAL BEHAVIOR

The tensile mechanical properties reflect structural changes that have occurred upon irradiation (no postirradiation treatment). PVF undergoes uniform deformation (no necking observed) when loaded parallel to the film machine direction. All the stress–strain curves include a clear yielding, unaffected by the irradiation. The PVF tensile modulus (Fig. 5b) first decreases by about 25% and then returns to its original value with increasing dose. However, the ultimate elongation decreases by about 14% at 5.0 Mrad and then remains unaffected by higher doses
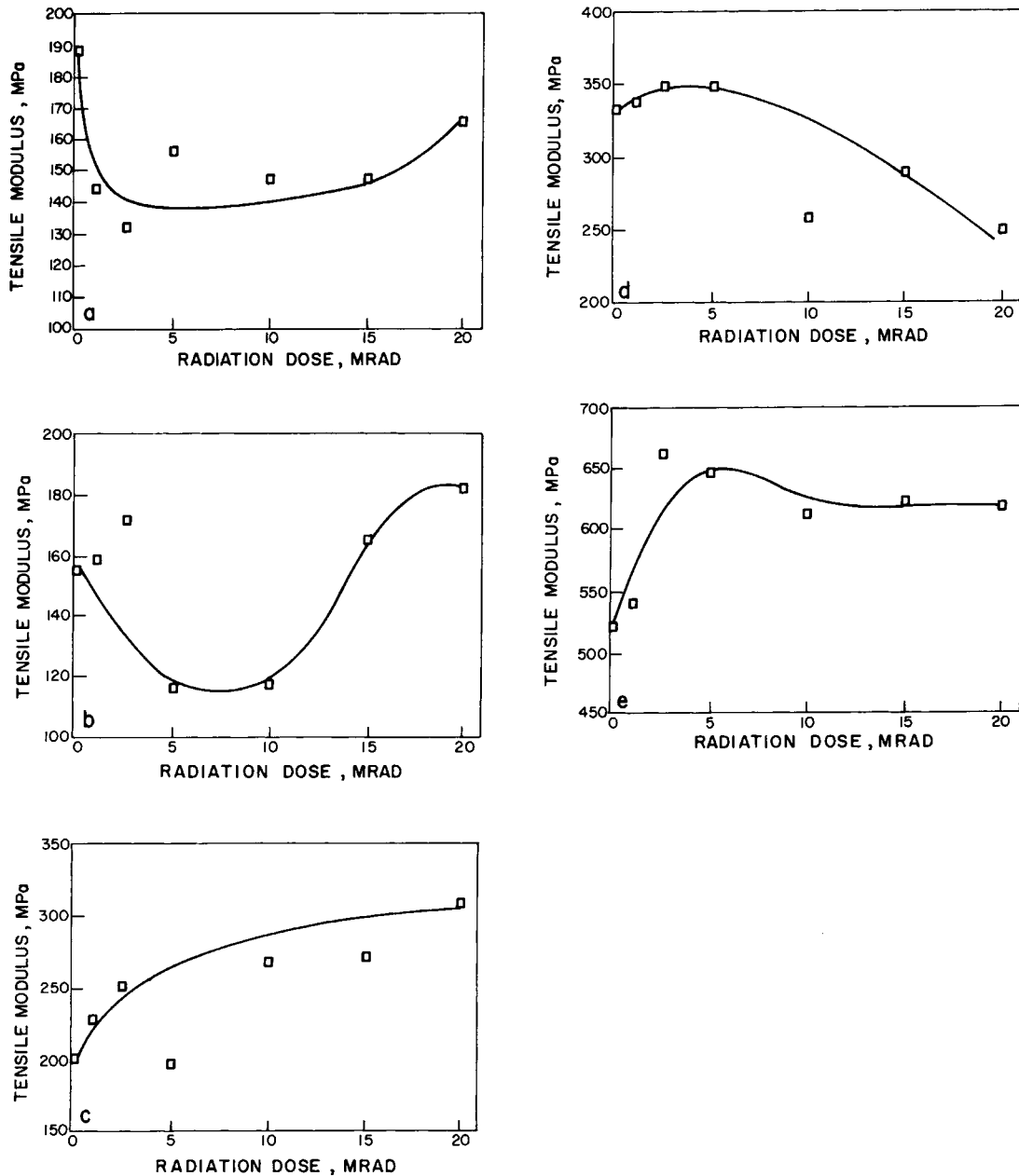
Figure 5   The tensile modulus, as affected by γ-irradiation, of (a) PVDF, (b) PVF, (c) PFA, (d) FEP, and (e) ETFE.

(Fig. 6b). Interestingly, the tensile strength of PVF (not shown) almost doubles upon irradiation of 1 Mrad and is not further affected. This behavior indicates the predominance of crosslinking; the drop in modulus (Fig. 5b) and elongation (Fig. 6b) is attributed to some chain scission (mainly of tie molecules), which is balanced by the main events of crosslinking. PVDF films deform through the formation of a neck, which becomes less prominent with increasing the dose, despite the constant elon-

gation at break maintained by all films (Fig. 6a). The latter suggests that the chain scission effect on elongation is compensated for by intermolecular crosslinking, despite its low density. The changes observed in the modulus (Fig. 5a) follow an upward trend, as in the degree of crystallinity only in films irradiated at the higher studied dose levels. Unexpected is the relatively large drop in modulus (31%) observed at low doses, whereas the crystallinity is just slightly changed. The initial changes thus occur
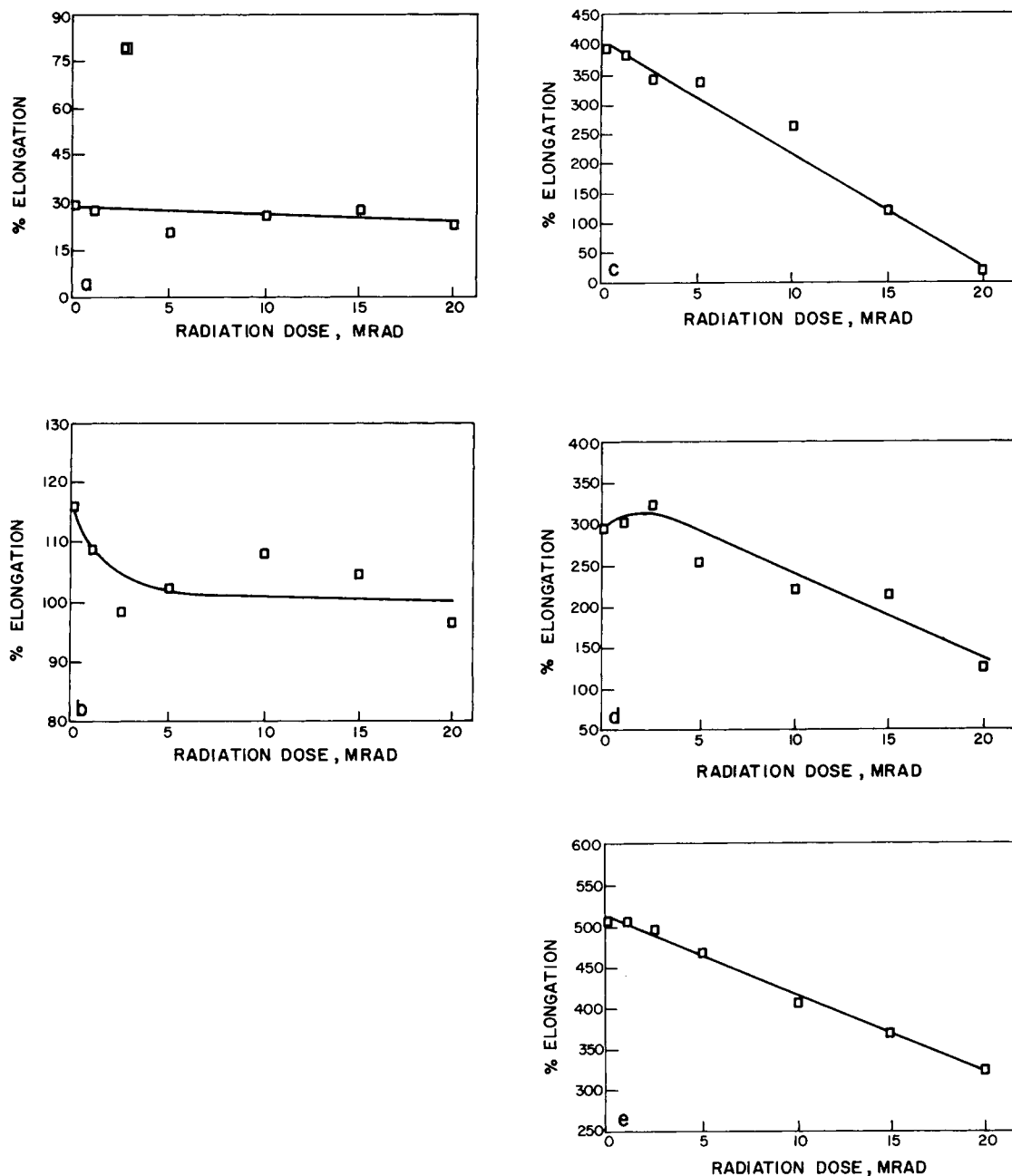
Figure 6   The effect of γ-irradiation on the ultimate elongation of (a) PVDF, (b) PVF, (c) PFA, (d) FEP, and (e) ETFE.

in the amorphous phase without significantly affecting the crystalline phase. It should be mentioned that the irradiation practically has not affected the PVDF films' strength.

The other three fluoropolymers studied (ETFE, FEP, and PFA) deform uniformly, without necking, in tension. The unirradiated films are all characterized by high ductility. Radiation does not affect the shape of their stress–strain curves, however, their

characteristic values are altered. The modulus of ETFE increases with an irradiation dose of up to 5 Mrad and then levels off (Fig. 5e). The modulus of FEP (Fig. 5d) continuously decreases with dose while the modulus of PFA (Fig. 5c) continuously increases. The tensile elongation of these three fluoropolymers is markedly decreased upon irradiation. In the dose range studied, the elongation of ETFE, FEP, and PFA is dropped by 40, 66, and 95%, re-

spectively; elongation is accompanied by a significant drop in their tensile strength (not shown). These losses in ultimate tensile properties are a consequence of chain scission and reflect its extent.

SURFACE MORPHOLOGY

The effect of γ-irradiation on the surface morphology of the fluoropolymers was studied via TEM by replicating NaOH treated surfaces. The NaOH etching effectiveness of irradiated fluoropolymers was found to depend on the polymers' chain structure and the irradiation dose.[19,34,35] Since crosslinking increases the fluoropolymers' resistance to etching, the TEM observations depend on the actual polymer morphology, as well as on its resistance to etching. FEP and PFA were not affected by NaOH; we were unable to study their morphology. In the other polymers studied, electron microscopy revealed only the changes in resistance to etching. With increasing radiation dose, the observed surface morphology changed from lamellar to granular. For example, the changes in surface morphology of PVDF, as seen in Figure 7, may stem either from changes of the surface resistance to etching or from real morphological changes, due to increased amorphous content in the polymer surface; more conclusive studies are required. The morphology of the extracted crosslinked PVDF (gel fraction) has been reported elsewhere[28]; there the resistance to etching was also found to increase with crosslinking density.

The crosslinking and degradation mechanisms in fluoropolymers are still debatable, however, it is commonly agreed that high energy irradiation products are mainly determined by the stability and mobility of the radicals formed.[9,31] The analysis of the thermal and mechanical data enables one to conclude that PVF has the strongest tendency to crosslink while PFA mainly undergoes degradation. The crosslinking in PVF is manifested by the polymer crystallization from the melt (2nd DSC run) and the marked enhancement in its tensile properties. The thermal and mechanical behavior of PVDF, ETFE, and FEP indicate the occurrence of both crosslinking and chain scission, with no obvious preference. However, the increase in PFA melting temperature and heat of fusion (in both DSC runs), in addition to the dramatic drop in its elongation, clearly suggest that PFA undergoes intensive degradation. These changes in the irradiation effects are consistent with the polymers structure. PVF, the most crosslinkable among the presently studied
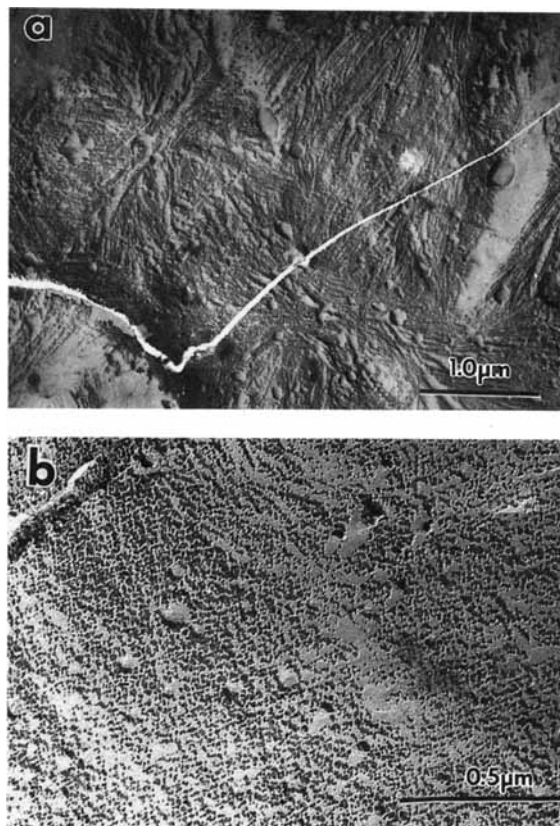

Figure 7   Electron micrographs of γ-irradiated PVDF film surface (etched with NaOH): (a) 0 and (b) 20 Mrads (replica).

polymers, consists of the highest main backbone H/ F ratio. These H atoms are responsible for the observed reaction to γ-irradiation, similar to that of polyethylene. In addition to the H/F ratio, these atoms' arrangement along the chain is an important parameter in determining the polymer reaction to irradiation. In PVDF and ETFE, the ratio of hydrogen to flourine is equal to unity, H/F = 1. The similar thermal behavior of the two irradiated polymers and their increased resistance to NaOH suggest that ETFE is also crosslinked (PVDF was recently shown to crosslink).[28] However, the stronger effect of radiation on the tensile properties of ETFE suggests that the TFE comonomer increases the polymer tendency to degrade. The marked decline in the mechanical properties of FEP and PFA indicates the occurrence of mainly chain scission, which, according to the thermal analysis data, is more severe in PFA. It has recently been reported that FEP tends to undergo partial crosslinking[12,17,20,21] and that PFA mainly undergoes degradation.[20,21] Therefore, the presently studied fluoropolymers can be listed ac-

cording to their reaction to ionizing irradiation as follows:

Crosslinkability

⟶

PFA, FEP, ETFE, PVDF, PVF

⟵

Degradability
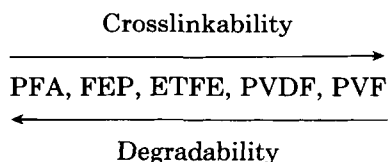
The chain scission/crosslinking events of three polymers with increasing F/H ratio (PVF, PVDF, and PTrFE) were studied.[12] The number of cross-linked chains per irradiation dose unit was found to decrease with increasing F/H ratio.
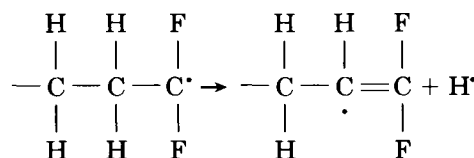
IRRADIATION INDUCED CHEMICAL CHANGES

Several studies have proposed crosslinking and chain-scission mechanisms occurring in high energy irradiated fluoropolymers.[13,14,18,37,38] The energy of a γ-quanta is approximately 10 times higher than the bond strength in organic substances. Thus, randomly multiple chain scission events, which are not selected by bond strength, may occur due to ionizing irradiation.[36] This reaction's products are likely to be determined mainly by the resulting radicals' stability, which is controlled by their structure and mobility. The reactions of radiation induced polymeric radicals are quite complex and not yet fully understood. The scission of C — C bonds in fluoropolymers may be related to the high electronegativity of the fluorine atom. It is suggested that the positive charge distribution surrounding carbon atoms results in the repulsion and weakening of the C — C bond in such structures as the following:

$$
\begin{array}{cc}
F^{\delta^-} & F^{\delta^-} \\
| & | \\
-C^{2\delta^+}-C^{2\delta^+}- \\
| & | \\
F^{\delta^-} & F^{\delta^-}
\end{array}
$$
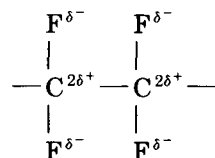
According to Fisher and Corelli,[13,14] ionizing radiation induced reactions in PTFE produce primary and secondary radicals, — (CF$_2$ — ĊF$_2$) and (CF$_2$ — ĊFCF$_2$) —: the formation of which can be related to C — and C — bond scission, respectively.

Fisher and Corelli have suggested that most primary radicals either react with each other, due to their low mobility, or are stabilized by the formation
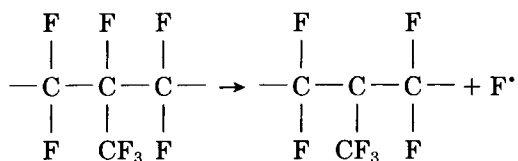
of double bonds at chain ends. As a result, more stable low molecular weight chains, which constitute the degraded products, are formed. Usually, higher hydrogen content enables intensive crosslinking since they supply favorable sites for crosslinks formation.[3] The present findings support this general statement. The radiation of PVF, which contains an H : F ratio of 3 : 1, yielded more crosslinking than in the other polymers studied. PVF's tensile strength increase and 2nd run crystallinity decrease reflect its tendency to crosslink. Although the H : F ratio in PVDF and in ETFE is identical, 1 : 1, ETFE is likely to undergo more intensive degradation, which is reflected by the marked decrease in its mechanical properties. Its resistivity to NaOH etching following radiation implies that the polymer was also crosslinked. It seems that the presence of the TFE comonomer in ETFE increases its radiation sensitivity compared with PVDF. This may be due to the formation of a stable double bond accompanied by the evolution of hydrogen radicals as follows:
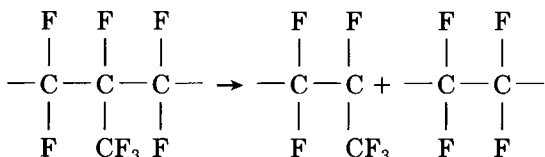
$$
\begin{array}{ccccccc}
H & H & F & & H & H & F \\
| & | & | & & | & | & | \\
-C & -C & -C^{\bullet} & \rightarrow & -C & -C & =C & +\ H^{\bullet} \\
| & | & | & & | & \bullet & | \\
H & H & F & & H & & F
\end{array}
$$

The H radical presumably continues to attack other chains.

Makuuchi et al.[38] investigated the influence of the presence of HF, which was formed during irradiation of PVDF, on the polymer chemical changes. Based on ESR analysis, a scheme of chemical changes due to the irradiation of PVDF in the presence of HF has been proposed. Applying the same analysis to ETFE, it may be suggested that the difference between the two polymers' response to irradiation rises from a more massive formation of — [CH$_2$ — ĊF$_2$] — radicals, [I], in ETFE than [ĊH$_2$ — CH$_2$] — , [II], or — [ĊH — CF$_2$] — , [III], radicals, which are less stable. Scission events in PVDF result in both [I] and [II] radicals in an approximate 1 : 1 ratio while scission of C — C bonds in the TFE comonomer can yield either only type [II] radicals or, like in PVDF, both in a 1 : 1 ratio. Thus, more type [II] radicals can be formed, which can be stabilized more readily than [I] radicals. The latter is less stable and therefore may react more readily with other radicals or chains. Radical [II], however, increases the degradation extent by lowering the polymer molecular weight and forming double bonds at chain ends.
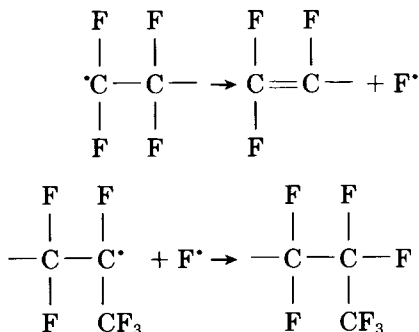
Upon the irradiation of FEP, stable radicals are presumably formed accompanied by the evolution of F radicals as follows:

$$
\begin{array}{ccccccc}
\text{F} & \text{F} & \text{F} & & \text{F} & & \text{F} \\
| & | & | & & | & & | \\
-\text{C}-\text{C}-\text{C}- & \rightarrow & & -\text{C}-\text{C}-\text{C}- & +\ \text{F}^{\bullet} \\
| & | & | & & | & & | \\
\text{F} & \text{CF}_3 & \text{F} & & \text{F} & \text{CF}_3 & \text{F}
\end{array}
$$

The radicals are well stabilized by the strong electronegative group and constitute possible cross-linked sites, which occurs to some extent in FEP.[12] Bond scission near the branching point of the fluoromethylic group causes massive chain degradation, while forming stable radicals and unsaturation at chain ends, accompanied by the evolution of F radicals as follows:
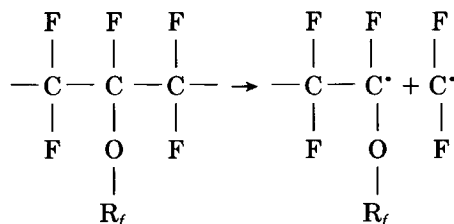
$$
\begin{array}{ccccccc}
\text{F} & \text{F} & \text{F} & & \text{F} & \text{F} & & \text{F} & \text{F} \\
| & | & | & & | & | & & | & | \\
-\text{C}-\text{C}-\text{C}- & \rightarrow & -\text{C}-\text{C}\ +\ -\text{C}-\text{C}- \\
| & | & | & & | & | & & | & | \\
\text{F} & \text{CF}_3 & \text{F} & & \text{F} & \text{CF}_3 & & \text{F} & \text{F}
\end{array}
$$

Reorganization of the radicals leads towards stable, lower molecular weight products, thus chain scission, as follows:

$$
\begin{array}{cccccc}
& \text{F} & \text{F} & & \text{F} & \text{F} \\
& | & | & & | & | \\
^{\bullet}\text{C}-\text{C}- & \rightarrow & \text{C}=\text{C}- & +\ \text{F}^{\bullet} \\
& | & | & & | \\
& \text{F} & \text{F} & & \text{F}
\end{array}
$$

$$
\begin{array}{ccccccc}
\text{F} & \text{F} & & & \text{F} & \text{F} \\
| & | & & & | & | \\
-\text{C}-\text{C}^{\bullet} & +\ \text{F}^{\bullet} & \rightarrow & -\text{C}-\text{C}-\text{F} \\
| & | & & & | & | \\
\text{F} & \text{CF}_3 & & & \text{F} & \text{CF}_3
\end{array}
$$

The mechanism proposed above supports the conclusions that FEP degrades more intensively than ETFE, as was also reflected in the mechanical and thermal behavior.

The mechanical properties of irradiated PFA sharply declined while its melting temperature and crystallinity (both runs) increased. This result undoubtedly indicates that PFA undergoes the most severe irradiation degradation among the presently studied fluoropolymers. This may be due to the

etheric bond connecting the long side branch to the main backbone. The oxygen in the etheric bond is very electronegative in nature, close to that of the F atom. The following degradation mechanism is proposed.

$$
\begin{array}{ccccccc}
\text{F} & \text{F} & \text{F} & & \text{F} & \text{F} & \text{F} \\
| & | & | & & | & | & | \\
-\text{C}-\text{C}-\text{C}- & \rightarrow & -\text{C}-\text{C}^{\bullet}\ +\ \text{C}^{\bullet} \\
| & | & | & & | & | & | \\
\text{F} & \text{O} & \text{F} & & \text{F} & \text{O} & \text{F} \\
& | & & & & | \\
& \text{R}_f & & & & \text{R}_f
\end{array}
$$

The two types of radicals formed are stable and, therefore, do not tend to crosslink.

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