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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

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To cite this Article Prasad, A. Vishwa and Singh, R. P.(1996) 'Studies of Radiation Effects on Fluoropolymers: Radiation-Induced Structural and Crystallinity Changes of Tefzel', *Journal of Macromolecular Science, Part A*, 33: 1, 91 – 101

To link to this Article: DOI: 10.1080/10601329608010856

URL: <http://dx.doi.org/10.1080/10601329608010856>

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STUDIES OF RADIATION EFFECTS ON FLUOROPOLYMERS: RADIATION-INDUCED STRUCTURAL AND CRYSTALLINITY CHANGES OF TEFZEL†

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ABSTRACT

Radiation-induced structural changes in the copolymer of tetrafluoroethylene and ethylene (Tefzel) were studied by FT-infrared spectroscopy, differential scanning calorimetry, and wide-angle x-ray diffraction. FT-IR data indicate a continuous increase in the number of free and bonded hydroperoxides and alcohols. The oxidized films were treated with SO₂ and NH₃ for the rapid identification and resolution of various carbonyl species and hydroperoxides. A continuous but marginal decrease in melting and crystallization temperature was observed in DSC thermograms. At room temperature, in the dose range examined, the crystallinity was observed to increase continuously with increasing dose and began to decrease after a certain dose for samples irradiated at 0.36 Mrad/h.

INTRODUCTION

Fluoropolymers are noted for their high thermal stability [1, 2]. Although they are often recommended for continuous use at higher temperatures, they do exhibit a small amount of degradation at processing temperatures. Despite its chemical inertness and thermal stability, fluoropolymers degrade readily when exposed

†National Chemical Laboratory Communication 6141.

to ionizing radiations. The γ -radiative degradation of fluoropolymers gives rise to primary and secondary radicals which can react with oxygen to give perfluoroalkoxy radicals and subsequently carbonyl groups [3, 4]. Fluoropolymers, however, have been reported to undergo crosslinking by ionizing radiations [5].

Although Tefzel (a fluoropolymer) is a high performance elastomeric tetrafluoroethylene/ethylene copolymer containing 0.5–2 mol% perfluorobutylethylene with excellent thermal stability and a good insulating material in nuclear power plants [6], little information is available on the nature of structural changes occurring during high energy radiation. The purpose of this work was to determine the nature of structural changes occurring when Tefzel is subjected to γ -irradiation. This knowledge is important in determining the useful lifetimes as well as the failure mechanism of Tefzel in such demanding applications as nuclear plants and fusion reactors.

EXPERIMENTAL

Material

The material in this study was a commercial sample of fluoropolymer (Tefzel) received from E. I. du Pont de Nemours & Co., USA. It is a terpolymer of 48 mol% ethylene, 0.5–2 mol% perfluorobutylethylene, and 50–51.5 mol% tetrafluoroethylene.

Experimental Procedure

The films ($\sim 120 \mu\text{m}$ thickness) were made by pressing the material between two plates at 270°C by applying $350 \text{ kg} \cdot \text{cm}^{-2}$ pressure for 50 seconds in a preheated hydraulic press. The films were quenched in cool tap water for 5 minutes. The films were kept for photoirradiation [7] in Sepap 12/24 at 60°C in air and under vacuum for different time intervals. The films for γ -irradiation were exposed in a uniform flux of ^{60}Co γ -rays (dose rate 0.36 Mrad/h) in a Gamma chamber 900 (Bhabha Atomic Research Center, Trombay/Bombay). All irradiations were done at room temperature in air for different time intervals (25–366 hours). The samples were intermittently withdrawn and analyzed.

Characterization

The extent of degradation was measured, and oxidative degradation products were identified by Fourier-transform infrared (FT-IR) spectroscopy (Perkin-Elmer 16 PC spectrometer). The γ -rays irradiated samples are unstable at room temperature and can continue to slow oxidize during dark storage [8]. Therefore, to minimize this effect all the irradiated samples were either analyzed immediately or stored at -20°C until analysis was performed. Some oxidized films were chemically treated with SO_2 and NH_3 gases at room temperature in a simple flow system that could be sealed off by valves to allow the reaction to proceed. Changes were detected by FT-IR spectra. The hydroperoxide group was derivatized by SO_2 and the acid group by NH_3 treatment of the oxidized film. The reactions were virtually completed in 4 hours.

The calorimetric measurements were made using a differential scanning calorimeter in the temperature range of 25–300°C at 10°C·min⁻¹ in nitrogen atmosphere with a Perkin-Elmer DSC-7 data station. The samples were cooled at the same rate. Wide-angle x-ray diffraction (WAXD) was recorded in the range of $2\theta = 5\text{--}50^\circ$ at a scan speed of 1–8° min⁻¹ at room temperature using a nickel-filtered CuK α radiation ($\lambda = 0.1542$ nm) from a Phillips PW 1730 x-ray generator. The crystallinity changes were evaluated by WAXS pattern following the conventional Alexander procedure [9] based on graphical separation of intensities due to crystalline and amorphous fractions of the material.

RESULTS AND DISCUSSION

Changes in FT-IR Spectra

The effect of γ -irradiation on Tefzel is shown in Figs. 1 and 2. The photooxidative degradation ($\lambda > 295$ nm) is practically negligible up to 6000 hours irradiation in Sepap 12/24. However, evidence of degradation appears after 1500 hours irradiation in vacuum (Figs. 1 and 2). The degradation of Tefzel by γ -rays in air is much more rapid than by UV irradiation in vacuum. This is because of a higher scission to crosslinking ratio during γ -irradiation than in vacuum. The rate of degradation was found to vary directly with energy. The principal mechanism of degradation was the scission of a carbon–carbon single bond [10]. The oxidative degradation was followed by FT-IR spectroscopy in the hydroxyl and carbonyl regions. A very broad hydroxyl absorption region (3700–3200 cm⁻¹) with a sharp peak at 3555 cm⁻¹ and a broad band at ~ 3380 cm⁻¹ was observed during γ -irradiation (Fig. 1). The band at 3555 cm⁻¹ is due to free (isolated) hydroperoxides, and the broad

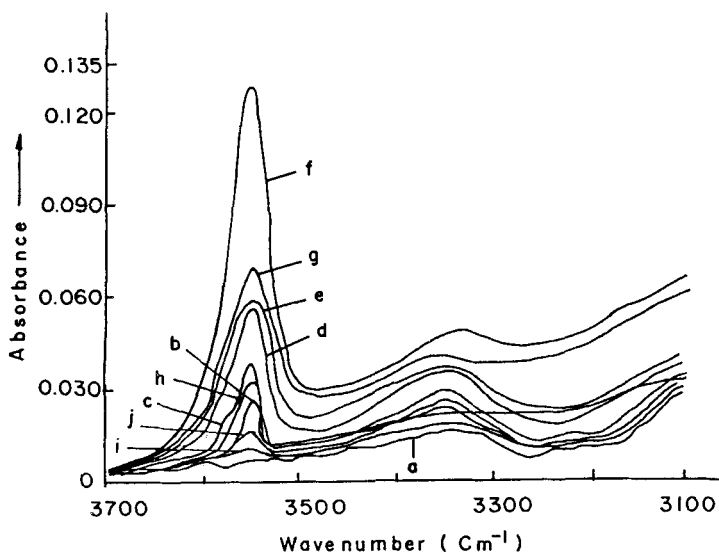


FIG. 1. FT-IR spectral changes in hydroxyl region for various doses of γ -irradiated Tefzel films in air.

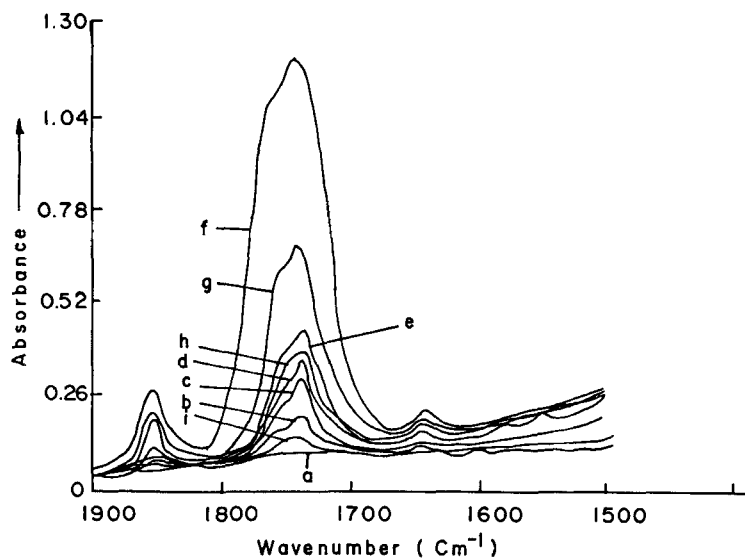
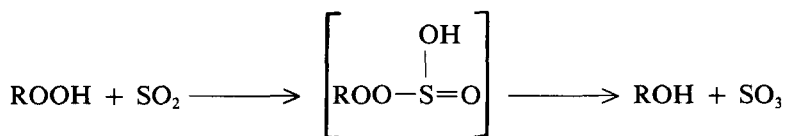


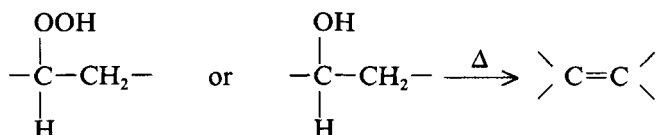
FIG. 2. FT-IR spectral changes in carbonyl region for different doses γ -irradiated Tefzel films in air.

absorption at $\sim 3380\text{ cm}^{-1}$ is because of neighboring intramolecular hydrogen-bonded hydroperoxides and associated alcohols. With increasing dose (up to 95.8 Mrad) a significant increase at these absorptions was observed and thereafter a slow decrease was followed. This is because the rate of hydroperoxidation is more than its decomposition in the initial doses (up to 95.8 Mrad). Exposure to SO_2 gas leads to a quantitative reaction with hydroperoxide groups [11] to give a product with a marked decrease in the hydroxyl region (Fig. 1):

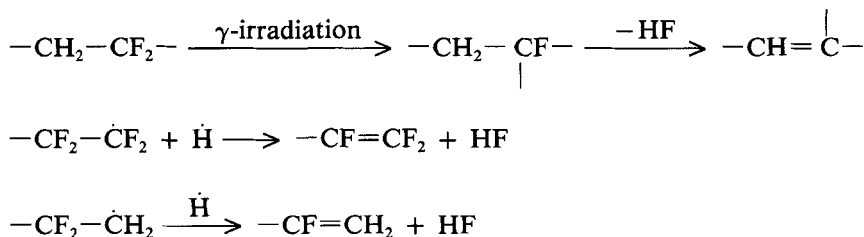


The broad carbonyl region ($1900\text{--}1550\text{ cm}^{-1}$) showed several overlapping absorption bands (Fig. 2). The absorptions at 1875, 1852, 1812, and 1775 cm^{-1} have been assigned to acid fluoride end group [3] in tetrafluoroethylene chain and ethylene chain, free carboxylic acid end group (1812 cm^{-1}), and carboxylic acid dimer or an associated form of carboxylic acid (1775 cm^{-1}) with a hydroxyl group [12]. The hydroxyl group comes in abundance from hydroperoxides in the oxidized ethylene chain. The sharp peaks at 1740 and 1720 cm^{-1} are due to ester and ketonic groups in the ethylene chain, respectively. On the basis of ESR work, Seguchi and Keizo [13] established that fluoropolymers give $-\text{CF}_2-\text{CF}_2-$ and $-\text{CH}_2-\text{CH}_2-$ random macroradicals on radiation-induced degradation in both the crystalline and amorphous regions. The tightly packed polymer chains in the crystalline regions render the diffusion of radicals to other sites difficult. Therefore, radiation-induced reactions are expected to occur predominantly in the amorphous region [14]. The radiation-induced crosslinking structures in Tefzel are expected to result from dif-

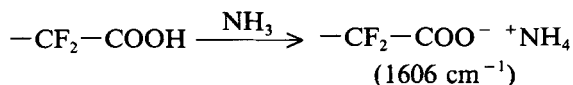
ferent combinations of these radicals. The unsaturated structures at 1640 cm^{-1} may be due to dehydration of hydroperoxide and hydroxyl groups:



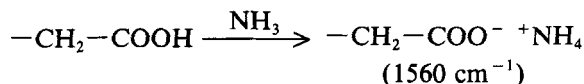
or may be attributed to the dehydrofluorination of crosslinks and/or branched structures:



The overlapping carbonyl region was separated and identified by derivatization reactions of polymeric acids. The ammonia vapors react with carboxylic acid in the polymer chain via the reaction:



and



After exposure to ammonia vapors, the absorption at 1775 cm^{-1} disappears and new peaks at 1606 and 1560 cm^{-1} for their respective ammonium carboxylates [15] are observed in Fig. 3.

The rate of carbonyl group formation increases with irradiation dose and time (Fig. 4), but carbonyl group concentration is a maximum at a dose of 95.8 Mrad (266 hours γ -irradiation). The same behavior was also observed in the amount of hydroperoxide/hydroxyl group formation. This is because the irradiation-unstable hydroperoxide/hydroxyl intermediates accumulate and then decompose to carbonyl groups on longer irradiation. The carbonyl groups subsequently also reach their saturation limits and decompose to end products. Thus the experimental results showed that $-\text{CF}_2-$ and $-\text{CH}_2-$ groups underwent structural changes during γ -irradiation.

Changes in DSC Thermograms

The ionizing radiations caused changes in melting and crystallization behavior due to structural changes (Fig. 5). The slight decrease in melting temperature (T_m) of Tefzel is due to radiation-induced scission [16, 17]. Owing to the increase in molecular mobility caused by radiation-scission, the crystallization temperature (T_c)

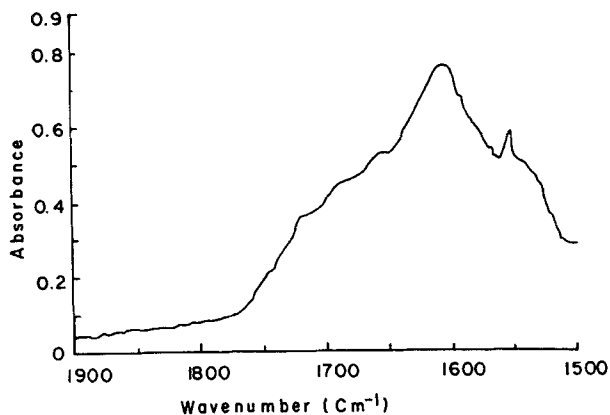


FIG. 3. FT-IR spectral changes of γ -irradiated (95.8 Mrad dose) and ammonia-treated Tefzel film.

and onset of crystallization temperature (T_{onset}) were also observed to decrease after γ -irradiation. The crystallization process is accelerated [18] by lowering T_c and T_{onset} . There is a slow decrease in the difference between T_{onset} and T_c on irradiation. Such a decrease can be attributed to an increase in the rate of crystallization. The half-width of the crystallization exotherm (ΔT_c) increases with irradiation, which means that irradiation facilitates crystallization. The decrease in T_c on irradiation means that chain-scission is the main radiation mechanism in the present system and the disorder in chemical structure caused by scission resulted in a lowering of T_m and T_c . The changes in T_m , T_c , T_{onset} , and ΔT_c are reported in Table 1. The decrease is also attributed to the presence of defects formed within the crystalline region after irradiation, which raise the free energy of the crystal and thereby lower T_m and T_c . The large decrease in T_m and T_c , especially at higher doses, may also be due to in

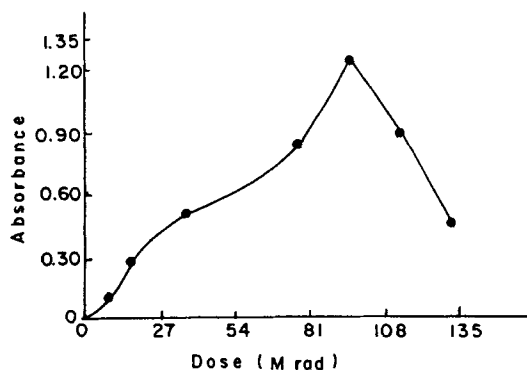


FIG. 4. Rate of carbonyl group formation with doses upon γ -irradiation of Tefzel film.

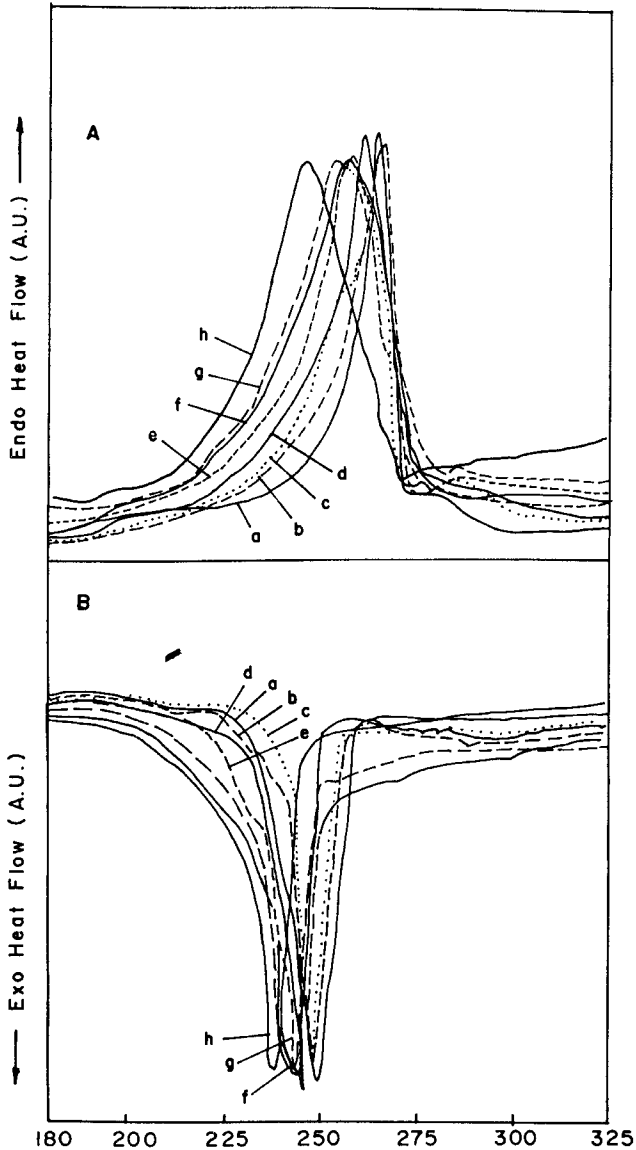


FIG. 5. Variations of DSC thermograms of γ -irradiated Tefzel films for different doses in air: (A) endotherm, (B) exotherm.

part to a decrease in superheating because of the lower molecular weight of highly irradiated material. The lower T_m values represent smaller crystallite size or closer packing. The thermodynamic T_m of semicrystalline polymers decreases as the molecular weight decreases or as the number of defects increases [19, 20]. Thus the decrease in T_m and T_c with increasing dose reflects the change in crystalline domains. DSC measurements showed a broadening of the melting range of Tefzel with dose.

TABLE 1. Changes in Melting (T_m), Crystallization (T_c), Crystallization Onset Temperature (T_{onset}), and Half-Width Crystallization Exotherm (ΔT_c) of Tefzel Film during γ -Irradiation in Air

Dose, Mrad	T_m , °C	T_c , °C	T_{onset} , °C	ΔT_c , °C
0	265.0	249.4	258.4	7.1
9	266.2	248.1	254.5	7.1
18	264.4	247.2	254.0	7.5
27	263.0	246.0	251.8	7.7
36	260.8	245.2	250.0	8.4
77.8	258.2	244.3	251.2	8.4
95.8	257.1	243.0	248.1	8.9
113.8	253.6	238.8	243.3	10.3
131.8	247.4	237.2	241.5	11.5

Thus the final effect of γ -irradiation is to increase the degree of order of polymer chains in irradiated Tefzel.

Changes in X-Ray Diffraction

Figure 6 shows the x-ray diffractograms of neat and γ -irradiated films. Table 2 lists the x-ray parameters of the most intense reflection of the WAXS diffractograms. A crystalline peak was observed at the scattering angle $2\theta = 19.6^\circ$. γ -Irradiation causes the crystallinity to increase up to a dose of 95.8 Mrad. The slow increase in full width at half maximum of the $2\theta = 19.6^\circ$ peak also indicates that crystallinity increases with irradiation. The increase in crystallinity is due to chain scission, preferentially in the amorphous region as it is more sensitive to radiation-induced scission [21, 22]. Because the lower molecular weight molecules (fragments) being more mobile, they are able to assume the lower free energy conformation of the regularly packed crystalline phase. γ -Irradiation has two main effects on the crystal structure of Tefzel. First, the residual stress existing in the amorphous region after crystallization will be partially removed, and thus there will be a further rise in crystallinity. Second, certain radiation-induced structural defects (crosslinks, branching, and chain-end structures), originally present in the crystalline and amorphous phases in different proportions, will be redistributed due to different sensitivities of the two phases to ionizing radiations. They are expected to be excluded from the crystalline regions or to exist in it only as defects. Therefore, the radiation that degrades the polymer is expected to increase its crystallinity further owing to the increase in mobility of the polymer chain.

The decrease in crystallinity at higher irradiation (>95.8 Mrad) is caused by the formation of a high concentration of defects within the crystalline region. The rate of formation of the crystalline defects with dose will be much less initially than the rate of chain scission. The oxygen molecules are unable to diffuse into the tightly packed crystalline phase. In the absence of oxygen, the recombination reactions are

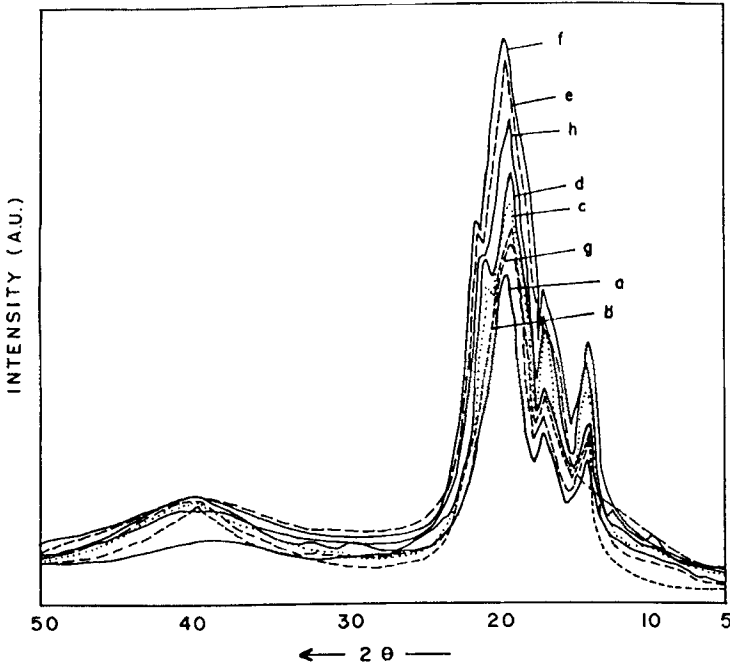


FIG. 6. Variations in x-ray diffractograms of γ -irradiated Tefzel films for different doses at room temperature in air.

TABLE 2. Changes in Percent Crystallinity ($X_c\%$) and Half-Width of the Crystallinity Peak during γ -Irradiation of Tefzel in Air

Dose, Mrad	Percent crystallinity, X_c	Half-width maximum of $2\theta = 19.6^\circ$ peak
0	31.9	2.2
9	35.9	2.6
18	36.9	2.8
27	37.9	3.0
36	38.8	3.1
77.8	41.3	3.2
95.8	43.5	3.5
113.8	36.5	2.7
131.8	41.8	2.4

important, especially in the crystalline region, where the mobility of the primary free-radical is limited by the cage effect. The secondary free-radicals remain unreacted or react to form branches, crosslinks, or end groups. Finally, at a high enough dose, the rate of crystalline defect formation exceeds that of crystallization reactions. Therefore, crystallinity decreases after a dose of 95.8 Mrad in the present system.

CONCLUSION

The structural changes in Tefzel during γ -irradiation were identified by FT-IR spectroscopy. The lowering of T_m , T_c , and T_{onset} is due to structural changes and indicates that the crystallizing ability of the copolymer is improved with increasing dose/time of irradiation. γ -Irradiation improves compatibility between the phases and hence the dispersion of soft segment domains in the matrix. The soft segment selectivity extracts steric defects, leaving a matrix of hard segment which causes higher crystallinity and reorganizes both phases. The soft segment (polyethylene phase) cocrystallizes with the hard segment (polytetrafluoroethylene), leading to a better alignment in the crystalline lattice. Thus the increase in crystallinity may be due to order in the crystal lattice which causes "regularity" in the polymer chain upon γ -irradiation. It was concluded from the crystallinity increase that Tefzel undergoes chain-scission rather than crosslinking under γ -irradiation.

ACKNOWLEDGMENTS

The authors are thankful to Dr. S. Sivaram, Deputy Director and Head, Polymer Chemistry Division, National Chemical Laboratory, Pune, India, for his encouragement and suggestions during these investigations. The authors express their thanks to TIFAC, New Delhi, for financial support of this work. The authors are also thankful to Department of Chemistry, Poona University, Poona, for providing γ -irradiation facilities.

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Received November 3, 1994

Revision received May 10, 1995