Free radicals and new end groups resulting from chain scission: 1. γ-Irradiation of polyethylene

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Measurements of the concentrations of free radicals by electron spin resonance (e.s.r.) and of new chemical species by Fourier transform infrared spectroscopy (FT i.r.) were carried out on polyethylene specimens exposed to γ-irradiation at dosages from 3 to 50 Mrads both in the presence and absence of oxygen. The improved signal-to-noise capability of the FT i.r. method permitted a direct comparison of the free radical concentration and the resultant concentration of new chemical groups. It was found that approximately 10 carbonyl groups and 2 carbon–carbon double bonds were formed per free radical. These results are comparable with previous estimates and form the basis for an investigation of chemical species formed during mechanical deformation and fracture which will be discussed in the second paper of this series.

INTRODUCTION

It has been proposed that covalent bond rupture might be monitored by infrared (i.r.) spectroscopy[1–4]. This laboratory has monitored the molecular changes associated with deformation and failure in polymers by electron spin resonance (e.s.r.) spectroscopy[5–10]. When homolytic bond rupture occurs in a polymer, two unpaired free electrons (free radicals) result. If these free radicals are produced in sufficient numbers and are stable enough to accumulate to detectable contentrations, they should be amenable to study by e.s.r. These limitations have curtailed e.s.r. studies to selected systems for relatively short term tests ($\sim$1 h or less). It has been suggested that when chain rupture occurs, new end groups are formed that may be detected by i.r. spectroscopy, indeed such studies have been reported. It has been reported that each free radical recorded by e.s.r. may represent a large number of bond ruptures ($>10^3$). These suggestions have stimulated supplemental studies of bond rupture due to mechanical damage. For example, studies have been made in the change in molecular weight resulting from fracture in polymers[11,12]. We and others have also made attempts to duplicate the i.r. studies of fracture. The studies were not as simple or straightforward as we had initially assumed after our reading the report of the pioneering work[1]. In our efforts, we have found that there are many additional changes in structure besides chain scission, associated with deformation and fracture of the films. The sensitivity of i.r. to these other changes has made our determinations ambiguous. However, the potential of the method is so great we believe that it merits further attempts at development and refinement. If it could be used reliably, it would allow bond rupture studies in polymers where e.s.r. is not useful (e.g. where free radicals are too unstable) as well as the important area of long term loading and rupture in polymers. A major problem encountered in trying to determine the new end groups resulting from fracture has been the sensitivity of i.r. to factors other than chain scission. When one pulls a polymer to fracture, the sample thickness changes, the surface condition may change, crystallinity may change, there may be alterations in chain alignment, etc. I.r. spectroscopy is sensitive to all these factors. In principle, it should be possible to separate the changes in end groups from these other factors; however, in practice it is very difficult.

Consequently, we felt it would be useful to devise a less ambiguous experiment in which bonds might be ruptured while keeping other effects more nearly constant. Irradiation is such a treatment. While our primary goal was the development of a sound basis for fracture studies, we also felt that these studies should have some basic fundamental interest on their own. There have been previous i.r. studies on the effect of irradiation of polyethylene[3,13,14] including the investigation by Tabb *et al.*[3] using Fourier transform i.r. (Ft i.r.) difference spectroscopy. The studies reported here may be viewed as a confirmation and continuation of the study by Tabb *et al.*[3] However, they do have one important and unique feature, that the same sample was studied by both e.s.r. and FT i.r. techniques after irradiation. In our opinion, this provides the most direct comparison between the two techniques to date.

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Sample preparation

Samples were high density (linear) polyethylene. Most of the samples were Marlex 6009*. For purposes of comparison, a few samples were made of commercial grade PE. We were unable to detect significant differences in the e.s.r. spectra and i.r. spectra between the materials. Samples were prepared by solvent casting. The polyethylene was dissolved in toluene at 118°C in an open container and was held at this same temperature until the liquid had evaporated. This left a film 0.02–0.1 mm thick depending on the amount of polymer and solvent present. These thin films were then cut to size ($\sim 2.5 \times 2.5$ cm) and rolled into small cylinders.

Testing procedures

The small cylinders were then inserted into suprasil sample tubes. Some of the tubes were evacuated and sealed while others were sealed with the sample in the presence of air. A liquid nitrogen dewar was built into a foam container such that it could be reproducibly placed in the same location of a cesium 137 source. Series of samples were then irradiated at liquid nitrogen temperature and at room temperatures ($23 \pm 1°$). Radiation times were varied to produce integrated levels of 3 to 50 Mrads.

Previous experience has demonstrated that free radicals produced in polyethylene are very stable at liquid nitrogen temperature. Free radicals produced by γ-irradiation or mechanical means can, for example, be held at liquid nitrogen temperature for days with no detectable change in e.s.r. spectra. It is reasonable, therefore, to assume that the e.s.r. spectra of the samples irradiated at liquid nitrogen temperature would provide a direct measure of the homolytic bond rupture resulting from the irradiation. Accordingly, these samples were removed from the radiation source at varying predetermined dosage levels and maintained in liquid nitrogen while the ends of the sealed quartz sample tubes were successively heated to remove colour centres and their associated e.s.r. spectra. The e.s.r. spectra of irradiated polyethylene samples were recorded at a temperature of $-160°$C. The resulting spectra were then digitized, and with the aid of a computer, doubly integrated and compared to the 'Standard Pitch Sample' to obtain the concentration of free radicals in the sample. The sample was then allowed to warm, causing the free radicals to decay away in the same environment in which they had been irradiated. At this point, the quartz tubes were opened and the films unrolled and mounted on i.r. sample holders. The lapsed time between opening the quartz tubes and recording the i.r. spectra was sufficiently long so as to assure equilibrium concentrations of the chemical species which had been generated by irradiation[14]. In this way, we were able to obtain i.r. spectra on the same samples that had been previously investigated with e.s.r.

E.s.r. spectra were recorded on a Varian E-3 Instrument. Some i.r. spectra were made on a Perkin Elmer 467 dispersion type instrument located at the University of Utah. Most of the i.r. spectra were taken on Fourier transform instruments located at the National Bureau of Standards in Gaithersburg, Maryland (DIGILAB Model 15) and the DIGILAB Incorporated facility at Columbia, Maryland (DIGILAB Model 20).

Fourier transform i.r. (FT i.r.) not only has the advantage of greater sensitivity, but the computer provides for easy storage and manipulation of spectra. The most useful manipulation of stored spectra involves subtraction of the spectrum of an untreated sample from that of the irradiated or fractured specimens. Such a procedure accentuates the spectrum due to chemical changes associated with degradation of the polymer. Typically, 500 scans were averaged to obtain an FT i.r. spectrum.

Electron spin resonance results

As noted previously, a major goal in this study was to relate chain scission as observed by i.r. to that observed by e.s.r. with the aim of laying a sound basis for studying mechanical fracture by the combined technique. Easily detectable e.s.r. signals are obtained at irradiation levels much lower than can be detected by changes in the i.r. spectra. For example, the spectrum of *Figure* 1*a* is for a 20 mg sample irradiated at only 3 Mrad in air. This signal is several orders of magnitude above the threshold sensitivity of the e.s.r. spectrometer, e.g. both the receiver gain and sample mass could be increased by 1 or 2 orders of magnitude to observe much smaller concentrations of radicals. The spectrum shown in *Figure* 1*b* is for 50 Mrad. The gain for this spectrum was decreased by a factor of 0.064 compared to that of *Figure* 1*a* while the ratio of irradiation dosages was 0.06. *Figures* 2*a* and 2*b* are similar curves for samples irradiated in vacuum, where the gain of the spectrum in *Figure* 2*b* is 0.1 of the spectrum shown in *Figure* 2*a*. In all these spectra, the spectrometer was at a power level of 1.25 mW, a field modulation of 10 gauss, a sweep time of 8 min and a time constant of 0.1 s. The spectra, such as those of *Figures* 1 and 2, were then analysed with the aid of a computer to yield the number of free radicals present in the microwave cavity. The samples were weighed and, with the above results, used to determine the radical concentration. This concentration of free radicals as a function of irradiation dosage is shown in *Figure* 3 for samples irradiated at 77K in air and vacuum. The free radical concentration appears to be quite linear with dosage with the possible exception of the data point for 37 Mrad in air. Similarly, as we shall see, the infrared measurements for this sample also falls off the linear plot in the same fashion.

Infrared results

Infrared measurements were carried out on polyethylene films which had been irradiated to achieve dosages from 3–50 Mrad either in a vacuum or in the presence of air at both room temperature and 77K. The infrared measurements were performed at room temperature in dry air or nitrogen. *Figure* 4 shows a comparison of the i.r. spectra taken on the dispersive instruments for the reference (unirradiated) and the specimen irradiated at 50 Mrad. These spectra illustrate one of the difficulties in using dispersive i.r., that is, even for samples with high irradiation levels, only

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* Certain commercial materials and equipment are identified in this paper in order to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply necessarily the best available for the purpose

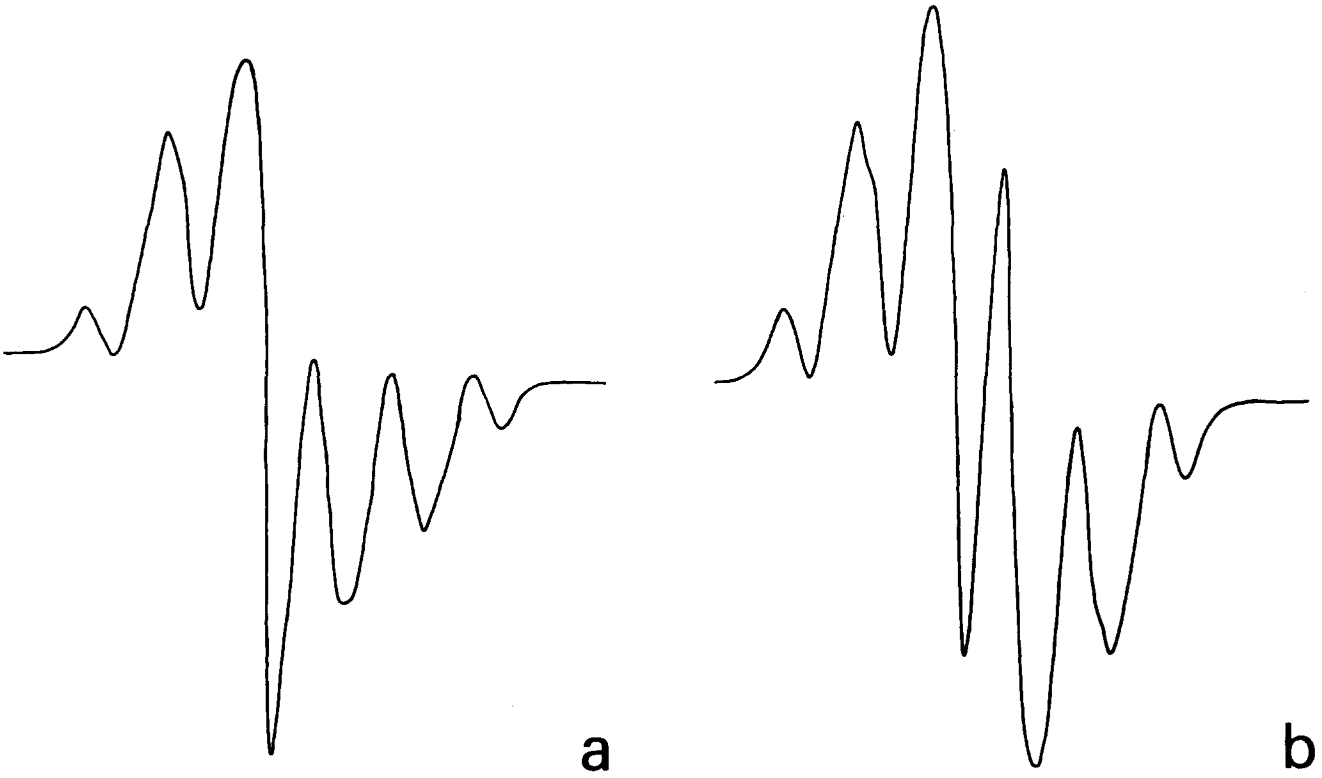

Figure 1 E.s.r. spectra for polyethylene irradiated in air at 77K (a) 3 Mrad, (b) 50 Mrad with instrument gain 0.064 of the value used to record (a)

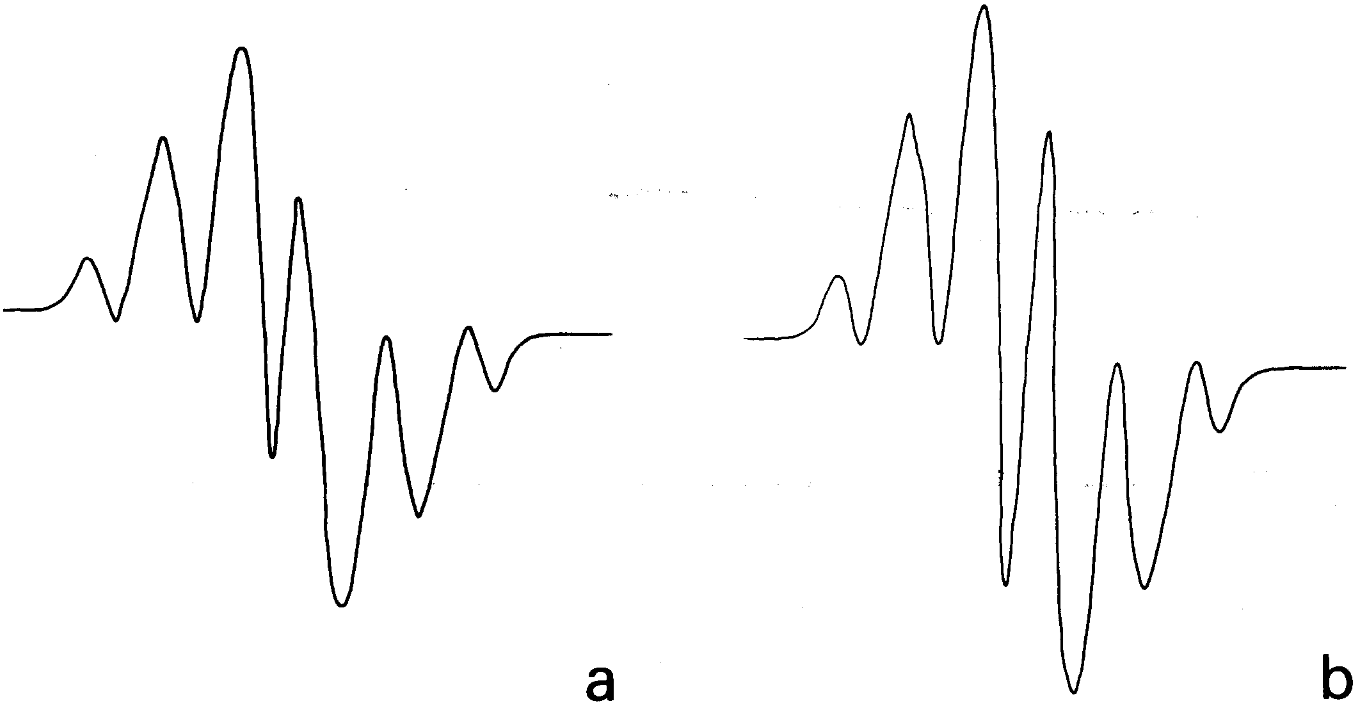

Figure 2 E.s.r. spectra for polyethylene irradiated in vacuum at 77K (a) Mrad, (b) 50 Mrad with instrument gain 0.1 of the value used to record (a)

the absorption band at 1716 cm^{-1} clearly shows a change in transmission level. Despite our efforts to enhance other spectral changes they were, at best, obscure, making it difficult to obtain quantitative results. The extent of spectral changes detectable by FT i.r. for films irradiated in air or in a vacuum at room temperature can be seen in *Figure* 5 by comparing the top two spectra with that of the reference sample shown at the bottom. The most prominent spectral variation in the 50 Mrad air spectrum is the band near 1700 cm^{-1} which has been assigned to $C=O$ stretching mode of carbonyl groups. The appearance of this band in the 50 Mrad vacuum spectrum is probably due to oxidation as a result of trapped oxygen. *Figures* 6 and 7 show comparisons of the 50 Mrad, 77K spectra with that of the reference spectrum. The experimental procedure was to allow the specimens which had been irradiated at 77K in a vacuum to warm to room temperature before exposing the samples to atmospheric oxygen. In addition to the spectral changes near 1700 cm^{-1}, there are readily discernible alterations in the frequency range 900–1000 cm^{-1} and near 1650 cm^{-1}. These spectral features are associated with vibrations of carbon–carbon double bond groups[15].

Small spectral variations are accentuated in difference spectra, an example of which is shown in *Figure* 8. All spectral variations are summarized in *Table* 1 where comparison is made with previous results. We find general agreement with prior results except for previously reported changes in the region between

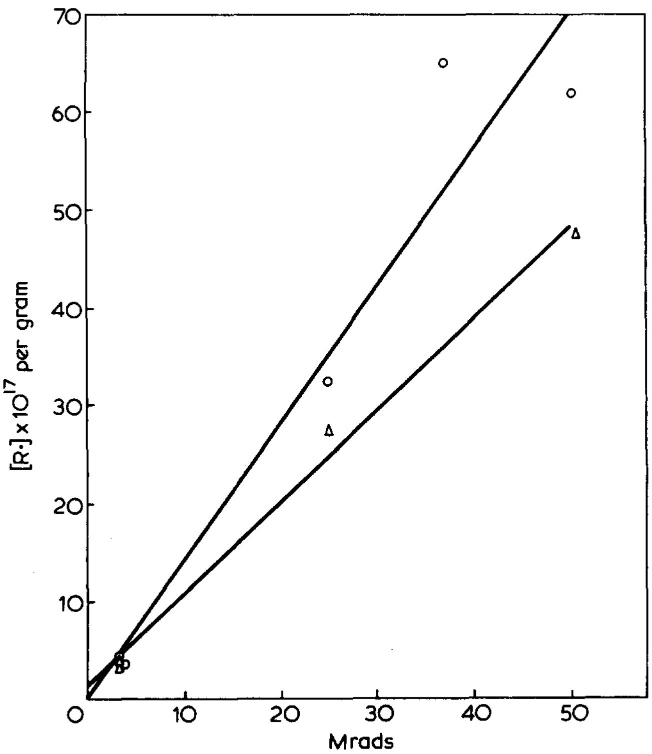

Figure 3 Free radical concentration as a function of irradiation dosage under the following conditions: ○, in air at 77K; and △, in vacuum at 77K

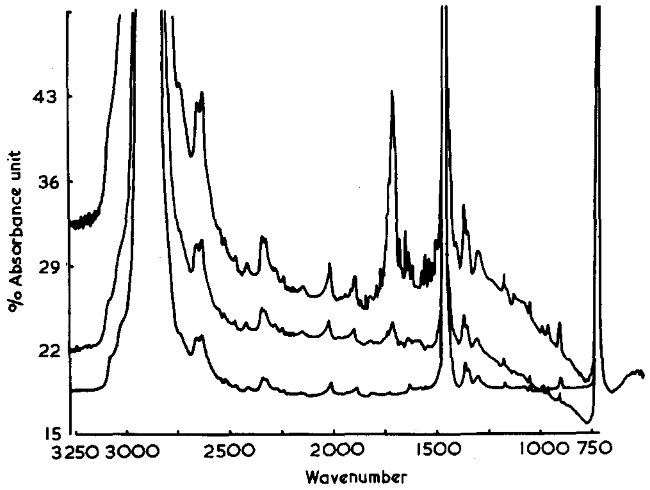

Figure 5 FT i.r. spectra of irradiated polyethylenes: top trace – 50 Mrad at room temperature in air; middle trace – 50 Mrad at room temperature in a vacuum, and reference polyethylene: bottom trace

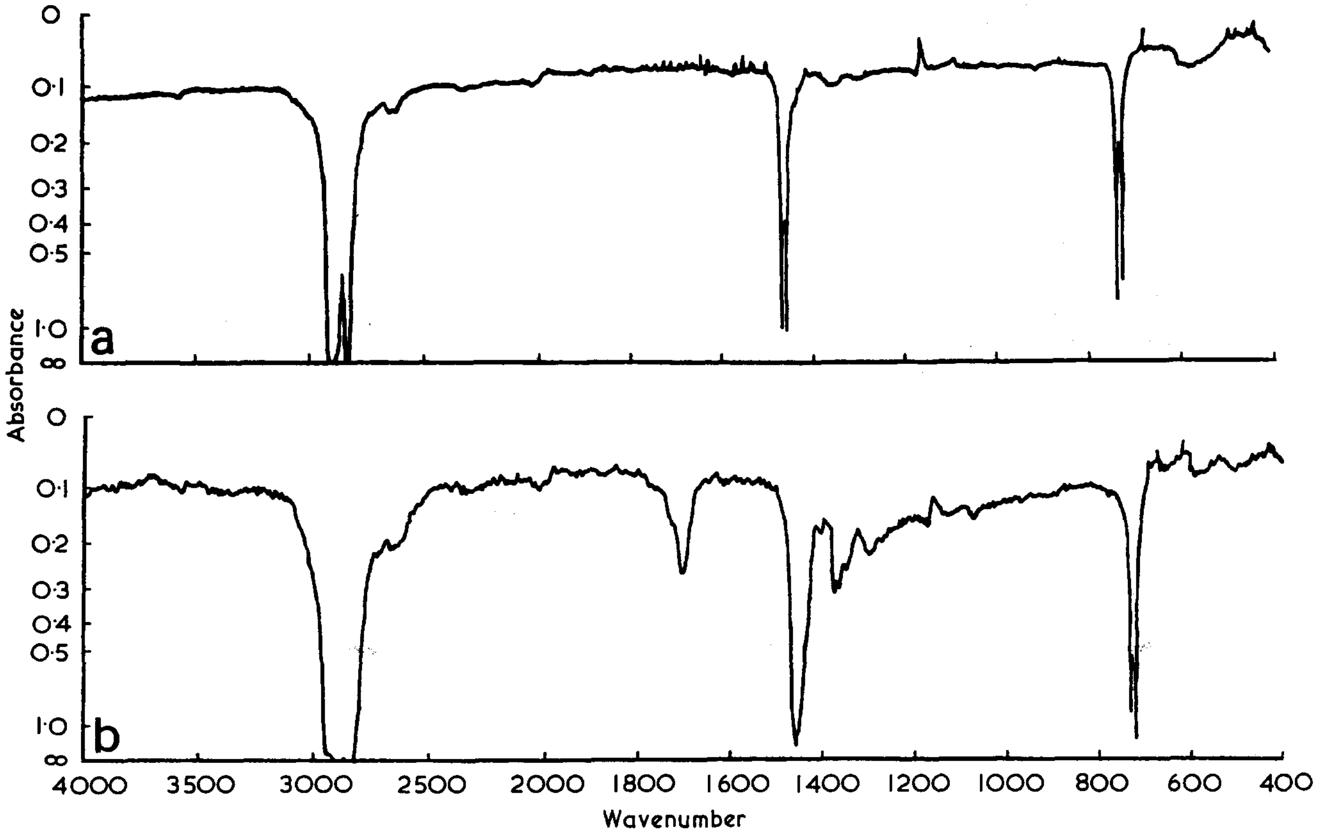

Figure 4 Dispersive i.r. transmission spectra of polyethylene (a) Reference, (b) Sample irradiated in air at room temperature to a dosage of 50 Mrad

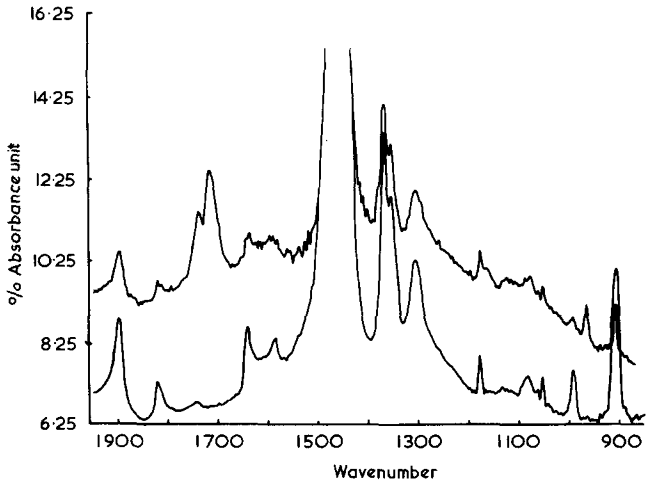

Figure 6 Comparison of FT i.r. spectrum between 800–2000 cm^{-1} of polyethylene irradiated to a dosage of 50 Mrad at 77K in a vacuum (top trace) to the reference polyethylene spectrum (bottom trace)

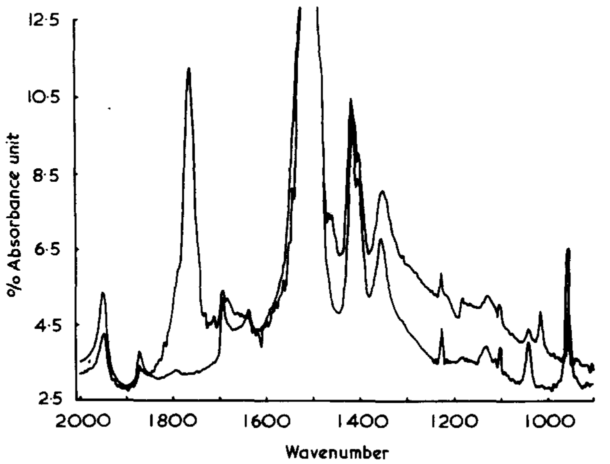

Figure 7 Comparison of FT i.r. spectrum between 800–2000 cm^{-1} of PE irradiated to a dosage of 50 Mrad at 77K in air (top trace) with the spectrum of reference PE (bottom trace)

1300–1450 cm^{-1} which we have not observed, presumably because of larger i.r. absorbancies in our specimens due to greater film thicknesses. The band assignments in *Table* 1 are those of Tabb, Sevcik and Koenig[3].

Our aim was to determine the number of specific chemical groups formed during irradiation and to correlate these findings with the e.s.r. measurements. Plots of the absorbance of the 1710 cm^{-1} band for each of the four different experimental conditions (two temperature and two environment, i.e., air and vacuum), as a function of the dosage is shown in *Figure* 9. Note that in the absence of air, these absorbancies appear to reach a limiting value between 25 and 50 Mrad and in the case of the room temperature samples, may actually decrease. By contrast, the number of free radicals increases much more linearly throughout the dosage range covered by these experiments. We will make our comparisons for the low temperature specimens on which free radical concentrations can be observed by e.s.r.

In order to convert the changes in i.r. band absorbancies to concentration differences of certain chemical species we use the Lambert–Beer Law,

$$\int \Delta A_v \mathrm{d}v = l \Delta c \int \varepsilon_v \mathrm{d}v \qquad (1)$$

where ΔA_v is the absorbance difference at v between the treated specimen and the reference sample, ε_v is the molar extinction coefficient at v, l is the specimen thickness in cm, and Δc is the concentration difference expressed as mol l^{-1}. In using Equation 1 we have assumed that the film thickness of the treated and reference materials is the same. Generally, these thicknesses differ and ΔA_v in Equation 1 is modified to

$$\Delta A_v = A_v^t l^r / l^t - A_v^r \qquad (2)$$

by multiplying the absorbance spectrum of the treated specimen by the ratio of the sample thickness of the reference film to that of the treated specimen film, l^r/l^t. With this treatment, the thickness, l, in Equation 1 is that of the reference specimen film. The spectral effects introduced by orientation in drawing leading to fracture need not be considered when the sample treatment is that of irradiation. An alternate procedure for arriving at the concentration difference, Δc, involves adaptation of a suitable internal standard i.r. band which is dependent only on the amount of material intercepting the i.r. beam. Apparently, no such band exists for polyethylene[3]. In absence of an internal standard band, the adopted procedure has been to treat the ratio of the sample film thicknesses as a parameter which is adjusted until a number of preselected bands in the difference spectrum disappear. These bands are selected on the assumption that the molecular vibration and its associated i.r. extinction coefficient are unaffected by the sample treatment. We have used this latter method as well as the more direct

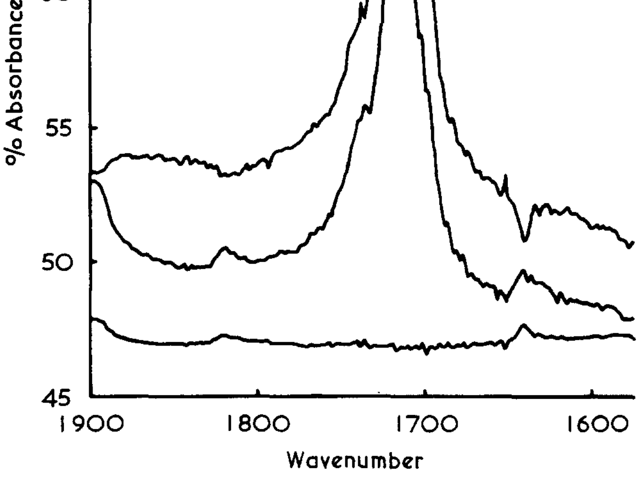

Figure 8 Difference spectra in the carbonyl stretch region: bottom trace, reference polyethylene; middle trace, 50 Mrad dosage in air at room temperature; top trace, difference spectrum

Table 1 Spectral variations associated with irradiation of polyethylene

Frequency (cm^{-1})	Assignments*	i.r. intensity Changes†				
		TSK*	O_2/RT	O_2/LN_2	VAC/RT	VAC/LN_2
1742	$R-\overset{\overset{O}{\|}}{C}-H$ ν(C=O)	–	U	U	U	+M
1716	$R-\overset{\overset{O}{\|}}{C}-R'$ ν(C=O)	+	+VL	+VL	+M	+M
1642	$R-C{=}CH_2$ ν(C=C)	–	–M	–M	–S	–M
1410	$R-CH_2-\overset{\overset{O}{\|}}{C}-CH_2R'$ δ(CH$_2$)	+	+S	+S	O	O
1378	$R-CH_3$ δ(CH$_3$)	+	+VS	U	U	U
1368 1353 1308 1261	$\gamma_w(CH_2)$–amorphous phase	–	ND	ND	ND	ND
1131	ν(C–O)	+	+VS	S	S	O
1068	ν(C–O)	+	O	O	O	O
991	$R-CH{=}CH_2$	–	U	–M	–M	–M
965	trans $R-CH{=}CH-R'$	+	+M	+M	+M	+M
909	$R-CH{=}CH_2$	–	–S	–M	–M	–M
806	amorphous phase	–	ND	ND	ND	ND

* Tabb, D. L., Sevcik, J. J., Koenig, J. L., ref 3

† O_2/RT, irradiated in air at room temperature; O_2/LN_2, irradiated in air at 77K; VAC/RT, irradiated in vacuum at room temperature; and VAC/LN_2, irradiated in vacuum at 77K. Magnitude of intensity changes: VL, very large; M, medium; S, small; VS, very small; U, unchanged; ND, not determined; O, obscured by near-by bands

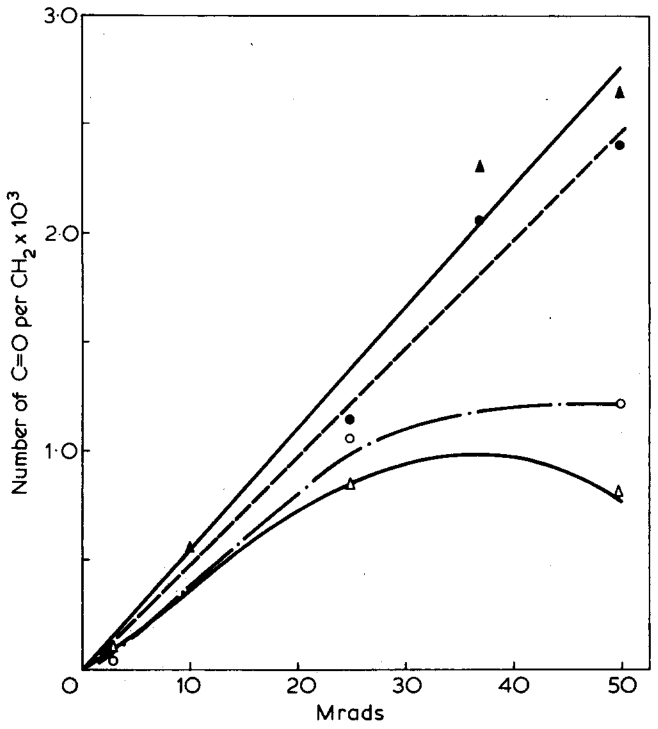

Figure 9 Plot of number of carbonyl groups formed as a function of irradiation dosage under the following conditions: ▲, in air at room temperature; ●, in air at 77K; △, in vacuum at room temperature; and ○, in vacuum at 77K

method illustrated by Equation 2 to arrive at values for the concentration differences. Generally, we find better overall consistency when we use the ratio of sample film thicknesses rather than a parameter value determined by the disappearance of a somewhat arbitrary selection of i.r. bands.

Table 2 Carbonyl concentration in irradiated polyethylene

Sample*	Number of $C{=}O/CH_2$	Number of radicals	Number of C=O/ radical
50 Mrad/O_2	$2.4 \pm 0.3 \times 10^{-3}$	$7 \pm 2 \times 10^{18}$	15 ± 6
50 Mrad/Vac	$1.2 \pm 0.2 \times 10^{-3}$	$4.8 \pm 1 \times 10^{18}$	11 ± 4
3 Mrad/O_2	$1.2 \pm 0.4 \times 10^{-4}$	$4.5 \pm 1 \times 10^{17}$	11.5 ± 6
3 Mrad/Vac	$3 \pm 2 \times 10^{-5}$	$3.9 \pm 1 \times 10^{17}$	3 ± 3

* All samples were irradiated at 77K

Concentration of carbonyl groups in irradiated polyethylene

The concentration of carbonyl groups in irradiated specimens of polyethylene were determined from integrated absorption band intensities and Beer's law (Equation 1). The values for the integrated absorption coefficient of both aldehyde and ketone groups were taken from published work[15] on acetaldehyde and acetone. Since the measured value as well as the calculated value of the integrated absorption coefficient for the carbonyl stretching mode in acetaldehyde is nearly identical to that for acetone, we carried out the integration procedure over both bands and determined the number of carbonyl groups. These values are tabulated in *Table* 2 and compared with the e.s.r. measurements of free radical concentrations.

Concentration of carbon–carbon double bonds in irradiated polyethylene

Carbon–carbon double bonds give rise to a number of i.r. bands, the most useful, of which for our purposes, are in the frequency range 900–1000 cm^{-1}. The corresponding modes consist of CH out of plane deformation which occurs at 965 cm^{-1} for the trans

Table 3 Trans vinylene double bond concentrations in irradiated polyethylene

Sample*	Number of R—CH=CH—R′/ CH_2	Number of radicals	Number of P—CH= CH—R′/ radical
50 Mrad/O_2	$4.3 \pm 0.9 \times 10^{-4}$	$7 \pm 2 \times 10^{18}$	2.6 ± 1.3
50 Mrad/Vac	$2.6 \pm 0.6 \times 10^{-4}$	$4.8 \pm 1 \times 10^{18}$	2.3 ± 1
3 Mrad/O_2	$1 \pm 0.5 \times 10^{-5}$	$4.5 \pm 1 \times 10^{17}$	1.0 ± 0.7
3 Mrad/Vac	$5 \pm 2 \times 10^{-5}$	$3.9 \pm 1 \times 10^{17}$	5.4 ± 3.5

* All specimens were irradiated at 77K

R–CH=CH–R′ group and at 993 cm^{-1} for the RCH =CH_2 group and of CH_2 wag of the RCH=CH_2 group which is found at 908 cm^{-1}. From *Figure* 9 we see that there are no detectable trans vinylene groups (R–CH=CH–R′) in the reference polyethylene whereas terminal carbon–carbon double bonds (R–CH=CH_2) are clearly evident. The spectral results for irradiated polyethylene, *Figure* 7, indicate, in agreement with previous results, that the concentration of the R–CH =CH_2 groups decreases while the number of R–CH =CH–R′ groups increases with dosage. The changes in concentration of the trans vinylene carbon–carbon double bonds are summarized in *Table* 3 where we have used integrated intensity values from mono-olefins[16] to convert bond intensities into number of double bonds.

DISCUSSION AND CONCLUSIONS

The results presented in the previous two sections provide a direct method for comparing infrared and e.s.r. measurements on the same samples of irradiated polyethylene. Overall, the e.s.r. data were found to be linear with dosage whereas the i.r. determined concentrations of carbonyl groups were found to be linear with dosage only for specimens irradiated in the presence of air. The specimens which were irradiated in vacuum did not follow a linear relationship with dosage. In both e.s.r. and i.r. measurements, the specimens irradiated in air gave higher values, although only slightly higher e.s.r. results whereas the i.r. changes were dramatically higher.

As shown in *Tables* 2 and 3, there is not exactly a one-to-one correspondence between the number of e.s.r. radicals produced and the number of resultant chemical groups as measured by i.r. This result was found for both carbonyl groups and for vinylene double bonds. Within the accuracy of these experiments, it appears that there were approximately ten carbonyl and two trans-vinylene groups detected by i.r. for each radical that was detected by e.s.r. Analyses of the plausible reaction paths subsequent to production of free radicals may lead to an understanding of the larger number of chemical groups formed than free radicals produced. An unstable free radical may react to form stable molecules by any one of the following paths:

(1) Two free radicals may recombine to form the same molecule or a similar molecule
(2) Formation of interchain crosslinks or intramolecular cyclization reactions
(3) Formation of unsaturated groups, methyl groups, ketones, aldehydes, etc.

It is expected that the first of these would occur only at very high free radical concentrations where the probability of two radicals interacting is high. End products of the first reaction pathway are not detectable by i.r., however, the apparent fall off in the number of carbonyl groups with dosage, *Figure* 9, may be attributable to this free radical decay mechanism. Mechanism (2) also produces end products which are undetectable by i.r. at least at the concentration levels which can be observed for carbonyl groups and carbon–carbon double bonds. Crosslinking occurs in irradiated polyethylene[17] and the G value (the number of a particular species produced per 100 eV of irradiation energy absorbed) for crosslinking is equal to or slightly higher than the value for carbon–carbon double bond formation[17–19].

The infrared results show clearly that chemical groups of the sort indicated under the third mechanism are found. Even though mechanisms (1) and (2) probably account for some free radicals, we find more carbonyl and vinylene groups formed than could be accounted for by experimental errors. Similarly, in infrared studies of fracture, it has been reported that more chemical groups are formed than radicals produced (as much as a thousand-fold increase in certain chemical species over the number of free radicals[1].) The results of this study for irradiated polyethylene suggest mechanisms in which the number of structural changes detected by i.r. is greater than the number of free radicals detected by e.s.r. Analysis of the results reported in *Tables* 2 and 3 indicates that they may differ by as much as an order of magnitude. The details of the reaction mechanisms of irradiation of the free radical produced are discussed in some of the references (e.g. 13–20). Our present aim is to illustrate the combined e.s.r.–FTi.r. technique and lay a firm basis for exploring new end groups in the concentration range anticipated for mechanical fracture. Since this work is to be the basis for fracture studies, it is appropriate to point out differences between the bond rupture mechanisms. In mechanical fracture, one might anticipate the primary chemical reaction to be chain scission, while γ ray irradiation of the sort used in the present study should break any bond with which it interacts. Hydrogen extraction would probably dominate in this latter case. The authors feel that the single most important observation of this part of the study is that FTi.r. can be used to detect the types and concentrations of chemical changes anticipated during mechanical damage leading to fracture. The second paper in this study will describe observation of molecular structural changes resulting from mechanical chain scission and fracture.

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