

Second Topical Meeting on Tritium Technology in Fission, Fusion, and Isotopic Applications, Dayton, Ohio, 30 April - 2 May 1985; also Fusion Technology, Special Supplement, September 1985

INTERACTION OF POLYETHYLENE AND TRITIUM GAS AS MONITORED BY RAMAN SPECTROSCOPY

J. T. Gill  
Monsanto Research Corporation - Mound\*  
Miamisburg, OH 45342  
(513) 865-3787

ABSTRACT

Irradiation of high-density polyethylene by an ~1 atm overpressure of T<sub>2</sub> gas at 23 ± 2°C has been shown to produce severe damage, ~200 kRad dose, within 6 months. Production rate of H<sub>2</sub> gas from irradiation due to polymer incorporation of tritium increased quickly within the first 2 months, after which it slowed considerably. It is proposed that outgassing of H<sub>2</sub> acted to inhibit diffusion of solubilized HT or T<sub>2</sub> into the bulk, thereby limiting increases in polymer T incorporation and thus damage rate. Damage to the HDPE sample was found to be nonuniform. Laser fluorescence from the sample surface irradiated by the supply of T<sub>2</sub> gas was ~10<sup>3</sup>-fold greater in the energy deposition layer than the fluorescence from bulk polymer after 2 months. This factor was within an order of magnitude of calculated dosages to surface and bulk. Fluorescence from the bulk, apparently caused by unsaturated polyene groups formed during irradiation, grew in time about proportionally to H<sub>2</sub> generation and thus dose. An appreciable concentration of radical or ion-radical polyenes at room temperature could be recombined by bleaching for 15 minutes at ~150°C; these species appeared to reform over night at room temperature.

INTRODUCTION

Large-scale systems, capable of handling tritium gas, are becoming increasingly important to the fusion community.<sup>1,2</sup> Primary containment of the gas, within the components of such systems, must be maintained reliably and with a minimum leakage to both plant and environment. Car-

tain performance requirements, particularly low-leakage non-static seals, such as in valves and pumps, virtually necessitate the use of polymers. The greater susceptibility to radiation damage of polymers, compared to metallic and ceramic materials, is generally recognized. Knowledge regarding interaction between tritium gas (T<sub>2</sub>) and polymers is therefore of some interest.

Damage to polymers by γ-radiation has been extensively studied.<sup>3,4</sup> Some data are available regarding the effects of T<sub>2</sub> gas on various polymers.<sup>5-7</sup> Extrapolation from γ-literature, toward a prediction or rationalization of effects under T<sub>2</sub> gas, is probably risky. Since T<sub>2</sub> cannot irradiate the bulk of a polymer without dissolving in it (tritium's 5.7 keV average energy β particle having a range of ~1 micron in polymers), bulk damage should be dependent upon solubility and diffusivity factors. The surface of a polymer under a column of T<sub>2</sub> gas should be subjected to far greater damage than the bulk. This derives from the much longer β range in the gas (2.6 mm for 5.7 keV β in 1 atm T<sub>2</sub>) and the higher density of T<sub>2</sub> in overgas (factor of ~10-100) than in the bulk.

The rather extensive γ-literature<sup>8</sup> and single β reference<sup>9</sup> concerning radiation damage to polyethylene suggested this polymer for additional study. Laser Raman spectroscopy<sup>9-10</sup> was chosen for analysis here because of its ability both to determine hydrogen isotopic content of overgas and also to monitor damage to portions of the sample employed.

\* Mound is operated by Monsanto Research Corporation for the U. S. Department of Energy under Contract No. DE-AC04-76-DP00053.

This document is  
**PUBLICLY RELEASABLE**  
*James K. Kasper*  
Authorizing Official  
Date: 6-18-09

#### EXPERIMENTAL

High density polyethylene (HDPE) was ordered as rod stock from a local supplier. Its density was determined to be  $0.948 \text{ g/cm}^3$ . Infrared analysis showed terminal vinyl, trans-vinylene, and vinylidene concentrations to be 52, 2, and 1 wt%, respectively, consistent with previous reports for high density polyethylene. From this stock was machined a right circular cylinder, with a  $45^\circ$  angular truncation at one end. The sample diameter was 3.85 mm and maximum length 12.7 mm. A small slot was cut along the minimum length to serve as a gas conductance path. This sample piece, of volume  $0.115 \text{ cm}^3$  and weight 0.109 g, was then press-fit into the bore of a borosilicate glass tube. One end of this tube had been fused closed while the other had been sealed to a stainless steel tube, the latter welded to a Cajon 4-VCR gland, this sample holder was in turn sealed via a copper gasket to a tee piece which held a valve and pressure transducer. Items used in the assembly of this apparatus (see Fig. 1) had previously been cleaned by detergent solution or alcohol, then rinsed and dried. The hermetic apparatus was shown to leak no greater than  $2 \times 10^{-7} \text{ cm}^3 \text{ (STP) N}_2/\text{s}$ . The 30 psia range pressure transducer was calibrated and accurate to  $<0.5\%$  of full scale.

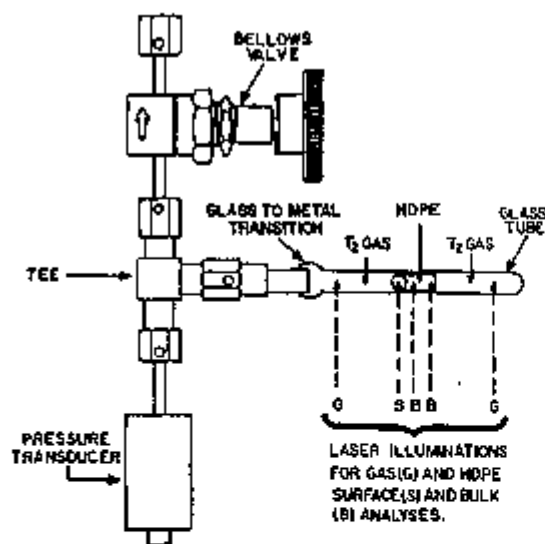


Fig. 1. Containment apparatus for  $T_2$ /HDPE interaction study.

The design of the laser Raman Spectrometer employed here is as proposed previously. Sample mounting areas of the instrument are housed within a tritium-compatible glovebox. A Spectra Physics Model 171-08 argon ion laser was used to illuminate the sample through a window mounted at the glovebox boundary. Laser output powers at 5145 Å were between 50 mW and 2.0 W, the latter normally used for gas analysis. A Spex model 14018 double monochromator, with 1800 groove/mm holographic gratings, analyzed photons scattered from the sample. A thermoelectrically cooled GaAs photomultiplier tube and pulse-counting electronics allowed the digital monitoring of photons. A Nicolet Model 1180 computer was used to drive the spectrometer and acquire and display data.

The sample cell was filled with 0.973 atm of gas at day zero. This gas was 96.5% tritium (as  $T_2$  and DT), 3.4% He, and 0.05% D, with other constituents (H, methane,  $N_2$ , and Ar) each less than 0.02%. Gas pressure and Raman spectrum were monitored periodically thereafter. The Raman gas spectrum, collected at  $40 \text{ cm}^{-1}$  resolution, showed a  $T_2$  peak with HT and  $H_2$  peaks increasingly larger with time. The H/(H+T) isotopic ratios were calculated by a simple ratio of Raman peak heights. This approximation was confirmed by a mass spectral analysis of gas at day 167, at which time the two values agreed within 7% relative.

HDPE spectra were also obtained periodically. The angled HDPE surface which was exposed to  $T_2$  gas was illuminated in a grazing fashion. The laser beam diameter at the sample was  $\sim 60$  microns. The area sampled was generally within 1 mm of the center of the elliptical surface. Areas of the HDPE which interfaced not with gas, but with the glass cell tube, were also illuminated for spectral analysis. The laser beam penetrated  $\sim$  perpendicular to the translucent HDPE a distance of  $\sim 0.5 \text{ mm}$ , with of course substantial internal scattering. Light scattered from the bulk of the specimen was collected with the attempted exclusion of that light resulting from glass or HDPE surfaces. Various points within the bulk of the sample were chosen for inspection.

Following 167 days of irradiation, the gas within the sample cell was analyzed by

mass spectrometry and then fully evacuated. The volume of the cell was later determined by calibration with a standard volume which had been filled with air. This determination, which lasted  $\sim \frac{1}{2}$  hr, yielded a value of 5.65 cm<sup>3</sup> for the volume of the cell holding the HDPE sample. The cell was then evacuated, valved off, and its contents monitored for an additional 42 days.

At day 202 the HDPE, still within its cell, was heated to  $\sim 150^\circ\text{C}$  for 15 min. A small heating tape was employed along with a manual voltage controller external to the glovebox. Temperature was monitored with a Type J thermocouple within a miniature sheath. Because of poor thermal contact between sample tube and thermocouple as well as an intermittent electrical connection to the thermocouple itself, it is estimated that the accuracy of the temperature above is  $\pm 15^\circ\text{C}$ .

Finally, at day 217, the HDPE specimen was removed from the cell into the H<sub>2</sub> atmosphere of the Raman glovebox. Attempts to melt or pulverize parts of the sample for use in ultraviolet or infrared spectroscopic analyses were futile. Several small pieces were fractured from the plastic. However, and two of these were analyzed by an air-atmosphere Nanometrics micro-infrared spectrometer. Infrared absorbance over a 700 to 4000 cm<sup>-1</sup> range was recorded for each sample piece.

## RESULTS

Changes in the composition of overgas in the sample cell are displayed in Fig. 2. Total partial pressures of both protium and tritium isotopes are plotted, these having been derived from total pressure results, isotopic ratio analyses, and predicted values of tritium decay. Values are shown both before and after the evacuation following mass spectral analysis (day 167). By comparison with the mass spectrum, H<sub>2</sub> partial pressures are estimated to be  $\leq 7\%$  low (relative) and T<sub>2</sub> values  $\leq 3\%$  high, since total pressures are known to  $\pm 0.5\%$ . No corrections were made. It can be seen from Fig. 2 that, while T<sub>2</sub> pressure dropped slightly, total H<sub>2</sub> pressure increased markedly over the course of the irradiation.

Raman spectra of the HDPE sample showed only one major change, as illustrated in Fig. 3. While Raman peaks remain unchanged

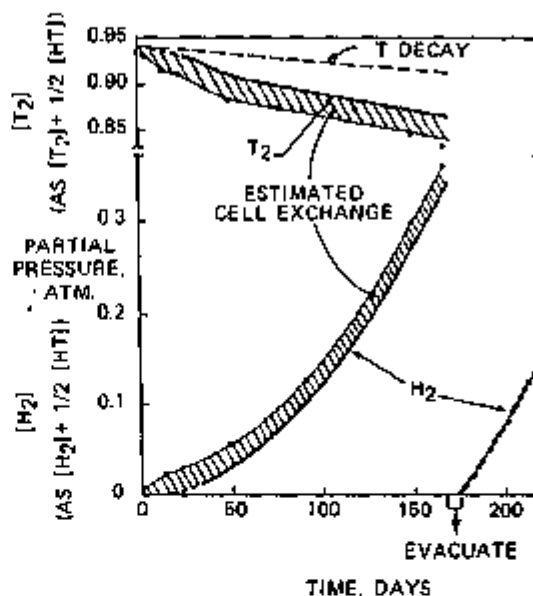


Fig. 2. Changes in composition of T<sub>2</sub> overgas with HDPE interaction time. Estimated cell contribution to changes are shown subtracted from the H<sub>2</sub> and T<sub>2</sub> curves and are shaded.

and no new peaks appeared upon irradiation by T<sub>2</sub>, the background fluorescence increased markedly with time. Such fluorescence is probably derived from electronically excitable unsaturations, radicals, or radical ions.

Therefore, the magnitude of this fluorescence, at its maximum (1800  $\pm$  100 cm<sup>-1</sup>), as referenced to the amplitude of the HDPE framework C-H band at 2884 cm<sup>-1</sup>, was monitored as an indication of radiation damage. Progress in time of this ratio, both for surface and bulk HDPE scans, is displayed in Fig. 4. At long times, the scatter of the data becomes large. This derives partly from the use of different sampling points but largely from the huge predominance of fluorescence over Raman scattering. Where the Raman peaks become barely visible or indiscernible, the uncertainty in the ratio employed here becomes quite large. Estimated error bars are given in Fig. 4 and it is apparent that relative errors of 30% or more are not uncommon. Nevertheless, it should be noted

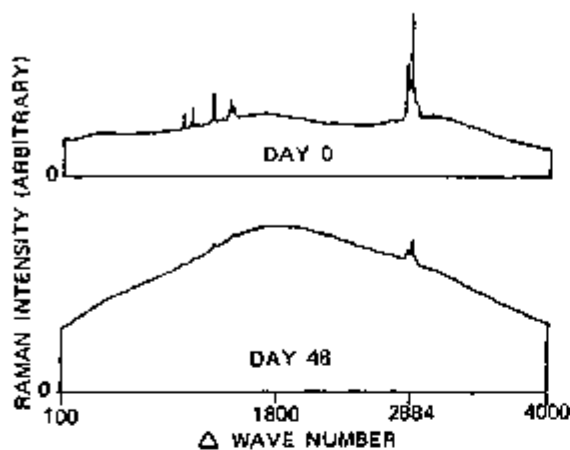


Fig. 3. Raman spectra from bulk HDPE at zero exposure and at 48 days exposure to 1 atm  $T_2$  gas.

that the ratios from surface scans are generally greater than those from bulk data. In addition, warming the sample to  $\sim 150^\circ\text{C}$  reduces substantially the fluorescence.

During the course of irradiation, the color of the HDPE changed markedly. The original sample was colorless and translucent. After  $\sim 70$  days of irradiation, the HDPE became yellowish, the color thereafter progressing rapidly to a dull orange (day  $\sim 120$ ) and then dark red-brown (day  $> 150$ ), the hue being slightly deeper toward the sample periphery. The translucence of the specimen remained throughout. Upon warming on day 202, however, the dark color was lost, the sample reverting to a pale yellow color more transparent than before. This annealing behavior coincided with a loss of fluorescence in the Raman. Overnight, however, the color of the HDPE returned to its pre-anneal dark red-brown state. The sample moreover appeared to have become loose in its mounting tube and fissured in numerous places, the cracks running perpendicular to the axis of the cylinder. After removing the HDPE from its cell, a thin disc was sectioned from the bulk of the cylinder with a scalpel. This disc was an almost clear pale yellow when annealed except for a

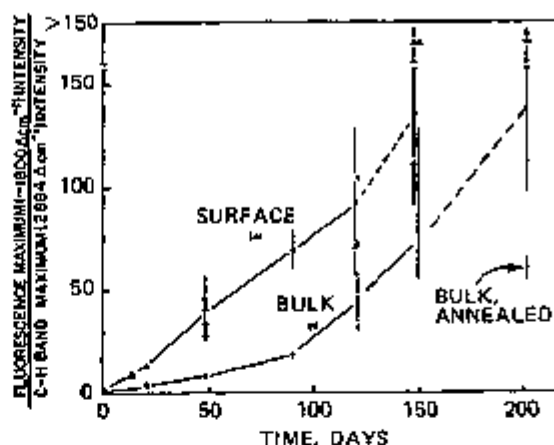


Fig. 4. Ratio of maximum fluorescence intensity to C-H Raman band intensity plotted for both surface and bulk HDPE as a function of  $T_2$  exposure time.

ring of darkened material along its circumference. A similar darkened film was observed on one of the small pieces fractured from the sample and used for micro-infrared analysis. The depth of the latter darkened film was  $\sim 10$  microns.

Micro-infrared absorption spectra of the two small HDPE fragments mentioned above were different from that of unirradiated material, most notably in two areas. The peaks at  $966\text{ cm}^{-1}$ , representative of trans-vinylene groups along the polyethylene backbone,<sup>11,12</sup> were greatly increased with respect to the peak at  $908\text{ cm}^{-1}$  for terminal vinyl groups. This behavior has been observed previously in the  $\gamma$ -irradiation of HDPE.<sup>11,13</sup> Even more dramatically, a large peak at  $1700\text{ cm}^{-1}$  was observed in irradiated samples where none was observed in virgin material. This peak position corresponds to that expected for both C-F bonds and carbonyl species. The absorbance of the  $1700\text{ cm}^{-1}$  band was  $\sim 1/10$  and  $\sim 1/5$  that of the C-H band in the large and small fragments respectively. The small fragment was that which displayed the darkened film. In addition,  $1700\text{ cm}^{-1}$  bands were observed to increase slowly with time.

## DISCUSSION

### Overgas

Previously published results indicate that the irradiation of polyethylene by tritium  $\beta$  particles releases  $H_2$  molecules from the plastic, presumably by crosslinking and desaturation. A G-factor for this release of 3.1  $H_2$  molecules/100 eV was determined. This was reasonably consistent with  $G(H_2)$  values determined under  $\gamma$ -radiation. Such  $G(H_2)$  factors have been shown invariant with  $H_2$  overpressure from 0.1 to 1.0 atm and with  $\gamma$ -dose up to 200 MRad, although the latter has been disputed.

Interpretation of the isotopics displayed in Fig. 2 is complicated by the simultaneous occurrence of several processes.  $T_2$  dissolves within the bulk sample, irradiates it from within, and presumably, to some extent, is incorporated into the polyethylene by exchange and addition. Tritium also irradiates the exposed surfaces of the HDPE, exchanging with the surface framework and perhaps decomposing the surface by production of methane. Finally, the  $T_2$  gas will exchange with protium on the surfaces of the sample cell itself and decompose to methane the carbonaceous residues left there following cleaning. Table I shows these mechanisms considered, along with their approximate relative contributions to  $H_2$  production, as discussed below.

Loss of some tritium to the exposed surface of the polymer by rapid exchange with C-H bonds (Table I.B.1) would be a reasonable contribution to the protium evolution observed. Full exchange of the top 1/3 micron of surface, about that observed previously, could, however, account for only  $\sim 0.002$  atm of the  $T_2$  loss (and  $H_2$  increase), a small fraction of that observed.

Progressive etching of the exposed surfaces by reduction of polymer to methane (Table I.B.2) is a possible mechanism for loss of  $T_2$  and increase of protium in the gas phase, assuming rapid distribution of isotopes among  $C(H/T)$  and  $(H/T)$ . An initial slow rise in concentration of methane noted in the Raman spectra may speak for some such etching, of perhaps the top

micron, but this largely ceases after day  $\sim 60$  and would account for only  $\sim 0.006$  atm of protium. An equilibrium process of creation and redeposition of methane species might then occur at the activated surfaces, effectively driving the exchange of isotopes deeper within the near surface. The depth to which such an effect could occur, however, would seem only a few Angstroms. Because methane concentration is observed to be small, reduction of cell wall organics (Table I.C.1) is also considered small.

The loss of gasified tritium shown in Fig. 2 is far greater than the solubility of  $T_2$  in the polyethylene sample. The solubility factor is dependent upon the crystallinity of the sample and may vary between 0.01 and 0.06 cm<sup>3</sup> (STP)/cm<sup>3</sup> atm. Even assuming the maximum factor, solution of  $T_2$  into the plastic would account for only a  $1.3 \times 10^{-3}$  atm loss of  $T_2$  overpressure. Moreover, dissolved  $T_2$  alone can account for an  $H_2$  production rate (Table I.A.1) of  $<0.01$  atm/100 days, far less than that observed.

One is left to conclude, therefore, that the trends noted in the  $H_2$  and  $T_2$  curves of Fig. 2 are not primarily the result of dissolved  $T_2$  or HDPE surface effects but rather derive from incorporation of tritium within the bulk of the polymer (Table I.A.2) and isotopic exchange with the cell walls (Table I.C.1). Exchange of D<sub>2</sub> gas with  $\gamma$ -irradiated polyethylene has previously been observed. Similarly, exchange of  $T_2$  with the surface protium of metal and glass containers is well-known.

If one assumes that the tritium lost within the gas phase has become fully incorporated within the sample of plastic, and then inspects the rate of protium increase, a G-factor of 2.2 may be calculated for  $H_2$  production at the end of the present experiment. A significant fraction of the lost tritium, however, has been incorporated not in HDPE, but into the surfaces of the sample cell. Assuming the previously published  $G(H_2)$  factor of 3.1 to be correct for HDPE, it is determined that 29% of the lost  $T_2$  at day 167 is incorporated in cell surfaces. The same procedure may be applied to earlier data. At day 48, the amount of  $T_2$  lost to surfaces is deter-

Table I. Some Possible Mechanisms Involved in the Present  $T_2$ -Irradiation of HDPE and Their Estimated Relative Contributions to  $H_2$  Production at Two Times

		Estimated Relative Contribution to $H_2$ Production At:	
		Day 48	Day 167
A. <u>HDPE BULK EFFECTS</u> ( $\times 180$ per T decay)			
1. Irradiation from decay of dissolved $T_2$ :			
$(CH_2)_n - T_2 \xrightarrow{\beta} C_n H_{2(n-x)} + xH_2 + \frac{1}{2}T_2 + \frac{1}{2}He$	1 to 4%	0.5 to 2%	
2. Irradiation from decay of incorporated T:			
$C_n H_{2n-1} T \xrightarrow{\beta} C_n H_{2(n-x)} + \frac{2x-1}{2} H_2 + \frac{1}{2} He$	$\sim 40\%$	$\sim 90\%$	
B. <u>HDPE SURFACE EFFECTS</u> (catalyzed by a high $\beta$ field)			
1. Exchange of surface protium:			
$(CH_2)_n + nT_2 \xrightarrow{\beta} (CT_2)_n + nH_2$	$\sim 4\%$	$\sim 0.5\%$	
2. Decomposition to methane (etching):*			
$(CH_2)_n + 2nT_2 \xrightarrow{\beta} nCT_4 + nH_2$	$\leq 7\%$	$\leq 3\%$	
C. <u>CELL WALL EFFECTS</u> (catalyzed by a high $\beta$ field)			
1. Reduction of cell wall organics:*			
$C_a H_b + 2aT_2 \xrightarrow{\beta} aCT_4 + \frac{b}{2} H_2$	$\leq 7\%$	$\leq 3\%$	
2. Exchange with cell wall protium:			
$MOH + \frac{1}{2}T_2 \xrightarrow{\beta} MOT + \frac{1}{2}H_2$	$\sim 45\%$	$\sim 7\%$	

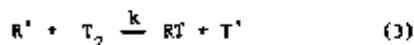
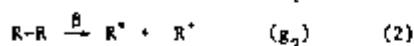
\* Note that the scrambling of H and T isotopes among hydrogen diatomic and methane product molecules does occur, but is not specified in this formula.

mined to be the same as at day 167. This is consistent with other results<sup>19</sup> which show similar container surfaces to be fully exchanged within 10-30 days. The inflection between days 10-50 in the  $H_2$  pressure curve would seem to confirm that here. Assuming then that cell surface isotope exchange remains essentially constant from day 20 onward, but is rather uncertain for days 0-20, hatched areas have been inserted in Fig. 2 to represent this exchange. For an incremental loss in tritium concentration to cell walls, an equal and opposite gain in protium concentration (from direct exchange) is also plotted.

The rate of increase of protium was shown above to be proportional to the amount of T incorporated into the plastic. This is reasonable if each T atom in the bulk is surrounded by an excess of H atoms: self-irradiation of the polymer would thus produce  $H_2$  almost exclusively. In fact, distribution of the  $T_2$  lost from the gas phase into the bulk polymer would result in an average of one T atom in  $\sim 600$  polymer H atoms at day 167.

Initially, the amount of T incorporated within the polymer might be expected to

increase exponentially following dissolution of  $T_2$  into the organic framework. The simplified mechanism (and associated g-values) below would be reasonable for this:



Then:  $\frac{d[RT]}{dt} = k[R^*][T_2]$

and

$$\frac{d[R^*]}{dt} = gk_B[2[T_2] + [RT]] - k[R^*][T_2],$$

where  $gk_B = (g_1 + 2g_2)k_B$  is the rate of production of organic radicals for a given concentration of tritium in the bulk. If one assumes a steady state for  $[R^*]$ , a constant  $[T_2] =$  gas solubility, and the absence of diffusion-control of Equation (3), the above can be solved for  $[RT]$ , yielding:

$$[RT] = 2[T_2] (\exp(gk_B t) - 1) \quad (4)$$

The rate of radiolytic  $H_2$  production should also increase exponentially during this time because:

$$\frac{d[H_2]}{dt} = G(H_2) k_B [2[T_2] + [RT]] =$$

$$2G(H_2) k_B [T_2] \exp(gk_B t),$$

and

$$[H_2] = \frac{2G(H_2) [T_2]}{g} [\exp(gk_B t) - 1] \quad (5)$$

The initial decrease of gasified  $T_2$  and increase of  $H_2$  as seen in Fig. 2 (corrected for container wall contribution) are fairly consistent with exponential rates. The data suggest  $g \sim 5$  for the first  $\sim 50$  days of the experiment, assuming  $T_2$  solubility of  $0.02 \text{ cm}^3 \text{ (STP)/cm}^3 \text{ atm}$ . This g-factor is larger than that for alkyl radical ( $R^*$ ) production

( $g_{alk} \sim 3.3$ ) previously observed in polyethylene,<sup>3,4</sup> but some radical recombination may have occurred in that study.

The production of  $H_2$  from irradiation of the HDPE does not continue to increase exponentially after day 50. Rather, the production rate slows toward a constant, steady rise in  $H_2$  pressure, not quite attained prior to mass spectral analysis and evacuation. The rate of loss of gasified  $T_2$  also appears to slow between the first and last 50 days. Some mechanism apparently causes the incorporation of T into the bulk plastic to slow from perhaps an exponential to a nearly zero rate of rise.

Incorporation presumably cannot occur without the presence of freshly solubilized  $T_2$  or RT molecules in the bulk plastic. Since calculations show diffusion of tritium gas into the plastic along the glass/HDPE interface to be facile, the exposed (highly irradiated) surfaces do not prevent tritium entry. Release of  $H_2$  from the irradiated HDPE might inhibit the entry of  $T_2$  or RT molecules, assuming that solution sites for  $H_2$ , RT, and  $T_2$  in the polymer matrix are limited in number and essentially the same at  $\sim 1$  atm pressure. The  $H_2$  outgassing rate at the end of the experiment is  $1.9 \times 10^{-7} \text{ cm}^3 \text{ (STP) } H_2/\text{s}$ . One can derive from Fick's law the concentration profiles of  $H_2$  within this outgassing sample. For a cylindrical geometry (calculations suggest that flux along glass/polymer interface should be large in comparison to outgassing rate), one may write:

$$\frac{\partial c}{\partial t} = D \left( \frac{\partial^2 c}{\partial r^2} + \frac{1}{r} \frac{\partial c}{\partial r} \right) + G, \quad (6)$$

where  $c$  is the concentration of  $H_2$  in polymer at time  $t$  and  $r$ , the radial distance from the axis,  $D$  is the diffusion constant, and  $G$  is the rate of production of radiolytic  $H_2$  in the bulk. Assuming an effective steady-state and a uniform distribution of  $H_2$  production, one equates the left side of Equation (6) to zero and obtains the differential equation:

$$\frac{\partial^2 c}{\partial r^2} + \frac{1}{r} \frac{\partial c}{\partial r} = -G/D \quad (7)$$

If it is also assumed that at sample radius  $R$ ,  $c = c_0$ , where  $c_0$  is the concentration at overgas pressure, and that, for continuity,

$$\frac{\partial c}{\partial r} = 0 \text{ at } r = 0,$$

the following solution is obtained:

$$c - c_0 = \frac{G}{4D} (R^2 - r^2) \quad (8)$$

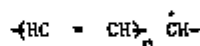
From Equation (8) above, and using  $D$  as determined at conditions approaching zero concentration,<sup>24,26,27</sup> the concentration of  $H_2$  at the sample axis on day 167 may be shown to be about two to three times the  $H_2 + T_2$  concentration at the sample periphery. Substantial  $H_2$  concentrations within the sample could cause a lowering of hydrogen solute's diffusivity, since a filling of less energetically favorable dissolution sites may likewise drive diffusion across higher potential energy barriers. While  $\gamma$ -irradiation of polyethylene has been shown not to affect hydrogen diffusivity up to 100 MRad<sup>18</sup> or solubility up to 30 MRad,<sup>20</sup> concentration-dependent diffusivity has been noted previously in several systems and may be more general than normally recognized.<sup>29,30</sup> Migration of dissolved  $H_2$  or  $T_2$  into the plastic could thus have been more difficult the deeper the penetration. In this way  $T$  incorporation in the polymer could have been significantly impeded once the  $H_2$  production rate became appreciable. Radiation damage rate to the bulk of the plastic therefore may essentially be self-limiting, as suggested by Fig. 2. Removal of all volatile  $T_2$  from the system at day 167 left only incorporated  $T$  within the HDPE framework; radiolytic  $H_2$  production remained linear in time thereafter.

A cross-section autoradiograph of the irradiated sample, performed after day 220, showed that incorporated tritium (and presumably radiation damage) was more concentrated toward the sample periphery than on axis. This tends to support the concentration-dependent diffusivity argument above.

#### Fluorescence

The appearance of the fluorescence curve for the bulk HDPE shown in Fig. 4 is qualitatively similar to the  $H_2$  release curve

of Fig. 2. This would appear reasonable, as damage to the plastic should be proportional to the  $H_2$  released, itself proportional to the dose received. The link between damage and fluorescence is, however, complicated. The dose imparted to the bulk plastic, averaged over the total bulk, may be calculated from  $H_2$  release to be  $1.8 \times 10^2$  MRad at day 167. Since polyethylene is known to experience severe damage from  $\sim 10^2$  MRad<sup>3</sup>  $\gamma$ -radiation, the darkening, shrinkage, and crazing of the sample seen here is expected. Upon irradiation, polyethylene has been shown to desaturate as well as crosslink, the latter being the dominant mechanism for mechanical damage,<sup>8</sup> but the former, along with the generation of stable free-radicals, undoubtedly giving rise to the observed fluorescence. The production of various unsaturated species is known to occur in a  $\gamma$  field. Isolated trans-vinylene groups appear to be formed initially as a linear function of dose, as are conjugated dienes, while tylenes are formed as the dose squared.<sup>31</sup> Dose dependencies of formation of higher polyene conjugations can only be estimated at present, but are surely non-linear. Radical species of significant lifetimes can also be formed.<sup>32,33</sup> Allyl radicals ( $n=1$ )



are formed with a nearly linear dose dependence, and higher polyenyls ( $n>1$ ) display a distinctly non-linear dependence.<sup>31,34</sup> Fluorescence from any of these electronically-excitable species requires that it display some absorption in its visible spectrum at the 514.5 nm green laser line employed here. Although all of the species noted above have absorbance maxima well into the ultraviolet, low energy tails from these bands appear to extend into the visible.<sup>12</sup> It has been shown that fluorescence (UV excited) from a  $\gamma$ -irradiated polyethylene sample is proportional to vinylene group concentration,<sup>35</sup> up to  $\sim 10$  MRad. Beyond this dose, [vinylene] approaches a limiting value and polyenes begin to contribute relatively more to total unsaturations.<sup>11,31</sup> The UV absorbance maxima of higher order species appear closer to the exciting laser line.<sup>31,34</sup> Visible fluorescence should thus become more efficient with increase in dose. It is then a bit surprising that bulk fluorescence does not increase even more rapidly in time than the radiolytic  $H_2$



evolution curve. As has been shown, however, the higher order polyenes themselves are formed with rather poor efficiency, their concentrations being < 0.1 times that of vinylene, diene, allyl, or dienyl species at 100 MRad.<sup>31</sup>

The presence of radical polyenes or radical ion color centers in the irradiated HDPE is indicated both by the color change and the loss of fluorescence upon annealing.<sup>23,33</sup> The rapidity with which the HDPE coloration and fluorescence disappear upon heating is presumably caused by a large increase in mobility of polymer chains and hydrogen gas within the material, allowing recombination of radicals or ions.<sup>36</sup> The overnight recovery of sample coloration may indicate an efficient trapping by polyenes of radicals generated along  $\beta$  tracks or facile ionization of polyenes, leading to some steady-state concentration of resulting species.

As expected, Fig. 4 shows that radiation damage at the exposed surface of the HDPE sample was larger than that in the bulk. By analogy with a previous calculation,<sup>37</sup> it can be shown that radiation flux at a planar surface of a material from an effectively infinitely deep and broad supply of tritium gas above the material should be  $\sim E_0 / 4\mu$ , where  $E_0$  is the specific volume activity of the gas in  $\text{eV sec}^{-1} \text{cm}^{-3}$  and  $\mu$  is the linear absorption coefficient in  $\text{cm}^{-1} \text{atm}^{-1}$  for the gas. The application of the concept of  $\mu$  to tritium  $\beta$  radiation is not strictly correct, but has been shown reasonable at least for gases.<sup>38</sup> A column of effectively infinite depth but restricted radius  $r$  (such as in the glass tube of the present experiment) should impart a smaller flux,  $F$ , at the center of a surface perpendicular to the tube axis, equal to  $\sim E_0 / 8\mu$  in this case.<sup>39</sup> If the normal to the surface is inclined at an angle  $\phi$  to the tube axis, flux should then roughly be  $F \cdot \cos \phi$ . Because in the present experiment  $\phi = 45^\circ$  and  $\mu = 2 \text{ cm}^{-1} \text{atm}^{-1}$  for both  $\text{H}_2$  and  $\text{T}_2$ ,<sup>38</sup> the flux at the surface should have been  $\sim 2 \times 10^4 \text{ eV day}^{-1} \text{cm}^{-2}$ . Backscattering or reemission was small. The range of the average tritium in the HDPE here should be 0.44 microns.<sup>40</sup> This value may actually be an upper bound for the effective damage layer, as the spectrum of the impinging  $\beta$

particles should be weighted toward lower energies,<sup>38</sup> given the partial absorption by the gas.<sup>22</sup> Roughly, however, a dose rate of  $5 \times 10^{22} \text{ eV day}^{-1} \text{cm}^{-3}$  or 700 MRad day<sup>-1</sup> should have been imparted in the topmost  $\beta$  penetration layer. The "near-surface" laser excitation, which illuminated a depth of  $\sim 60$  microns, sampled HDPE material in which the average dose rate was  $\sim 3 \times 10^{20} \text{ eV day}^{-1} \text{cm}^{-3}$ , assuming negligible bulk dose. The dose at day 50 was thus  $1.5 \times 10^{22} \text{ eV cm}^{-3}$ . By contrast the bulk dose at day 50, determined from the H evolution curve, is calculated to be  $1.3 \times 10^{21} \text{ eV cm}^{-3}$ . The near-surface to bulk dose rate ratio should thus be  $\sim 10$ , while the observed fluorescence ratio is 5. The discrepancy factor between calculated dose and observed fluorescence ratios is about 2 from days 50-120. Observed near-surface fluorescence is always low. Discrepancies at earlier times appear larger, probably because of uncertainties in the  $\text{H}_2$  evolution curve, but are still  $< 10$ .

The discrepancies may indicate that the contribution to fluorescence from doses  $>> 100$  MRad is less efficient than at lower doses. As noted before, unsaturated group concentrations tend toward limiting values with dose. The near-surface fluorescence curve parallels that of the bulk after day  $\sim 90$ . This may suggest that the surface contribution to fluorescence had indeed reached a limiting value at about that time.<sup>3</sup> The surface dose at day 90,  $4 \times 10^{24} \text{ eV cm}^{-3}$  or  $6.5 \times 10^{10} \text{ Rad}$ , could account for complete desaturation of the 0.44  $\mu$  HDPE layer if an average  $g$ -value for unsaturation of 1.1 were assumed. This contrasts with the  $g$  (vinylene) of 2.4 at the beginning of an irradiation of HDPE.<sup>12</sup> Surely then, at day 90, a large portion of the surface  $\beta$ -range layer was drastically altered. Some of the discrepancy above may also be attributed to a surface etching mechanism suggested in the previous section. An etch rate of 1 micron/60 days,<sup>3</sup> together with a  $\mu$  (HDPE) =  $1.2 \times 10^4 \text{ cm}^{-1}$ , would decrease integrated surface dose by 25-50% during the first 60 days. Underestimation of bulk dose near the sample periphery may also contribute to the discrepancy.

Following removal of the HDPE sample from the tritium irradiation apparatus, a

thin ~ 10 micron band of darkened material was observed to "coat" the cylindrical surface of the plastic. Since a sample cell volume calibration had been performed with air some 2 months earlier, since a micro-infrared analysis showed that the absorbance at  $1700\text{ cm}^{-1}$ , a known band of the C=O group, was larger near that surface, and since that band increased overnight when further exposed to air, the discolored layer is attributed to oxidation of the irradiated material during volume calibration. Oxygen appears to have migrated along the HDPE/glass interface where the material separation distance was small but finite. Given this migration,  $\text{O}_2$  probably diffused into the sample, with simultaneous scavenging by organic radicals, to the ~ 10 micron depth observed. As the optical absorbance bands of polyene-aldehydes or acids tend to fall closer to the visible regions of the spectrum than those of polyenes of comparable length,<sup>4</sup> the relative darkening of the layer is reasonable. Greater fluorescence observed from this boundary layer than that from the center of the thin disc section, even when annealed, is also consistent with an oxidation interpretation.

#### CONCLUSION

Irradiation of high-density polyethylene by an ~ 1 atm overpressure of  $\text{T}_2$  gas at  $23 \pm 2^\circ\text{C}$  has been shown to produce severe damage, ~ 200 MRad dose, within 6 months. Production rate of  $\text{H}_2$  gas from irradiation due to polymer T incorporation increased quickly within the first 2 months, after which it slowed considerably. It was proposed that outgassing of  $\text{H}_2$  acted to inhibit diffusion of solubilized HT or  $\text{T}_2$  into the bulk, thereby limiting increases in polymer T incorporation and thus damage rate. Damage to the HDPE sample was found to be nonuniform. Laser fluorescence from the sample surface irradiated by a supply of  $\text{T}_2$  gas was ~  $10^3$ -fold greater in the energy deposition layer than the fluorescence from bulk polymer after 2 months. This factor was within an order of magnitude of calculated dosages to surface and bulk. Fluorescence from the bulk, apparently caused by unsaturated polyene groups formed during irradiation, grew in time about proportionally to  $\text{H}_2$  generation and thus dose. An appreciable concentration of radical or ion-radical polyenes at room temperature could be recombined by bleaching for 15 min.

at ~150°C; these species appeared to reform overnight at room temperature.

The nature of the mechanism proposed above for the inhibition of ever-increasing T incorporation and thus dose rate is subject to some question. The evidence alone, however, suggests that an outflux of  $\text{H}_2$  could be useful in this and other systems (where the  $\text{H}_2$  outgas could be tolerated) to reduce damage and contamination of materials by  $\text{T}_2$  gas. Investigations of diffusion in the  $\text{H}_2/\text{T}_2/\text{HDPE}$  system as a function of concentration should be undertaken to clarify the present observations.

Characterization of unsaturated groups present in  $\text{T}_2$ -irradiated HDPE and correlation with observed fluorescence is also of interest. Particularly, the nature of the species which are readily bleached but return overnight is intriguing. Ultraviolet/visible spectroscopy could help settle such questions.

#### ACKNOWLEDGEMENTS

The author wishes to thank Dr. R. S. Carlson for his micro-infrared analyses of irradiated polyethylene, R. L. Anderson for art work, J. A. Blanton for mass spectral analysis of overgas, V. D. Jones for autoradiographic analysis, and Drs. C. C. Abell and R. E. Ellefson for helpful reviews and discussions.

#### REFERENCES

1. J. L. ANDERSON, D. O. COFFIN, and C. R. WALTERS, J. Vac. Sci. Technol., **A1**, 849(1983).
2. J. T. GILL, B. E. ANDERSON, R. A. WATKINS, and C. W. PIERCE, J. Vac. Sci. Technol., **A1**, 856(1983).
3. R. O. BOLT and J. G. CARROLL, Radiation Effects on Organic Materials, Academic Press, New York, 1963.
4. F. A. MAKHLIS, Radiation Physics and Chemistry of Polymers, J. Wiley and Sons, New York, 1975.
5. L. M. DORFMAN, B. A. MEMER, and C. F. PACHUCKI, "The Interaction of Tritium with Polymeric Materials," KAPL-980 (del.), Knolls Atomic Power Laboratory, Schenectady, NY, 1953.

6. P. M. S. JONES and R. GIBSON, "The Interaction of Tritium Gas with Polythene," AWRE-O-16/63, Atomic Weapons Research Establishment, United Kingdom, 1963.
7. a) P. E. ZAPP, "Effects of Tritium in Elastomers," DP-MS-82-54, Savannah River Laboratory, Aiken, SC, 1982; b) K. F. WYLLIE, J. E. HOCKETT, and T. L. BUXTON, J. Vac. Sci. Technol., 20, 1138 (1982).
8. For recent reviews see: M. DOLE, J. Macromol. Sci.-Chem., A15, 1403(1981); and M. DOLE, C. GUPTA, and N. GVOZDIC, Radiat. Phys. Chem., 14, 711(1979).
9. S. M. CRAVEN and J. T. GILL, "Proposed Implementation of Laser Raman Scattering Spectroscopy for Analysis of Hydrogen Isotopes", MM-2583, Monsanto Research Corporation, Miamisburg, OH, 1979.
10. R. W. SIESLER and K. HOLLAND-NORITZ, Infrared and Raman Spectroscopy of Polymers, Marcel Dekker, New York, 1980.
11. M. DOLE, D. C. MILNER, and T. F. WILLIAMS, J. Amer. Chem. Soc., 80, 1580(1958).
12. M. E. FALLGATTER and M. DOLE, J. Phys. Chem., 68, 1988(1964).
13. D. L. TABB, J. J. SEVCIK, and J. L. KOENIG, J. Polym. Sci., Polym. Phys. Ed., 13, 815(1975).
14. M. DOLE, T. F. WILLIAMS, and A. J. ARVIA, Second Intl. Conf. Peaceful Uses Atomic Energy, Geneva, Switzerland, Vol. 29, 171(1958).
15. H. MITSUI, F. HOSOI, and T. KAYIGA, Polym. J., 4, 79(1973).
16. E. J. LAWTON, P. D. ZEMANY, and J. S. BALWIT, J. Amer. Chem. Soc., 76, 3437(1954).
17. K. SHUMACHER, Kolloid Z. Z. Polym., 157, 16(1958).
18. H. MITSUI and Y. SHIMIZU, J. Polym. Sci., Polym. Chem. Ed., 17, 2805(1979).
19. J. T. GILL, J. Vac. Sci. Technol., 17, 645(1980).
20. S. XOSO and M. DOLE, Macromolecules, 7, 190(1974).
21. M. E. LAND and M. DOLE, Macromolecules, 9, 960(1976).
22. M. E. LAND and M. DOLE, Proc. Symp. Struct.-Solubility Relat. Polym., 123(1977).
23. M. DOLE and F. CRACCO, J. Phys. Chem., 66, 191(1962).
24. N. MIYAKE et al., J. Vac. Sci. Technol., A1, 1447(1983).
25. I. A. VARSHAVSKII et al., Doklady Acad. Nauk SSSR, 118, 315(1958).
26. F. P. EVANS et al., "Permeation and Diffusion of Hydrogen Isotopes and Helium through Polymeric Materials," AWRE-O-45/63, Atomic Weapons Research Establishment, United Kingdom, 1963.
27. R. ASH, F. M. BARRER, and D. G. PALMER, Polymer, 11, 421(1970).
28. M. N. ALEKSEENKO et al., Radiats. Bezop. Zashch. AES, 4, 258(1980).
29. J. CRANK and G. S. PARK in Diffusion in Polymers, Academic Press, New York, 1968, p. 15ff.
30. P. E. ROUSE, Jr., J. Amer. Chem. Soc., 69, 1068(1947).
31. D. H. BODILY and M. DOLE, J. Chem. Phys., 45, 1433(1966).
32. E. J. LAWTON, J. S. BALWIT, and R. S. POWELL, J. Chem. Phys., 33, 405(1960).
33. S. OHMISKI et al., J. Polym. Sci., 47, 503(1960).
34. D. C. WATERMAN and M. DOLE, J. Phys. Chem., 74, 1906(1970).
35. K. YAHAGI and K. TAKAHASHI, Annu. Rep. Conf. Elec. Insul. Dielec. Phenomena, 38(1970).

36. N. DOLE, J. SAIK, and N. GVOZDIC, Fundam. Res. Homogeneous Catal., 3, 83(1979).
37. P.M.S. JONES, P. ELLIS, and C. G. HUTCHESON, "The Exchange of Hydrogen Isotopes between Methane and Erbium Tritide," AWRE-0-93/66, Atomic Weapons Research Establishment, United Kingdom, 1966.
38. H. N. MUELLER, "A Calculation of the Beta Energy Absorbed by Tritiated Gases in Spherical Vessels," LAMS-2580, Los Alamos National Laboratory, Los Alamos, NM, 1961.
39. Developing further the equation A4 of Reference 37:

$$F = \int_{\theta=0}^{\pi/2} \int_{r=0}^{r'/\cos\theta} \frac{E_0}{2} e^{-\mu r} \sin\theta \cos\theta \, dr d\theta =$$

$$\frac{E_0}{2\mu} \int_{\theta=0}^{\pi/2} \sin\theta \cos\theta \left(1 - e^{-\mu r'/\cos\theta}\right) d\theta,$$

which may be further integrated. Here,  $\theta$  is the angle from the surface toward its normal and  $r$  is the radial distance in tritium gas from the surface center, restricted to a maximum of  $r'/\cos\theta$  by the tube interior.

40. I. KAPLAN, Nuclear Physics, 2nd ed. Addison-Wesley, Reading, MA, 1963, pp. 346-353.
41. H. H. JAFFE and M. ORCHIN, Theory and Applications of Ultraviolet Spectroscopy, J. Wiley and Sons, New York, 1962, pp. 228,236.