Reactions of Irradiated Polytetrafluoroethylene Resin

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INTRODUCTION

It has been known for a number of years that polytetrafluoroethylene degrades when subjected to ionizing radiation in ordinary atmospheres.[1,2] More recently, radiation experiments have been conducted in inert atmospheres[3] leading to materials with tensile breaking strengths far superior to samples irradiated at equivalent dosages in air. Electron spin resonance (ESR) measurements have shown the presence of $\sim\!CF_2\dot{C}FCF_2\!\sim$ groups,[4–7] and $\sim\!CF_2\!-\!CF_2\cdot$ [13] and reactions of these radicals with oxygen and other radical acceptors have been described. The irradiation experiments were conducted, for the most part, on sintered, fabricated forms of the resin.

In the present work, compacted virgin resin was used and all irradiations were carried out in high vacuum. Changes in molecular weight were followed using specific gravity and melt viscosity measurements on the subsequently melted samples. Additional information concerning the reactions that occur during and after irradiation is also presented.

EXPERIMENTAL

Irradiation

(1) The irradiation source was a 3-m.e.v. Van de Graaff accelerator. The samples were passed under a beam of 2-m.e.v. electrons at 250 μamp. at a rate to provide exposure to 11 w.-sec./cm.² per pass.

(2) For the studies relating the molecular weight changes in polytetrafluoroethylene to irradiation, samples were prepared by placing three grams of Teflon 1 TFE-fluorocarbon resin in a cylindrical mold cavity $1^1/_2$ in. in diameter and subjecting the resin to pressures of 2000 psi for 3 min. at room temperature. Care was taken to distribute the resin evenly in the mold cavity to produce test specimens of uniform thickness and density. Pressure was applied and released gradually to allow escape of air and prevent impact stresses in the specimens.

(3) Samples for ESR measurements were irradiated in 8 mm. O.D. quartz tubes 5 in. long which fit the cavity of the instrument for measuring the electron spin resonance (ESR) of the radicals produced. These tubes were one-third filled with one gram of the resin (fine powder) and sealed with

ether resin to a vacuum stopcock for evacuation. The evacuations were carried out overnight using a mercury diffusion pump capable of reducing the pressure to 10^{-5} mm. mercury. The evacuated tubes were partially immersed in ice and subjected to ten passes at 250 μamp and 2 m.e.v. in a Van de Graaff generator. The stopcocks were protected with lead shielding. This exposure was sufficient to produce a concentration of radicals in excess of 10^{17}/cc. of polymer. Before these radicals could be examined by ESR measurements, the radicals simultaneously produced in the quartz tube itself were destroyed by heating. During this procedure, the radicals in the polymer were protected by inverting the tube while the tip was heated. The section of the tube containing the polymer was kept cool with a moistened towel. The ESR measurements were made at frequencies in the range of 9300 Mcycles/sec. and fields of about 3300 gauss.

(4) For the graft polymerization experiments, 1 and 2 g. samples of Teflon 1 resin powder were irradiated in vacuum in 50 cc., round-bottomed flasks. The flasks were equipped with tungsten leads to avoid cracking during the irradiation, puncturable rubber tips to provide means for injection of reactants with hypodermic syringes after irradiation, and three-way stopcocks to facilitate additions and evacuations. Glass-covered magnetic stirring bars were placed in the flasks with the polymer before the evacuations. The evacuations (3–12 hr. duration) were accomplished in the manner described in Section 3.

The flasks were exposed to 10 passes under the Van de Graaff generator while partially immersed in an ice/water slurry. The stopcocks were protected by lead shielding and the flasks were covered with screening to prevent damage to the Van de Graaff window in the event the flasks shattered during irradiation. The same irradiation procedure was used for all the graft polymerization experiments.

After irradiation, the flasks containing polytetrafluoroethylene were connected to a supply of purified tetrafluoroethylene (TFE). In order to keep the oxygen concentration below 10 ppm, copper lines were used exclusively. Connections of the glass equipment to the copper lines were made with very short lengths of butyl rubber tubing. Monomer consumption was measured with a gas burette which fed directly to the reaction flask. Before polymerization was initiated, lines were carefully evacuated and purged with monomer. Perfluorodimethylcyclobutane solvent (5 cc.) was added through the puncturable stopper by a syringe and the entire flask was immersed in an ice/water slurry. The contents of the flasks were stirred magnetically to provide good heat transfer. The rate of monomer absorption was high initially until the flask was filled and the solvent was saturated with monomer. Within 2 min., the rate reduced to a constant level.

Melt Viscosity Measurements

Viscosities of the molten polymer were measured in a parallel plate plastometer at 380°C.[8] Specimens 1.905 cm. in diameter and 0.317 cm.

thick were placed in the cavity of the instrument and loaded with a piston 1.905 cm. in diameter attached to a dial gauge for measuring piston travel. Piston height was then measured as a function of time and the melt viscosity calculated from the relation:

$$\eta = [2FH^3/3\pi R^4(dH/dt)]$$

where η is the melt viscosity in poises, F is the force on the piston in dynes, H is the thickness of the specimen in centimeters, R is the radius in centimeters, and dH/dt is the absolute magnitude of the rate of change of sample thickness in centimeters per second.

DISCUSSION

Changes in Molecular Weight

The changes in molecular weight of polytetrafluoroethylene on irradiation with high energy electrons at various conditions were followed using two techniques. The first involved measurement of the inherent polymer specific gravity (ISpG) by comparing the intensities of the infrared absorption at 778 and 2367 cm.$^{-1}$ as described by Moynihan[9] of samples which had been subjected to the standard heating and cooling cycle described in ASTM D 1457–56T.[10] The method, which is independent of void content, is based on the principle that crystallization rates of lower molecular weight linear polymers are faster than high molecular weight resins, resulting in a higher specific gravity. The procedure employed in this work differed from the published method only in that the heating and cooling cycles were conducted in vacuum in some experiments. The specific gravity as obtained by this method has been related to the number average molecular weight as determined by endgroup analysis.[11] The second technique involved the determination of the melt viscosity at 380°C. using a parallel plate plastometer[8] as described in the experimental section above.

The results of these various experiments are shown in Table I.

Samples of unsintered polytetrafluoroethylene cold pressed into chips and irradiated under high vacuum (samples 2, 3, and 4) had higher ISpG values, lower apparent melt viscosities and poorer mechanical properties on sintering in vacuum than did the unirradiated control (sample 1). This indicates that some degradation of molecular weight occurs during irradiation in inert atmospheres presumably due to direct carbon-carbon bond cleavage. ESR measurements on irradiated unsintered samples indicated a high concentration of secondary radicals from carbon-fluorine bond cleavage as well. A sample (sample 5) irradiated under high vacuum and sintered in air had an even higher ISpG value and lower melt viscosity indicating a severe degradation in molecular weight. Infrared spectrometric analysis indicated the presence of more carboxyl endgroups than observed in the samples irradiated and sintered in vacuum. Samples in some cases were slightly porous. Porosity can be introduced during the sintering step from the escape of gaseous degradation products formed during radiation.[1,2,6]

TABLE I

Evidence for Molecular Weight Changes in Polytetrafluoroethylene on High Energy Irradiation

Sample no.	Treatment, preformed chip	ISpG	$\bar{M}_n \times 10^{-6}$	Apparent melt viscosity (380°C.), poises	Bend test, % of original
1	Evacuated, sintered in vacuum (control)	2.163	>10	3.2×10^{11}	100
2	Evacuated, irradiated (10 passes), sintered in vacuum	2.240	2.5	2.8×10^{9}	60
3	Evacuated, irradiated (50 passes), sintered in vacuum	2.245 (slight porosity)	2.1	1.4×10^{8}	50
4	Same as above	2.243 (slight porosity)	2.3	2.3×10^{8}	50
5	Evacuated, irradiated (50 passes), sintered in air	2.266 (porous)	0.9	8.0×10^{8}	10
6	Resin sample A, unirradiated	2.237	2.8	4.9×10^{11}	100
7	Resin sample B, unirradiated	2.250	1.7	6.7×10^{9}	80
8	Resin sample C, unirradiated	2.264	1.0	5.8×10^{8}	70

These observed differences in degradation are in agreement with earlier work by Florin and Wall[3] who showed clearly that the relative breaking strengths of polytetrafluoroethylene samples irradiated in vacuum were superior to those given equivalent dosages in air. While the radiation conditions and sample preparations in our work were different from those of Nishioka et al.,[12] melt viscosities as determined by the parallel plate plastometer are not inconsistent with melt viscosity measurements made by these workers.

Further examination of the data in Table I reveals that the bending strengths of the irradiated samples are inferior to unirradiated samples having similar ISpG values (compared samples 2 with 6; 3, 4, with 6, 7; and 5 with 8). The melt viscosities of the irradiated samples appear to be more consistent with the mechanical strengths observed. While more definitive experiments are required, the data are consistent with branching during irradiation or sintering which would inhibit crystallization and lead to a lower specific gravity for a given molecular weight. A number of species produced in the irradiation process can react in a manner to introduce branches in the fluorocarbon chain. Mechanisms by which branches can be formed are discussed later in this paper.

Thermal Stability and Chemical Reactivity of Radicals Produced by Ionizing Radiation

The molecular degradation of polytetrafluoroethylene under ionizing radiation in high vacuum suggests that primary radicals as well as second-
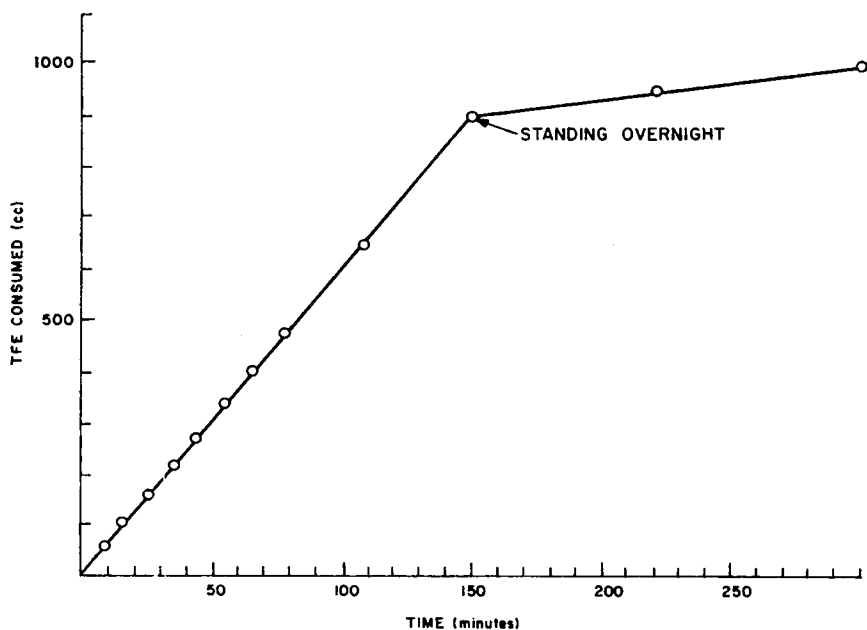

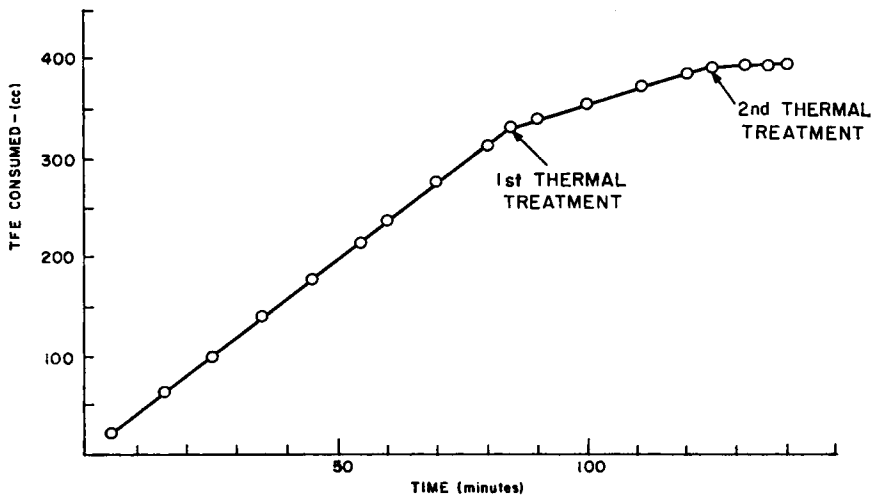Fig. 1. Polymerization of TFE on irradiated polytetrafluoroethylene. (15 psia, 0°C.).

Fig. 2. Polymerization of TFE on irradiated polytetrafluoroethylene showing effects of thermal treatment on rate. (15 psia, 0°C.).

ary radicals are formed. Secondary radicals were shown in the present work to possess unusual thermal stability. ESR measurements on samples heated for 30 min. in vacuum at 200°C. showed no decrease in radical content. Similar experiments showed that 10–25% of the secondary radicals initially detected survived treatment at 400°C. for 60 min.

The presence of primary radicals in irradiated polymer has recently been indicated by Matsugashita[13] by differentiating the ESR spectrum of peroxy radicals formed from primary radicals from that formed from secondary radicals. We have carried out a series of typical radical reactions that further indicate the presence of primary radicals and establishes their order of thermal stability. Polytetrafluoroethylene fine powder which had been irradiated in high vacuum was allowed to react with tetrafluoroethylene (TFE) monomer at 0°C. in a stirred vessel using the perfluorocarbon solvent. Uptake of monomer was rapid as shown in Figure 1. This was accompanied by the disappearance of secondary radicals, as followed by ESR. A graft was thus produced at the site of the secondary radical forming a branched polymer with primary radicals terminating the growing branched chain. Uptake of monomer continued at a constant rate (5.8 cc./min.) for 2.5 hr. Addition of monomer was arbitrarily terminated and the vessel allowed to stand at room temperature for 18 hr. On resumption of monomer addition, uptake proceeded steadily at one-fourth the rate of the first addition indicating that termination of some growing primary radicals had occurred on standing. Polymerization continued at a constant rate (1.3 cc./min.) for 2.5 hr. The total weight of polymer increased 230% which was in good agreement with the volume of tetrafluoroethylene absorbed. Reactivity of the resin was lost on complete exposure of the sample to the atmosphere.
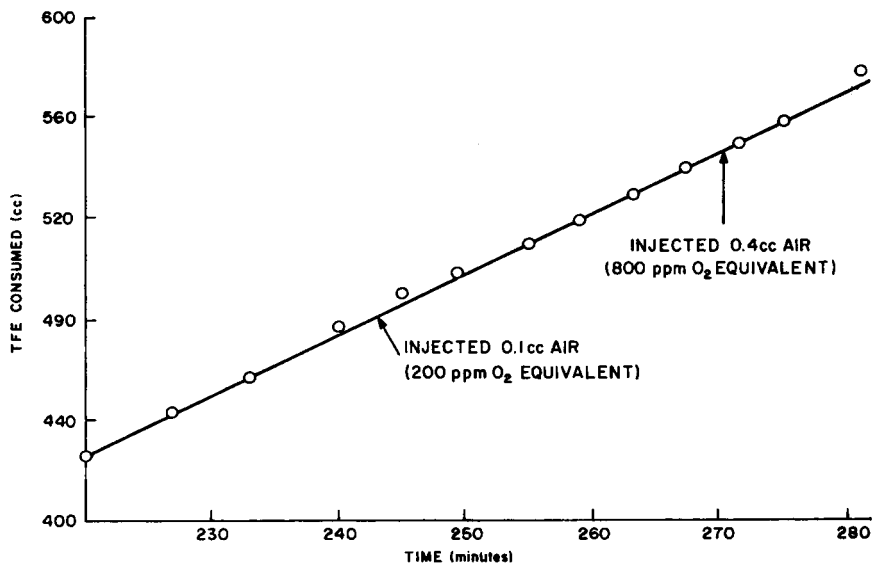
Fig. 3. Polymerization of TFE on irradiated polytetrafluoroethylene showing effects of oxygen on rate. (15 psia, 0°C.).

A second polymerization experiment shown in Figure 2 gave additional indication of the thermal stability of primary radicals. After the rate of polymerization had been established at 0°C. (4.0 cc./min.), the reactive resin was heated in vacuum 1 hr. at 70–75°C. On resumption of the polymerization, the rate of monomer uptake had decreased 70% (1.2 cc./min.). After the evacuation and heating process was repeated, the rate was only 5% (0.2 cc./min.) of that observed with the unheated irradiated material. Primary perfluoroalkyl radicals appear then to be destroyed in about 2 hr. at 70–75°C.

A third set of polymerization experiments indicated the reactivity of primary radicals to oxygen. After establishing the rate of polymerization in an irradiated sample (Fig. 3), dry air was admitted to the polymerization. No change in polymerization rate was noted after two such additions of significantly large quantities of air. Oxygen present in the air reacted with the primary radicals present to produce peroxy radicals. These reacted rapidly with additional TFE to produce a polymeric chain having the suggested structure —OO—(CF$_2$—CF$_2$)$_n$—O—O—(CF$_2$—CF$_2$)$_n$—OO—. The formation of $\sim$CF$_2$—CF$_2$—O—O· radicals is consistent with the findings of Tsvetkov.[14] Further evidence for this reaction series was obtained in a group of experiments in which oxygen was allowed to react with irradiated resin under various conditions as outlined in Figure 4. Irradiated polytetrafluoroethylene powder was allowed to react alternately with TFE and oxygen, the vessel being evacuated rigorously between each reaction. The ESR of Product II no longer included the typical ESR spectrum of the secondary radical so evident in irradiated Resin I. The
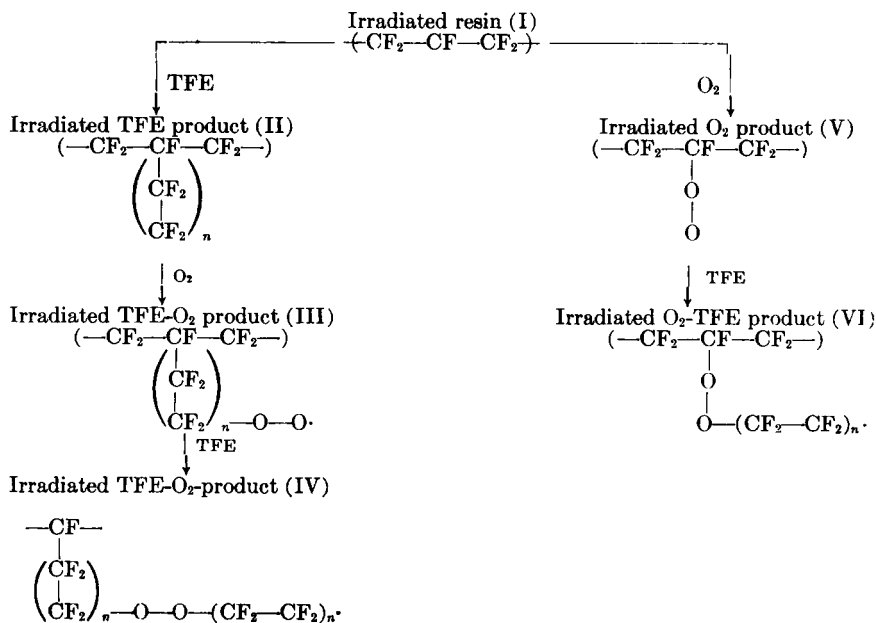
Irradiated resin (I)
$(-CF_2-CF-CF_2-)$

| TFE

Irradiated TFE product (II)
$(-CF_2-CF-CF_2-)$
$$\left(\begin{array}{c} CF_2 \\ | \\ CF_2 \end{array}\right)_n$$

| O₂

Irradiated TFE-O₂ product (III)
$(-CF_2-CF-CF_2-)$
$$\left(\begin{array}{c} CF_2 \\ | \\ CF_2 \end{array}\right)_n -O-O\cdot$$
| TFE

Irradiated TFE-O₂-product (IV)

$-CF-$
$$\left(\begin{array}{c} CF_2 \\ | \\ CF_2 \end{array}\right)_n -O-O-(CF_2-CF_2)_n\cdot$$

Irradiated O₂ product (V)
$(-CF_2-CF-CF_2-)$
O
O

| TFE

Irradiated O₂-TFE product (VI)
$(-CF_2-CF-CF_2-)$
O
$O-(CF_2-CF_2)_n\cdot$

Fig. 4. Reactions of irradiated polytetrafluoroethylene in various atmospheres. Similar reaction schemes are visualized for $(-CF_2-CF_2-)_nCF_2\cdot$.

ESR of Product III was clearly identified with the peroxy radical structure of previous workers. The ESR spectrum of Product IV showed a partial reduction in the peroxy structure and a partial recovery of the diffuse fluorocarbon radical spectrum associated with Product II. Product V showed an ESR spectrum similar to Product III and that of Product VI similar to Product IV.

Additional evidence supporting the reaction of oxygen with the resin lay in pyrolysis experiments. The various products were heated in vacuum at 400°C. for 1 hr. and the off-gases were analyzed for the CO_2 arising from decarboxylation of endgroups and decomposition of peroxy radicals and linkages. Comparisons are summarized in Table II.

TABLE II

Analysis of CO_2 Content of Off-Gases from Pyrolysis of Various Irradiated TFE Resin Products

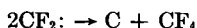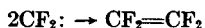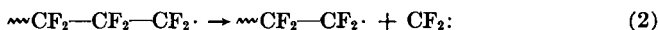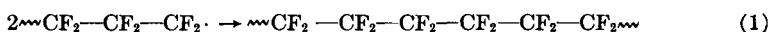| Product	CO_2 evolved[a]
I	1.0
II	1.0
III	9.6
IV	10.2
V	13.9
VI	14.4

[a] The results are unitized for easy comparison.

The presence of much larger concentrations of CO_2 in the off-gases of Products III, IV, V, and VI over that found in the controls I and II established clearly that oxygen combined with the polymer.

Mechanism of Degradation by Ionizing Radiation

Much has been written concerning the mechanisms of the reactions involved when polymeric materials are subjected to high energy radiation. While the reactions are extremely complex and may involve both ions and radicals, in polytetrafluoroethylene they appear to lead ultimately to $\sim CF_2\text{—}CF\text{—}CF_2\sim$ and $\sim CF_2\text{—}CF_2\text{—}CF_2\cdot$ as quasi-stable intermediates when the irradiation is carried out at 0°C. in the absence of air. The radicals may be highly excited when formed and, as such, may enter into quite unusual reactions.

A short review of the various reactions presented by previous workers together with recent observations made in this laboratory are presented in the following paragraphs. Reactions which are postulated for primary radicals in the absence of air are shown in eqs. (1)–(5).

$$2\sim CF_2\text{—}CF_2\text{—}CF_2\cdot \rightarrow \sim CF_2\text{—}CF_2\text{—}CF_2\text{—}CF_2\text{—}CF_2\text{—}CF_2\sim \qquad (1)$$

$$\sim CF_2\text{—}CF_2\text{—}CF_2\cdot \rightarrow \sim CF_2\text{—}CF_2\cdot + CF_2\text{:} \qquad (2)$$

$$2CF_2\text{:} \rightarrow CF_2\text{=}CF_2$$

$$2CF_2\text{:} \rightarrow C + CF_4$$

$$\sim CF_2\text{—}CF_2\text{—}CF_2\cdot \rightleftarrows \sim CF_2\cdot + CF_2\text{=}CF_2 \qquad (3)$$

$$CF_2\text{=}CF_2 \rightarrow C + CF_4$$

$$\sim CF_2\text{—}CF_2\text{—}CF_2\cdot + F\cdot \rightarrow \sim CF_2\text{—}CF_2\text{—}CF_3 \qquad (4)$$

$$2\sim CF_2\text{—}CF_2\text{—}CF_2\cdot \rightarrow \sim CF_2\text{—}CF_2\text{—}CF_3 + CF_2\text{=}CF\text{—}CF_2\sim \qquad (5)$$
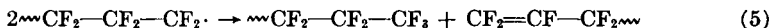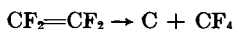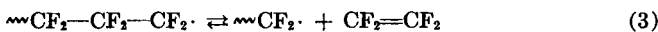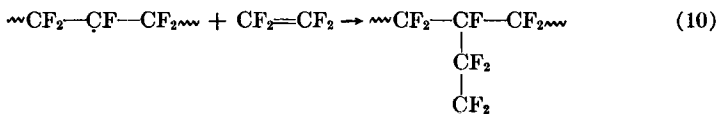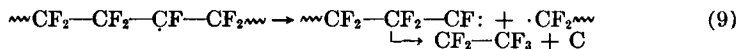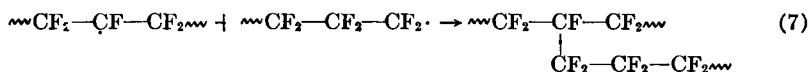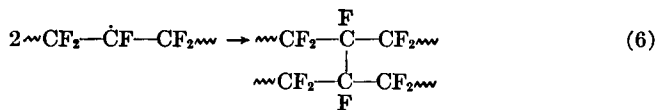
Reaction (1) describes the coupling of radical fragments, especially at the point of scission. Due to the high crystallinity[11] and the rigidity[15] of the fluorocarbon chain, the "caged" structure suggested by Watanabe[17] appears reasonable.

Reactions (2) and (3) postulate the formation of small quantities of carbon and provide a plausible mechanism for the formation of the small amounts of carbon tetrafluoride observed in our work as well as that of previous workers. That carbon is formed was shown in the present work by observing the change in color of samples of unsintered resin sheets subjected to 500–1000 passes in air. The grey-brown hue obtained during irradiation was removed by heating in air at 250°C. or washing in aqua regia. The feasibility of these reactions is supported by known high temperature reactions of polytetrafluoroethylene, difluorocarbene[18] and TFE.[19] The reversed arrow in reaction (3) also indicates repolymerization of product $CF_2\text{=}CF_2$. Due to the high reactivity of this compound, as shown by our grafting experiments (even when unexcited by electron bombardment), the repolymerization reaction undoubtedly is rapid. The postulated reactions for TFE also appear consistent with the relative

abundance of carbon tetrafluoride and the dearth of TFE observed in the reaction products by other workers as well as ourselves.

Reaction (4) represents a termination reaction involving coupling of primary radicals with F·, a major intermediate produced in the reaction. Reaction (5) postulates a disproportionation to form perfluoromethyl and olefinic endgroups. Little evidence exists for the formation of $\sim CF_2—CF=CF_2$ as an important intermediate or end-product of the radiation reaction under the usual conditions of irradiation. No terminal olefins have been detected in our irradiation experiments with polytetrafluoroethylene or lower molecular weight model compounds.[20] Similar observations were made by Florin et al[21] in experiments in which linear perfluoroheptane was irradiated with gamma rays.

Although the stability of the secondary free radical $\sim CF_2—\dot{C}F—CF_2\sim$ is greater than that of the primary radicals, the fate of this structure on heating at elevated temperatures is of equal concern. Some of those reactions which may occur are shown in eqs. (6)–(10).
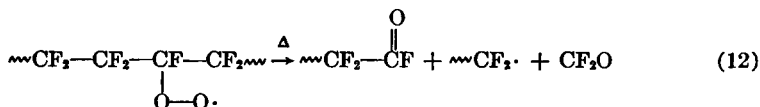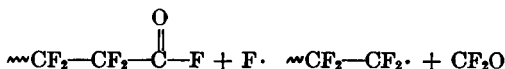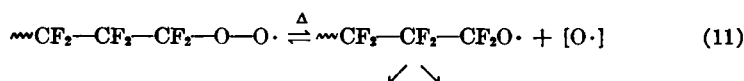
$$2\sim CF_2—\dot{C}F—CF_2\sim \rightarrow \begin{array}{c} F \\ | \\ \sim CF_2—C—CF_2\sim \\ | \\ \sim CF_2—C—CF_2\sim \\ | \\ F \end{array} \quad (6)$$

$$\sim CF_2—\dot{C}F—CF_2\sim \;+\; \sim CF_2—CF_2—CF_2· \rightarrow \begin{array}{c} \sim CF_2—CF—CF_2\sim \\ | \\ CF_2—CF_2—CF_2\sim \end{array} \quad (7)$$

$$\sim CF_2—\dot{C}F—CF_2\sim + F· \rightarrow \sim CF_2—CF_2—CF_2\sim \quad (8)$$

$$\sim CF_2—CF_2—\dot{C}F—CF_2\sim \rightarrow \begin{array}{c} \sim CF_2—CF_2—CF: + ·CF_2\sim \\ \hookrightarrow CF_2—CF_3 + C \end{array} \quad (9)$$

$$\sim CF_2—\dot{C}F—CF_2\sim + CF_2{=}CF_2 \rightarrow \begin{array}{c} \sim CF_2—CF—CF_2\sim \\ | \\ CF_2 \\ | \\ \dot{C}F_2 \end{array} \quad (10)$$

Reaction (6) is highly unlikely for reasons of steric hindrance and thermal stability.[21] Reaction (7) has previously been postulated by Wall and Florin[3] and appears feasible at elevated temperatures where a degree of chain mobility exists. It provides one mechanism for producing branched molecules. Recombination of F· with secondary radicals in reaction (8) probably constitutes a major reaction during irradiation. Reaction (9) results from cleavage of the carbon-carbon bond adjacent to the secondary radical to form a primary radical and a highly unstable substituted carbene. The unstable carbene would be expected to rearrange to produce carbon and the stable —CF_3 endgroup. Alternatively, the rearrangement of a fluorine atom from the second carbon to the terminal carbon would produce a terminal olefin[22] but this easily identifiable group[23] was not found in our products.
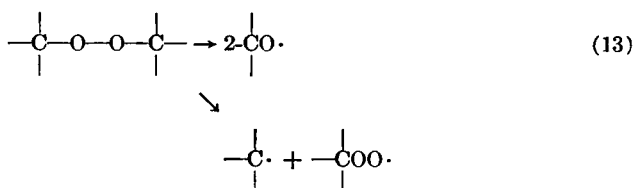
The rapidity with which irradiated polytetrafluoroethylene reacts with TFE monomer as shown in our grafting experiments provides validity for reaction (10). This reaction would be expected to be highly favorable in

thick samples where the rate of diffusion of gases to the surface would be comparatively slow. The reactive primary radical thus produced could react further in a coupling reaction to produce a branched chain. The comparatively high mobility and reactivity of the primary radicals suggest this to be the major branching reaction during heat treatment. Elimination of a fluorine atom from the carbon adjacent to the one containing a secondary radical to produce internal unsaturation would appear highly unfavorable thermodynamically[24] and no indication of the presence of this bond was found in our work.
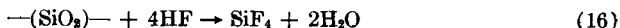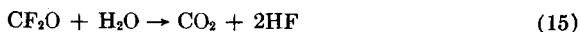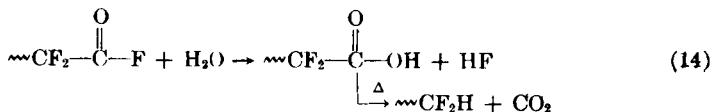
The reactions of secondary radicals with oxygen have been described in several previous papers and the graft polymerization experiments presented above as well as the work of Matsugashita[13] indicate that primary radicals react similarly. We have studied the fate of these oxygenated radicals on heating in anhydrous atmospheres. The presence of carbonyl fluoride in the off-gases of the pyrolysis products was detected by infrared analysis. In addition, acid fluoride endgroups were observed in the polymers using infrared methods. These products have also been previously identified by Golden[25] in similar types of experiments. Reactions leading to these end-products are postulated in eqs. (11) and (12).

$$\text{\textasciitilde CF}_2\text{—CF}_2\text{—CF}_2\text{—O—O} \cdot \;\underset{\Delta}{\rightleftharpoons}\; \text{\textasciitilde CF}_2\text{—CF}_2\text{—CF}_2\text{O} \cdot \; + \; [\text{O} \cdot] \tag{11}$$

$$\swarrow \quad \searrow$$

$$\overset{\displaystyle O}{\underset{}{\text{\textasciitilde CF}_2\text{—CF}_2\text{—}\overset{\|}{C}\text{—F}}} + \text{F} \cdot \quad \text{\textasciitilde CF}_2\text{—CF}_2 \cdot \; + \; \text{CF}_2\text{O}$$

$$\text{\textasciitilde CF}_2\text{—CF}_2\text{—}\underset{\underset{\text{O—O} \cdot}{|}}{\text{CF}}\text{—CF}_2\text{\textasciitilde} \;\overset{\Delta}{\rightarrow}\; \text{\textasciitilde CF}_2\text{—}\overset{\overset{\displaystyle O}{\|}}{\text{CF}} + \text{\textasciitilde CF}_2 \cdot \; + \; \text{CF}_2\text{O} \tag{12}$$

Perfluorinated peroxides —(—CF$_2$—O—O—CF$_2$—)— which may be produced during irradiation in dry oxygen atmospheres probably break down at elevated temperatures to various intermediates described above which degrade further to the end-products observed.

$$\overset{|}{\underset{|}{\text{C}}}\text{—O—O—}\overset{|}{\underset{|}{\text{C}}}\text{—} \;\rightarrow\; 2\text{-}\overset{|}{\underset{|}{\text{C}}}\text{O} \cdot \tag{13}$$

$$\searrow$$

$$\overset{|}{\underset{|}{\text{C}}} \cdot \; + \; \overset{|}{\underset{|}{\text{C}}}\text{OO} \cdot$$

The resin, in general commercial applications, encounters radiation atmospheres in which both moisture and oxygen are present at wide ranges of temperature. The reactive end-products outlined in reactions (11)–(13) react further with water to give still simple products, as shown in eqs. (14)–(16).

$$\underset{\substack{\| \\ O}}{\text{$\sim$CF}_2\text{—C—F}} + H_2O \rightarrow \underset{\substack{\| \\ O}}{\text{$\sim$CF}_2\text{—C—OH}} + HF \tag{14}$$

$$\xrightarrow{\Delta} \sim CF_2H + CO_2$$

$$CF_2O + H_2O \rightarrow CO_2 + 2HF \tag{15}$$

$$-(SiO_2)- + 4HF \rightarrow SiF_4 + 2H_2O \tag{16}$$

These well-known reactions account for the presence of carbon dioxide in the off-gases from irradiation experiments and posttreatment at various elevated temperatures, and for the formation of silicon tetrafluoride in experiments carried out in glass equipment.

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Synopsis

Powders and compacted preforms of virgin unmelted polytetrafluoroethylene were subjected to ionizing radiation in high vacuum. The specific gravities, melt viscosities, and mechanical strengths of the irradiated samples after a standard heating cycle in air or at reduced pressures indicate that degradation is more pronounced in the presence of oxygen than in vacuum. The presence of oxygen in the excessively degraded sample was shown by electron spin resonance and pyrolysis experiments. It is suggested that some branched molecules are also formed on heating the irradiated samples resulting in a broadening of the molecular weight distribution. Primary fluorocarbon radicals of the type $\sim\sim CF_2$—$CF_2\cdot$ disappear rapidly when heated at 75°C. in vacuum while secondary radicals $\sim\sim CF_2$—$\dot{C}F$—$CF_2\sim\sim$ are stable thermally at 200°C. and disappear only slowly at 400°C. Both types of radicals react rapidly with oxygen and tetrafluoroethylene at 0°C. The reactions which occur in irradiated polytetrafluoroethylene in various atmospheres and at several temperatures are reviewed in light of the information developed during this research.

Résumé

On a soumis du polytétrafluoroéthylène nonfondu et vierge, sous forme de poudres et de préformés compactes à un rayonnement ionisant dans le vide poussé. Les densités spécifiques, les viscosités à l'état fondu et les résistances mécaniques des échantillons irradiés après un cycle standard de chauffage à l'air ou à pression réduite, indiquent que la dégradation est plus prononcée en présence d'oxygène que dans le vide. On a montré la présence d'oxygène dans l'échantillon fortement dégradé par résonance de spin électronique et des expériences de pyrolyse. On sugère qu'il se forme également quelques molécules ramifiées en chauffant les échantillons irradiés ce qui a pour résultant un élargissement de la distribution des poids moléculaires. Des radicaux fluorocarbonés primaires du type $\sim\sim CF_2$—$\dot{C}F$—$CF_2\sim\sim$ sont thermiquement stables à 200°C. et disparaissent seulement lentement à 400°C. Ces deux type de radicaux réagissent rapidement avec l'oxygène et le tétrafluoroéthylène à 0°C. A la lumière des informations obtenues pendant ce travail de recherche on passe en revue les réactions qui ont lieu à différentes pressions et températures.

Zusammenfassung

Pulver und zusammengepresste Formlinge aus unverarbeitetem, ungeschmolzenem Polytetrafluoräthylen wurden ionisierender Strahlung im Hochvakuum ausgesetzt. Das spezifische Gewicht, die Schmelzviskosität und die mechanische Festigkeit der bestrahlten Proben nach einem Standard-Erhitzungscyklus unter Luft oder bei vermindertem Druck lassen erkennen, dass in Gegenwart von Sauerstoff der Abbau stärker hervortritt als im Vakuum. Die Anwesenheit von Sauerstoff in der übermässig abgebauten Probe wurde durch Elektronspinresonanz- und Pyrolyseversuche bewiesen. Es wird angenommen, dass bei der Erhitzung der bestrahlten Proben auch einige verzweigte Moleküle gebildet werden, was zu einer Verbreiterung der Molekulargewichtsverteilung führt. Primäre Fluorkohlenstoffradikale vom Typ $\sim\sim CF_2$—$CF_2\cdot$ verschwinden beim Erhitzen auf 75°C im Vakuum rasch, während sekundäre Radikale $\sim\sim CF_2$—$\dot{C}F$—$CF_2\sim\sim$ bei 200°C thermisch stabil sind und bei 400°C nur langsam verschwinden. Beide Radikaltypen reagieren bei 0°C rasch mit Sauerstoff und mit Tetrafluoräthylen. Ein Überblick über die in bestrahltem Polytetrafluoräthylen mit verschiedenen Gasen und bei mehreren Temperaturen auftretenden Reaktionen wird im Lichte der während der vorliegenden Untersuchung gewonnenen Erkenntnisse gegeben.