# Radiation Chemistry of Poly(tetrafluoroethylene-*co*perfluoromethyl vinyl ether): Effects of Oxygen and Crystallinity

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ABSTRACT: The presence of oxygen had a varied effect on the  $\gamma$ -radiolysis of the amorphous copolymer, poly[tetrafluoroethylene-*co*-perfluoro(methylvinyl ether)] (TFE/PMVE), depending upon radiolysis conditions. Radiolysis undertaken in stages, up to a dose of 1500 kGy (1 rad =  $10^{-5}$  kGy) in the presence of air, resulted predominantly in chain scission and a wax-like substance was produced; whereas, other studies have shown that continuous radiolysis of the polymer produced a crosslinked network. Radiolysis of semicrystalline TFE/PMVE in vacuum up to a dose of 4200 kGy produced little change in the crystalline content. Crosslinking, however, predominated in the amorphous regions, which had the effect of lowering the crystallization temperature upon cooling from above the crystalline melt. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 807–812, 1999

**Key words:** radiolysis; poly[tetrafluoroethylene-*co*-perfluoro(methylvinyl ether)]; oxy-gen effect; crystallinity

#### INTRODUCTION

The radiolysis of fluoropolymers in the presence of oxygen enhances the degradation of the polymer chains, but this effect is greatly influenced by such factors as the sample dimensions and the dose rate.<sup>1,2</sup> It has been known for some time that the radiation degradation of polytetrafluoroethylene (PTFE) is accelerated in the presence of oxygen, and mechanisms similar to those observed for radiolysis of hydrocarbons in the presence of oxygen have been established.<sup>1,3</sup> Zhong et al.<sup>4</sup> recently suggested oxygen influenced the radiation stability of PTFE to a much lesser extent than what was previously thought and showed that most oxidative damage was limited to the surface.

Main chain and chain end radicals have been identified in irradiated PTFE, indicating scission of both the C—C and C—F bonds.<sup>5–7</sup> In the presence of oxygen, these radicals react to form perfluoroperoxy radicals,<sup>6,8</sup> which by thermal activation or reaction with other radicals are converted to perfluoroalkoxy radicals (Fig. 1A).<sup>3,9</sup> Decompo-

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**Figure 1** Proposed mechanisms for the radiolytic oxidation of PTFE.

sition of the perfluoroalkoxy radicals located along the polymer backbone leads to main chain scission and the formation of acid fluoride chain ends. Carboxylic acid end groups are formed as a result of hydrolysis of the acid fluoride end groups with moisture in the atmosphere, particularly near the surface of the polymer. Burger et al.<sup>10</sup> and Fisher et al.<sup>9</sup> identified both associated and isolated acid end groups in irradiated PTFE and in the copolymer of tetrafluoroethylene and hexafluoropropylene (FEP), and the copolymer of tetrafluoroethylene and perfluoro(propylvinyl ether) (PFA). Chain end perfluoroalkoxy radicals undergo  $\alpha$ -cleavages, forming carbonyl fluoride, which also regenerates the chain end radicals (Fig. 1B). Carbonyl fluoride is a major volatile product of PTFE when it is irradiated in the presence of air.<sup>11</sup>

The effect of crystallinity on the radiation induced changes in polyolefins has been reviewed.<sup>1,12</sup> Zhong et al.<sup>4,13</sup> found the yields of chain scission to be inversely proportional to the crystalline content of PTFE and the decrease in the molecular weight as a function of crystallinity indicated that most of the chain scission was occurring in the amorphous region. Radicals trapped in the crystalline regions were thought to recombine because of the cage effect, which explained the increased radiation resistance observed for polymers with a higher crystalline content. The crystallinity of PTFE increased upon irradiation because of crystallization of smaller chain segments formed in the amorphous region. The driving force for this process was the relief of stress originally present in this region. Burger et al.<sup>10</sup> irradiated PTFE in air and showed the crystallinity to increase initially up to a dose of 7 kGy. However, a continual drop in the crystallinity above 2 MGy was observed and attributed to radiation-induced crystal lattice defects.

The fluoroelastomer, TFE/PMVE (Fig. 2), undergoes both crosslinking and chain scission upon radiolysis at room temperature. Uschold<sup>14</sup> irradiated TFE/PMVE and found the modulus of the elastomer to increase, indicating crosslinking of the polymer chains. Forsythe et al.<sup>15</sup> used <sup>19</sup>F NMR to find the *G*-values for chain scission (G(S) = 1.4), and crosslinking (G(X) = 0.9). Mechanisms for the formation of radiation-induced crosslinks and chain ends have been described elsewhere.<sup>15,17,18</sup> In the present study, we investigate further the effect of oxygen on the radiation chemistry of TFE/PMVE, as well as the effect of crystallinity.



Figure 2 Structure of TFE/PMVE random copolymer.

## **EXPERIMENTAL**

#### **Materials**

The perfluoroelastomer, TFE/PMVE was supplied by Du Pont Dow Elastomers L.L.C. in the form of a crumb. The material was synthesized in an emulsion polymerization with a free radical initiator, as described by Logothetis.<sup>16,19,20</sup> The TFE/ PMVE was free of additives and the ratio of TFE to PMVE was 2 : 1, as determined from an <sup>19</sup>F NMR analysis.<sup>15</sup> The semicrystalline TFE/PMVE used was also in the form of a crumb and the mole ratio of TFE to PMVE was 4.2 : 1.

#### **Radiolysis**

Both the TFE/PMVE amorphous elastomer and the semicrystalline elastomer were  $\gamma$ -irradiated in vacuum in Pyrex tubes at a dose rate of 20 kGy h<sup>-1</sup> at the Takasaki Research Establishment of the Japan Atomic Energy Research Institute (JAERI). The Pyrex tubes were opened to the atmosphere and left in a vacuum oven overnight at 373 K to expel evolved volatiles.

#### Method

Glass transition temperature measurements were obtained from a Perkin–Elmer Differential Scanning Calorimeter DSC7/TAC7 using a scanning rate of 40 K min<sup>-1</sup>. Crystallization temperatures were determined by annealing the polymer at 600 K for 5 minutes then cooling at a rate of 10 K min<sup>-1</sup>.

Fourier transform infrared (FTIR) spectra were obtained on a Perkin–Elmer 2000 FTIR using an MTEC photoacoustic model 2000 accessory. Spectra were acquired using 4 cm<sup>-1</sup> resolution and an optical path distance, OPD, velocity of  $0.10 \text{ cm s}^{-1}$ .

The NMR spectra were obtained on a Bruker MSL200 spectrometer. <sup>19</sup>F spectra were obtained using a  $\pi/2$  pulse-decay of 5  $\mu$ s with a 2-s recycle delay period between pulses at a temperature of 420 K. Sufficiently long delay times were used to ensure quantitative integrated peak intensities. Trifluoroacetic acid was used as an external standard, and chemical shifts were reported relative to trichlorofluoromethane.

X-ray diffraction data were measured using graphite monochromated Cu K $\alpha$  radiation on a Philips PW1050 diffractometer. Patterns from the pressed powders of the as-received material and materials  $\gamma$ -irradiated to 4200 kGy were recorded



**Figure 3** PAS FTIR spectra of TFE/PMVE: A) unirradiated; B)  $\gamma$ -irradiated to a dose of 1500 kGy in vacuum; C)  $\gamma$ -irradiated to a dose of 1500 kGy in air.

from 5 to 90°  $2\theta$  in 0.05° steps. Deconvolution of the observed peaks yielded information on the crystalline dimensions as broadening of the Lorenztian components of the diffraction peaks is attributable to the size of the coherent blocks.<sup>21</sup>

# **RESULTS AND DISCUSSION**

#### Effect of Oxygen on the Radiolysis of TFE/PMVE

The effect of oxygen on the radiolysis of TFE/ PMVE varies dramatically, depending upon the irradiation conditions. The radiolysis of the TFE/ PMVE elastomer was carried out in stages to a dose of 1500 kGy in the presence of oxygen, causing a drastic deterioration in the physical properties and producing a viscous wax. The glass transition temperature of the unirradiated elastomer was 276 K and was reduced to 267 K after radiolysis. The infrared spectrum of the wax is shown in Figure 3C and shows a large absorbance centred at  $1775 \text{ cm}^{-1}$ , which has been assigned to the carbonyl stretch of associated carboxylic acid end groups.<sup>9,10</sup> The infrared spectrum of the unirradiated elastomer (Fig. 3A) and of the elastomer irradiated to 1500 kGy in vacuum (Fig. 3B) are shown for comparison. The carbonyl stretch of the elastomer irradiated in air (Fig. 3C) was significantly broader than that for the elastomer irradiated in vacuum (Fig. 3B), indicating a higher proportion of new carboxyl chain ends. In vacuum, the acid chain ends must result from chain scission at the PMVE units, because this is the only source of oxygen in the elastomer. Initial cleavage of the fluoromethyl group from the side chain produces an oxygen-centred radical and a  $\cdot CF_3$  radical (Fig. 4). A major gaseous product identified from the radiolysis of TFE/PMVE is



Carboxylic acid

**Figure 4** Mechanism for side chain cleavage of TFE/ PMVE forming  $CF_4$  and new carboxylic acid end groups.

 $\mathrm{CF}_4(G=0.93)$ , which is formed from the recombination of the  $\cdot\mathrm{CF}_3$  radical with a F·radical.<sup>18</sup> An  $\alpha$ -cleavage of the oxygen-centered radical yields an acid fluoride chain end, which has been identified in TFE/PMVE by Pacansky et al.<sup>18</sup> The acid fluoride chain ends readily hydrolyze with atmospheric moisture to give carboxylic acid chain ends and hydrogen fluoride.

By conducting the radiolysis in stages, oxygen was allowed to diffuse into the bulk of the polymer and react with polymeric radicals, forming peroxy radicals and, ultimately, new acid end groups. Mechanisms for this process would be expected to be similar to the oxidative damage of PTFE shown in Figure 1. Reaction of oxygen with

the polymeric radicals promoted chain scission but also prevented crosslinking. The inhibition of crosslinking under these conditions caused a dramatic drop in the glass transition temperature and the formation of a low molecular weight wax. Figure 5A shows the <sup>19</sup>F NMR spectrum of TFE/ PMVE crumb irradiated to 1500 kGy in vacuum. The new absorbance at -181.3 ppm was attributed to a tertiary fluorine formed at the branch site on the main chain. The crosslinking of the TFE/PMVE polymer chains, therefore, occurs by a Y-linking mechanism.<sup>15</sup> As expected, the crosslink peak at -181.3 ppm was not present in the <sup>19</sup>F NMR spectrum of TFE/PMVE irradiated in air (Fig. 5B). The NMR line widths in Figure 5B are reduced because of the increased chain mobility of the lower molecular weight polymer. It was, therefore, concluded that oxygen was scavenging the polymeric radicals, thus inhibiting the crosslinking reaction.

Reaction of oxygen with radical intermediates in polymers is diffusion controlled.<sup>2,17</sup> Homogeneous oxidation of the polymer initially takes place; however, the oxygen present in the bulk of the elastomer is rapidly depleted by the formation of new carboxylic acid and acid fluoride end groups. The renewal of oxygen into the bulk of the polymer may be inhibited for relatively thick samples, high dose rates, high consumption of oxygen,



**Figure 5** <sup>19</sup>F NMR spectra of TFE/PMVE crumb: A)  $\gamma$ -irradiated to 1500 kGy in vacuum; and B)  $\gamma$ -irradiated to 1500 kGy in air; spectra were acquired at 420 K.



**Figure 6** XRD pattern of unirradiated semicrystalline TFE/PMVE pressed powder acquired at room temperature.

and low oxygen permeation rates.<sup>2</sup> Logothetis irradiated TFE/PMVE O-rings, which were relatively thick, using high-energy electrons and found that oxygen had little effect on the crosslinking reaction. Oxidation of the polymer sample is, in many cases, heterogeneous and limited to the surface of the polymer. However, conducting the radiolysis in steps may provide a mechanism of the renewal of oxygen in the bulk polymer, thus maintaining homogeneous oxidative damage.

# Effect of Crystallinity on the Radiation Chemistry of TFE/PMVE

Copolymerization of TFE with 33 mol % PMVE yields a fully amorphous elastomer. The bulky perfluoromethyl ether side chain of PMVE disrupts chain packing, which decreases the TFE homopolymer crystallinity.<sup>22</sup> However, decreasing the PMVE comonomer content to 19.2 mol %gives a semicrystalline elastomer. The X-ray intensity versus diffraction angle of the unirradiated semicrystalline elastomer is shown in Figure 6. A major crystalline scattering peak was observed at 17.9°, which was superimposed on the broad amorphous scattering peak. The crystalline content of the unirradiated semicrystalline elastomer was 13.2%, which was determined from the ratio of the areas of the crystalline to amorphous peaks. The crystalline content of the elastomer irradiated to a dose of 4200 kGy was 13.8%, indicating little or no change in the crystalline content after irradiation. The full width at half maximum (FWHM) of the crystalline peak in the unirradiated elastomer was 0.680°, and did not change after a dose of 4200 kGy, indicating no increase in the disorder of the crystalline structures. Thus, most of the radiolytic processes, such as crosslinking and chain scission, probably occurred in the amorphous region because of the higher polymer chain mobility. Radicals formed in the crystalline region would most likely recombine because of the cage effect.

The glass transition temperature of the semicrystalline elastomer increased with an irradiation dose higher than 200 kGy, indicating crosslinking in the amorphous region (Fig. 7). The DSC melting curve of the semicrystalline elastomer showed a small, broad crystalline melt, characteristic of low crystallinity and small crystallites, which did not allow reliable values of  $T_m$  and the melting endotherms to be obtained, because the transition was so ill defined. However the crystallization transition upon cooling from above the  $T_m$  was better defined, and the crystallization temperatures  $T_c$  were determined. The  $T_c$  was strongly influenced by irradiation and showed a general decrease with irradiation attributable to the formation of crosslinks in the amorphous region (Fig. 8). Rosenberg et al.<sup>23</sup> found the crystallization temperature of the copolymer of ethylene and tetrafluoroethylene (ETFE) to decrease with increasing irradiation attributable to the formation of crosslinks. In comparison, such fluoropolymers as FEP and PFA, which undergo chain scission



**Figure 7** The glass transition temperature of  $\gamma$ -irradiated TFE/PMVE determined by DSC; Fully amorphous ( $\bullet$ ) and semicrystalline ( $\bigcirc$ ).



**Figure 8** Crystallization temperatures of semicrystalline TFE/PMVE as a function of  $\gamma$ -irradiation dose.

when irradiated at room temperature, had increasing crystallization temperatures.

### **CONCLUSIONS**

Depending upon the conditions of irradiation, oxygen had varying degrees of impact on the radiation crosslinking of TFE/PMVE. Irradiations carried out in stages allowed oxygen to diffuse into the bulk of the elastomer, thus maintaining a high oxygen concentration and, consequently, significant oxidative damage. The formation of a low molecular weight wax in the presence of oxygen indicated a predominance of chain scission of the polymeric chains and an inhibited yield of crosslinking. However TFE/PMVE may be crosslinked in the presence of oxygen when irradiated continuously or if thick samples are used.<sup>17</sup>

Radiation had little effect on the crystalline regions of semicrystalline TFE/PMVE up to a dose of 4200 kGy. This behavior differs from that obtained for the radiolysis of PTFE, where the crystallinity increases upon irradiation.<sup>4</sup> The difference can be attributed to the crosslinking in the amorphous regions of TFE/PMVE attributable to the higher chain mobility of TFE/PMVE as compared to PTFE. The formation of crosslinks hinders crystallization of the polymer chains and also lowers the crystallization temperature. Mandelkern et al.<sup>24</sup> showed that crosslinked chain units of polyethylene were similarly excluded from the crystalline regions because of steric factors.

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