Nature of the side chain branches in low density polyethylene: volatile products from gamma radiolysis

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Measurements of the yields of low molecular weight hydrocarbons after γ-irradiation of low density polyethylene (LDPE) in the solid and liquid phases have confirmed that the main products are ethane and butane. Alkene yields were small, contrary to some previous reports. Irradiation at 150°C doubled the total yield of hydrocarbons, but the relative proportions of different hydrocarbons did not change markedly. The compatibility of these results with ^{13}C n.m.r. determinations of the distributions of short chain branches in the same samples of LDPE is considered.

INTRODUCTION

Polyethylene is a generic name given to a variety of polymers in which gradations in crystallinity, density and related properties depend on the frequency of short chain branches[1]. There may be up to 50 short branches per 1000 main chain carbon atoms and also up to 5 long branches, the latter affecting mainly the molecular weight distribution and the rheology of the polymer[2]. It is generally accepted that the long branches are formed by intermolecular hydrogen atom abstraction between growing polymer chain radicals and 'dead' polymer molecules[3]. However, the formation and nature of the short branches are still matters of controversy.

The presence of branches in low density polyethylene (LDPE) produced by the high pressure polymerization of ethylene was deduced from the intensity of the methyl vibration at 2960 cm^{-1} (3.38 μm) in the infra-red spectrum by Fox and Martin[4] and their frequency determined by Cross et al.[5] and Bryant and Voter[6] using the 1378 cm^{-1} (7.26 μm) methyl absorption with suitable corrections for overlapping methylene absorptions. The branches were postulated to be n-butyl groups by Roedel[7], who proposed an intramolecular hydrogen atom abstraction reaction (back-biting) involving a 6-membered cyclic transition state. Willbourn[8] subsequently resolved two small peaks at 745 and 770 cm^{-1} in the infra-red spectrum and attributed them to butyl and ethyl branches, respectively. He deduced that the branches were 67% ethyl and 33% butyl and proposed a secondary intramolecular hydrogen atom transfer reaction to form ethyl branches.

Wilbourn's infra-red analysis has been supported by a number of measurements of the composition of the volatile products from the radiolysis of polyethylene[9–20]. The main product is hydrogen, but hydrocarbon yields from 2 to 15% have been reported, comprising mainly C_2 and C_4 with smaller amounts of C_1, C_3, C_5, C_6 and C_7. Yields of alkenes have been claimed up to 350% of the corresponding alkanes. The hydrocarbons have been attributed to elimination of entire branches; and the high specificity of C–C scission at the branch points has been proposed on the basis of product yields from the radiolysis of branched polymethylenes[12] and ethylene–α-olefin copolymers[20]. Boyle et al.[17] deduced that there was a distribution of branch lengths in LDPE with maxima at C_4 and C_2, but Kamath and Barlow[20] determined the branches to be ethyl and butyl in the ratio 2:1 in exact agreement with Willbourn, attributing the other hydro-

carbon products to C–C cleavage at the ends of the main chains.

Seeger and Barrall[21] have analysed the pyrolysis products from HDPE, LDPE and various copolymers. C–C fracture occ.rred in a pattern attributed to 6-membered, cyclic transition states and from the distribution of isoalkane yields they also deduced the presence of ethyl and butyl branches in LDPE in the ratio 2:1.

Recently, ^{13}C n.m.r. studies by Randall[22] and Bovey et al.[23,24] have indicated that the branches are mainly n-butyl, with some n-amyl and only about 10% ethyl. In particular, Bovey concluded that 2-ethyl hexyl and pairs of ethyl branches, which would result from Willbourn's double back-biting mechanism[8], were not present. ^{13}C n.m.r. spectra of a variety of LDPE samples obtained by Cudby and Bunn[25] indicated that the branch length distribution may vary, but confirmed the predominance of butyl branches. However, they suggested that a significant proportion of the ethyl branches could be in pairs or possibly 2-ethyl hexyl structures as required by the double back-biting mechanism[8].

The apparent incompatability of the ^{13}C n.m.r. and radiolytic results is a matter of serious concern and in this paper we report a re-examination of the radiolysis products from two polyethylene samples of different density, and a comparison with the branch length distributions deduced from ^{13}C n.m.r. spectra of the same samples. In particular, (a) gas chromatographic analysis was used to determine absolute product yields and to separate alkenes from the corresponding alkanes; (b) the glass ampoules containing the irradiated polymer samples were heated and crushed in the inlet of the gas chromatograph to ensure quantitative detection of products volatile at 150°C; (c) the polymers were irradiated in the solid and liquid phases in order to detect any differences in the relative proportions of different hydrocarbon products due to varying crystalline content.

EXPERIMENTAL

Polymers and characterization

Two low-density polyethylenes (LDPE-I and LDPE-II) produced by a high pressure process (ICI) were selected for investigation, LDPE-II having a lower density and molecular weight than LDPE-I. The polymers were characterized by density with a density gradient column[26] and total branch content (methyl group concentration from infra-red spectra
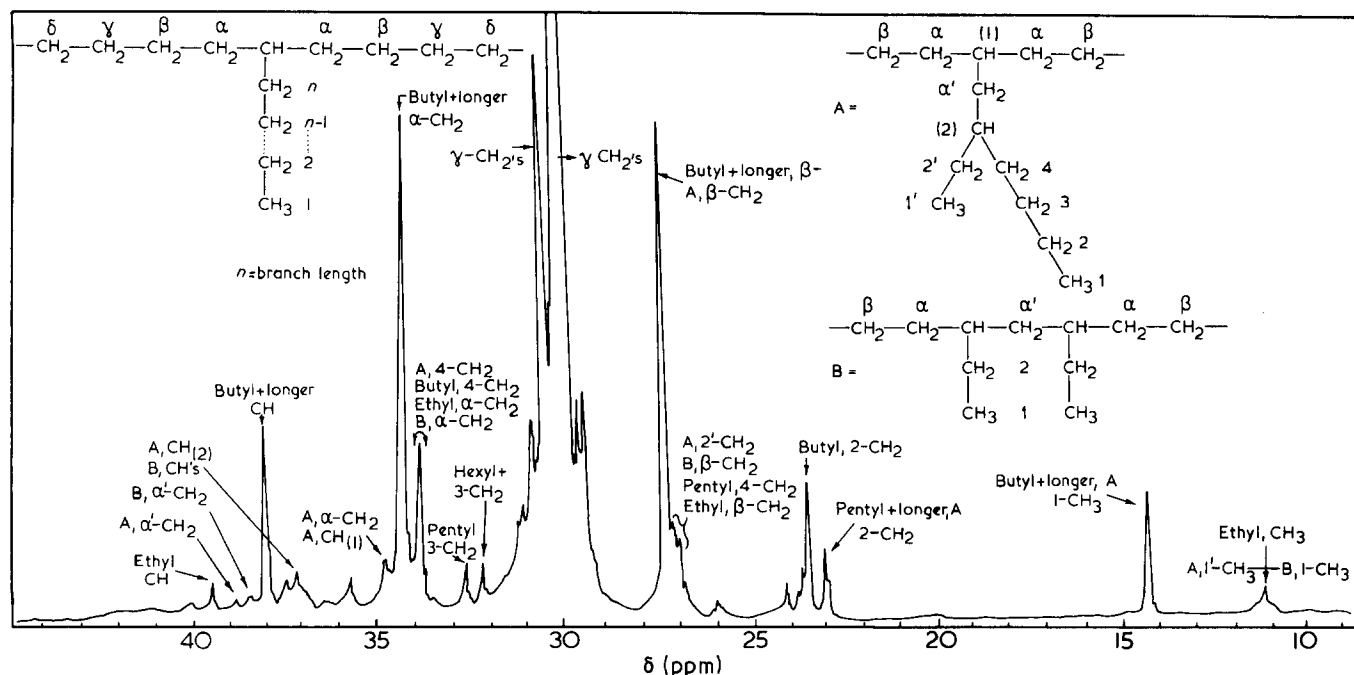
Figure 1 $^{13}C-\{^1H\}$ n.m.r. spectrum of 20% solution of LDPE-II in trichlorobenzene

Table 1 Polymer characterization

Polyethylene	$\bar{M}_v$ (g/mol)	Main chain ends per 1000 C atoms	Density (g/cm^3)	CH$_3$/1000 C atoms from i.r.	Branches/1000 C atoms	
					From ^{13}C n.m.r.	From i.r.
LDPE-I	55 000	4	0.919	30.5	15	27
LDPE-II	18 500	10	0.909	40	22	31
HDPE	90 000	2.1	0.972	3.3	—	1.6

at 1378 cm^{-1} using pressed films[6]. Solution viscosities were measured in decalin at 70°C with phenyl-α-naphthylamine as antioxidant and $\bar{M}_v$ found from[27]:

$$[\eta] = 3.87 \times 10^{-2}\bar{M}_v^{0.738} \text{ cm}^3/\text{g}$$

^{13}C–$\{^1$H$\}$ n.m.r. spectra of the LDPE samples were obtained in trichlorobenzene at 100°C with a Bruker HX-130 spectrometer (67.89 MHz) and were similar to those reported by Randall[22] and Bovey *et al.*[23,24]. The pulse width was 18 μsec and the pulse interval 1.0 or 5.0 sec. The spectra were collected over approximately 30 000 scans with the protons decoupled from the carbon nuclei using a random noise decoupling field. Hexamethyldisiloxane (HMDS) was employed as internal reference (2.0 ppm vs. TMS). Dimethylsulphoxide-d_6 provided the deuterium lock signal.

The ^{13}C n.m.r. spectrum of LDPE-II is shown in *Figure 1*; the spectrum of LDPE-I was similar, but resolution was not as good due to the lower concentration of polymer as a result of its higher molecular weight. Details of the polymers are given in *Table 1*. A high density Ziegler polyethylene (HDPE) was also studied as a relatively unbranched reference polymer.

Sample preparation and irradiation

Large (0.5–2.5 g) samples of polyethylene were evacuated (50 h, 10^{-2} Pa, some samples heated to 100°C) and sealed in radiolysis tubes (15 mm diameter × 175 mm) with breakseals.

Heating the polymer during evacuation had no effect on the product yields. Therefore, pre-irradiation evacuation for 50 h at ambient temperature was considered sufficient to out-gas polymer samples. Small (5–35 mg) samples were evacuated and sealed in thin-wall glass ampoules (4 mm diameter × 35 mm).

The polymers were irradiated with γ-rays in the ^{60}Co pond facility of the Australian Atomic Energy Commission (2 Mrad/h) and in a Gammacell (0.5 Mrad/h) using Fricke dosimetry[28] with G(Fe^{3+}) = 15.5 and the correction factor of dose (PE) = 1.028 × dose (Fricke)[29]. Ceric dosimetry[30] was also used for the 2 Mrad/h radiation. Irradiations were at ambient temperature (25°C at 0.5 Mrad/h and 30°C at 2 Mrad/h) and at 150°C using an aluminium block heater.

Volatile product analysis

The large samples were heated at 150°–200°C for 60–90 min and the total volatile product yield measured in a gas burette. The components were then analysed by injection into a gas chromatograph via a loop on the gas burette. The small ampoules were inserted into a modified inlet system on the gas chromatograph, heated at 150°–200°C and the ampoule crushed by a plunger (*Figure 2*).

The H$_2$ was measured with a Poropak Q column at 90°C using a thermal conductivity detector and the hydrocarbons analysed with the same column, a flame ionization detector and temperature programming from 80° to 200°C. Nitrogen was used as carrier gas for both procedures. Alkane/alkene
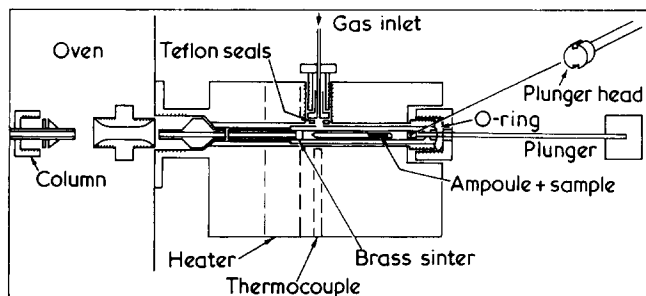
Figure 2 Ampoule injection system for gas chromatograph

Table 2 Retention of hydrocarbon radiolysis products in LDPE-I without post-irradiation heating

Hydrocarbon	Retained in irradiated polymer (%)
C_1	1
C_2	5.9
C_3	17.9
C_4	43.4
C_5	71.5
C_6	86.1
C_7	95.4
C_8	100
$>C_8$	100

ratios were checked by using a molecular sieve 5A column which gave enhanced separations. The identities and yields of the individual products were determined by calibrations with pure compounds.

Radical scavenging

The radical species formed on irradiation of polyethylene were investigated using iodine as a radical scavenger. Iodine concentrations of 0.001–0.005 M, which have been found suitable for alkanes[31,32], were used in irradiations of small ampoules at 150°C. The alkyl iodides were analysed by gas chromatography on a silicone QF-1/Chromosorb column programmed from 80° to 200°C.

RESULTS

Sample treatment

Post-irradiation heating above the melting point of the polymer was found to be essential to release all the volatile products from the irradiated polyethylene samples. Typical values for the proportions of different hydrocarbon products retained by the polymer in the absence of post-irradiation heating are shown in *Table 2*. Trial experiments showed that post-irradiation heating at 150°C for 60 min was sufficient to release more than 98% of the gaseous products.

Volatile product yields

The dose dependence of the product yields is illustrated in *Figure 3*. Linearity in hydrogen yields and decreasing rates of hydrocarbon production were observed for the three polymers at both temperatures.

The volatile product yields from the three polyethylenes at 25°–30°C and 150°C are shown in *Figures 4–6* as abso-

lute *G* values (number of moles per 16 aJ (100 eV) of energy absorbed).

Hydrocarbons up to C_{10} were detected for all three polyethylenes. Both alkenes and alkanes were present, but the alkene yields were small (usually 1–3% of the corresponding alkane). Ethane and n-butane were the major products from both LDPE samples. Hydrocarbon yields were approximately doubled for irradiation at 150°C compared to 25°C. The
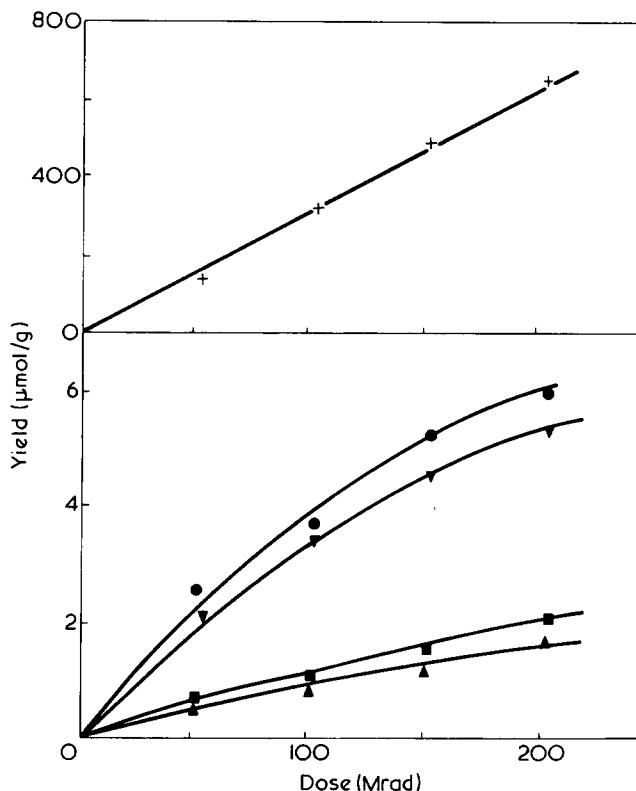

Figure 3 Dose dependence of volatile products: +, H_2; ■, CH_4; ●, C_2H_6; ▲, C_3H_8; ▼, C_4H_{10}
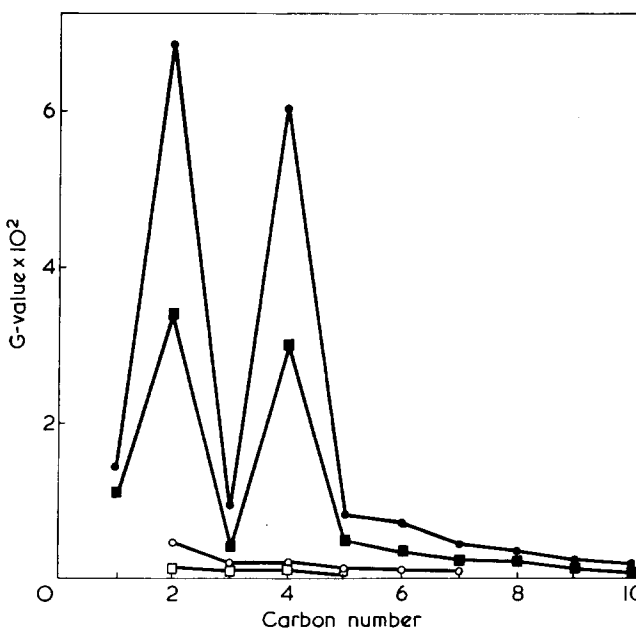

Figure 4 Yields of hydrocarbon radiolysis products from LDPE-I Irradiations at 150°C: ●, alkanes; ○, alkenes. Irradiations at ambient temperatures: ■, alkanes; □, alkenes
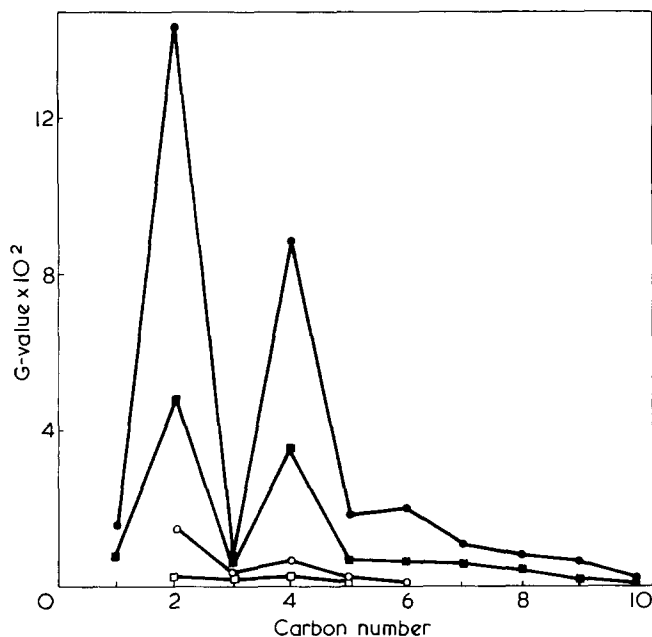
Figure 5 Yields of hydrocarbon radiolysis products from LDPE-II; symbols as in *Figure 4*
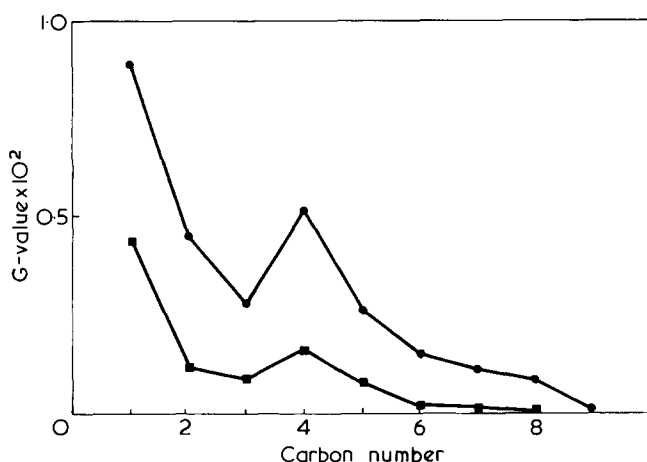

Figure 6 Yields of hydrocarbon radiolysis products from HDPE, symbols as in *Figure 4*, alkenes < 1% alkanes

These observations indicate that the low mobility of the iodine and the radicals in the highly viscous polymer melt at $150°C$ prevents effective scavenging at these concentrations. Non-scavengable reactions may also occur.

^{13}C n.m.r. analysis

Using the parameters of Lindeman and Adams[33] we have calculated the ^{13}C--$\{^1H\}$ n.m.r. spectra to be expected for a variety of branch structures. These predictions and the spectra reported for ethylene–α-olefin copolymers[22,23] were used to determine the assignments in our ^{13}C n.m.r. spectra (*Figure 1*). Quantitative branch distributions were then obtained for LDPE-I and LDPE-II by defining the intensities (areas) of the resonances algebraically[22] in terms of the branch type, and solving by a least squares analysis. The methyl carbon resonances showed a greatly decreased sensitivity compared with the other carbon resonances for a pulse interval of 1.0 sec and were not used in the analysis of these spectra. This phenomenon is also evident in spectra published by other workers[22]. It is attributable to different relaxation times of carbon atoms in different environments and could be overcome by using a pulse interval of 5 sec.

In both polymers n-butyl branches were found to predominate. Resonances attributable to branch structures resulting from the double back-biting mechanism[8] (i.e. pairs of ethyl branches and 2-ethyl hexyl branches) were seen at 38.88, 38.4, 37.4, 37.0 and 34.8 ppm. The other resonances from these structures (determined by the use of the Lindeman and Adams[33] parameters) coincide with the more intense resonances of other structures (e.g. butyl branches and main chain carbon atoms). The resulting branch distributions are given in *Table 6*.

DISCUSSION

Comparison of results from small ampoules and large tubes

The technique of irradiating a small sample of polymer (<50 mg) in an ampoule which is heated and crushed in the inlet of the gas chromatograph was shown to be more satisfactory than the gas-burette technique, which requires larger samples and radiation doses.

The lower yields of H_2 found with large samples (*Table 3*)

yields from LDPE-II were approximately 40% greater than from LDPE-I which were an order of magnitude greater than the yields from HDPE. Total product yields are given in *Table 3* and representative hydrocarbon values in *Table 4*.

Radical scavenging

A wide variety of alkyl iodides were detected by scavenging free radical intermediates with iodine in the liquid phase at $150°C$ and the yields are given in *Table 5*. The alkyl iodide yields showed an inverse relationship with the size of the alkyl radical. Also, there was a distribution of isomers (primary, secondary, etc.). This is more likely to result from rearrangement of primary alkyl radicals before reaction with iodine than the direct production of these radicals from radiolytic scission of C–C bonds in the LDPE. Only about 15% of the alkyl free radicals were scavenged, estimated from the hydrocarbon yields in the absence of added iodine assuming that the hydrocarbon products result from hydrogen abstraction or addition reactions of intermediate free radicals.

Table 3 G-Values for volatile radiolysis products

| Irradiation conditions | Polyethylene | | | |
	HDPE	LDPE-I	LDPE-II	Product*
Ambient 12–50 Mrad in ampoules	2.90	3.50	3.10	H_2
	0.0088	0.092	0.11	hc
150°C 12–40 Mrad in ampoules	4.45	3.90	3.50	H_2
	0.026	0.18	0.36	hc
Ambient 25–200 Mrad in large tubes	2.30	2.67	2.50	H_2
	0.0035	0.062	0.075	hc
150°C 25–200 Mrad in large tubes	4.0	3.0	2.80	H_2
	0.01	0.14	0.22	hc

* hc = total hydrocarbon yield

Table 4   G-Values for hydrocarbon radiolysis products[a] from LDPE-I (C_n' indicates alkene)

Irradiation temperature (°C)	Hydrocarbon															
	C_1	C_2	C_2'	C_3	C_3'	C_4	C_4'	C_5	C_5'	C_6	C_6'	C_7	C_7'	C_8	C_9	C_{10}
25	1.03	3.4	0.015	0.38	b	2.9	b	0.37	0.01	0.35	0.005	0.2	b	0.25	0.05	b
150	1.39	6.8	0.5	0.84	0.08	5.9	0.05	0.85	0.05	0.72	b	0.45	b	0.29	0.2	0.05

a, G-values x 10^2; b, yields <0.005

Table 5   Alkyl iodide yields

Alkyl iodide	G-value X 10^3	Alkyl iodide	G-value X 10^3
CH_3I	11.0	$2\text{-}C_7H_{15}I$	0.04
C_2H_5I	5.6	$3\text{-}C_7H_{15}I$	0.30
$1\text{-}C_3H_7I$	3.9	$4\text{-}C_7H_{15}I$	0.50
$1\text{-}C_4H_9I$	1.69	$1\text{-}C_8H_{17}I$	0.46
$1\text{-}C_5H_{11}I$	0.41	$3\text{-}C_8H_{17}I$	0.20
$3\text{-}C_5H_{11}I$	0.85	$4\text{-}C_8H_{17}I$	0.39
$1\text{-}C_6H_{13}I$	0.21	$1\text{-}C_9H_{19}I$	0.13
$2\text{-}C_6H_{13}I$	0.53	$5\text{-}C_9H_{19}I$	0.66
$3\text{-}C_6H_{13}I$	0.32	$1\text{-}C_{10}H_{21}I$	0.10
$1\text{-}C_7H_{15}I$	0.32	$5\text{-}C_{10}H_{21}I$	0.64

G-value for total Alkyl Iodides = 0.0283

Table 6   Branch distribution from ^{13}C n.m.r.

Branch species	Total Branches (%)	
	LDPE-I	LDPE-II
n-Butyl	67.3	65.7
n-Amyl	11.8	11.2
n-Ethyl	7.6	10.0
n-Hexyl + longer	5.4	5.5
2-Ethyl hexyl	3.8	3.7
Pairs of ethyl branches	3.8	3.7

can be explained by reactions of double bonds and trapped polymer radicals with hydrogen atoms and molecules[34]. These reactions have been observed by Varshavskii *et al.*[35] by irradiating polyethylene in the presence of deuterium gas, when transfer of D to the polymer occurred. They would be less important in the small ampoules on account of the smaller particle size of the polymer and the lower hydrogen pressure (by an order of magnitude) resulting from the greater free volume: polymer ratio and the smaller radiation doses.

The less volatile hydrocarbons are inefficiently released from the irradiated polymer and transferred to the gas chromatograph from the large tubes. Thus the measured C_6 and C_7 hydrocarbon yields were appreciably lower than from the ampoules and C_8, C_9 and C_{10} hydrocarbons were not detected.

Comparison with other radiolysis results

Previous workers using mass spectral analysis have observed substantial alkene yields; for example Lawton *et al.*[10] found alkene: alkane = 2.5 and Harlen *et al.*[12] reported alkene:alkane ratios from 0.2 to 2.0. Contrary to these results we have found only small amounts of alkenes, using gas chromatographic analysis to separate alkenes and alkanes. There was no unusual dose dependence for any of the samples to suggest that the alkenes were reacting after irradiation. Although some radical scavenging must be suspected, we conclude that the previously reported high alkene yields are a result of the mass spectral analysis.

Hydrogen yields vary with the molecular weight of polyethylene due to unsaturation associated with chain ends[36]. Our results for $G(H_2)$ are in accord with the relationship of Okoda and Mandelkern using estimated values for $\overline{M}_n$ of the polyethylenes.

The increase in hydrogen yield $\Delta G(H_2)$ for irradiation at 150°C compared with 25°C increased in the order LDPE-II, LDPE-I, HDPE. This correlates with the degree of crystallinity and indicates the important role of the mobility of the polymer chains in at least some of the hydrogen forming reactions. Increased H_2 yields for irradiation above the mel-

ting temperature have also been reported by other workers[37-41].

Our experiments show that serious underestimation of the yields of the less volatile hydrocarbon products occurs (resulting in an erroneous bias towards the lower molecular weight products) unless the irradiated polymer is heated above its melting temperature (*Table 3*). The effect of the post-irradiation heating is readily explained by liberation of trapped volatile products from the crystalline regions in the polymer and enhanced diffusion out of the amorphous regions. However, excessive heating can cause thermal degradation; thus we detected small amounts of methane and ethane (<4% of the radiolytic yield) from unirradiated LDPE after heating at 200°C.

Thermal annealing of the irradiated polymer is also necessary to ensure complete reaction of free radical intermediates. These radicals, if exposed to air, could result in the alternative formation of peroxy radicals and oxidation products — perhaps the source of CO and CO_2 reported by other workers[16]. We did not find any CO or CO_2 above the detection limit of $G \approx 0.01$ imposed under our irradiation conditions by the relatively insensitive thermal conductivity detector which must be used (with He as carrier gas) for these compounds.

Comparison of our G values for hydrocarbon products with previous literature on these radiolysis products from low density polyethylenes is limited because hydrocarbon yields have usually been reported relative to hydrogen. The $G(H_2)$ value varies with the preparation (e.g. molecular weight) and treatment of the polymer and is not an adequate reference yield.

However, our results confirm that C_2 and C_4 hydrocarbons are the major products in addition to hydrogen. Consideration of the various factors discussed above (e.g. post-irradiation heating, annealing, analytical technique, etc.) can explain discrepancies between reported product distributions.

Branch length and radiolysis product distributions

Elimination efficiencies. If the alkyl branches are fractured exclusively at the tertiary carbon atom with equal efficiency, then the relative yields of hydrocarbons in the radiolysis products will give the distribution of branch lengths in the

Table 7 Branch detection efficiencies (Boyle et al.[17])

Branch species	Branch detection efficiency
n-Ethyl	2.4
n-Butyl	1.0
n-Pentyl	0.78
n-Hexyl	0.67
n-Heptyl	0.56
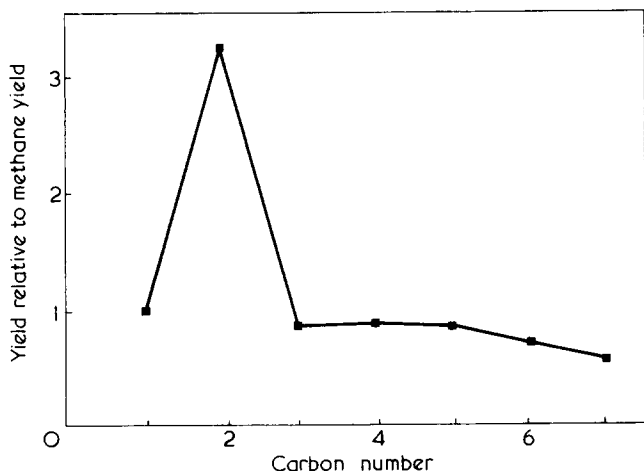
Figure 7 Radiolysis product distribution from n-docosane, $C_{22}H_{46}$

polymer. Kamath and Barlow[20] deduced from their studies of ethylene–α-olefin copolymers that these two conditions applied to LDPE and hence derived $C_2:C_4$ branches = 2:1 in close agreement with Willbourn[8]. These results are in direct conflict with the estimate of Dorman et al.[23] from ^{13}C n.m.r. that the branches in LDPE were predominantly n-butyl.

The efficiency of elimination of alkyl branches can be expected to vary with the length of the branch. Very long branches should have lower efficiencies than very short branches due to the cage effect. Boyle et al.[17] examined a variety of model branched polymers including substituted polymethylenes and ethylene–α-olefin copolymers prepared using Ziegler and Phillips catalysts and although the yields from branch elimination varied considerably with the type of polymer, the relative proportion of hydrocarbon eliminated (i.e. the branch detection efficiency) was deduced to be greatest for C_2 branches (*Table 7*). Boyle's calculated branch distribution, after correcting for the branch detection efficiencies, showed a dominance of n-butyl branches, which is qualitatively similar to the ^{13}C n.m.r. results. Unfortunately Boyle's radiolysis products apparently included large alkene yields and the validity of ignoring them in the calculations is questionable.

Fragmentation of chain ends

The radiolytic fragmentation of the polymer main chain ends would be expected to produce a product distribution similar to long chain hydrocarbons[13,42,43]. Salovey[42,43] has reported product distributions from long chain (C_{16} and C_{17}) hydrocarbons which show a preferential cleavage of the second carbon–carbon bond to produce ethane. Our product distribution from the radiolysis of n-docosane ($C_{22}H_{46}$) shown in *Figure 7* confirms this preferential cleavage.

To determine the relative probability (x) of production of volatile products from fracture of main chain ends to production of volatile products from fracture of short branches, we have considered the total hydrocarbon yield, $G(hc) = K$ [(no. of branches/1000 C atoms) + x (no. of main chain ends/1000 C atoms)], where (i) K is a proportionality constant, (ii) the number of main chain ends/1000 C atoms is calculated from estimated $\bar{M}_n$ values, and (iii) the number of branches/1000 C atoms is determined by either ^{13}C n.m.r. or infra-red spectroscopy (see Discussion).

Using the total hydrocarbon yields in *Table 3* we find the relationship (average for small ampoules, large tubes, 25° and 150°C):

$$G^{LDPE-II}(hc) = 1.5\ G^{LDPE-I}(hc) = 18\ G^{HDPE}(hc)$$

which eliminates the proportionality constant K. Comparison of LDPE-I and LDPE-II with HDPE using total branch frequencies from either ^{13}C n.m.r. or infra-red analysis give $x \approx 0.3$. Although this value of x is subject to some uncertainity, it is reasonable for the relative ease of cleavage.

Fragmentation of branches

The longer alkyl branches can be considered similar to a main chain end. Therefore, an alkyl branch — of length n — should show some tendency to fragment (similar to the main chain end), modified by the preferential cleavage at the tertiary carbon atom. Using product yields from branched polymers (e.g. ethylene–α-olefin copolymers)[12,17] the probable product distribution is shown in *Table 8*.

Total number of short branches

There is a discrepancy (see *Table 1*) between the total number of branches calculated from infra-red and ^{13}C n.m.r. spectroscopy. The infra-red determination is based on calibrations with model compounds[8,44] to establish extinction coefficients. Problems arise from (1) the methyl absorption at 1378 cm^{-1} having different extinction coefficients[44] for different branch species, and (2) the overlapping methylene absorptions at 1372 and 1355 cm^{-1} being dependent on the degree of crystallinity[45].

^{13}C n.m.r. spectroscopy is an absolute method and should provide a more reliable total branch frequency and also a more reliable branch distribution than the infra-red method. However, the peak intensities in the ^{13}C– {^1H} n.m.r. spectrum are dependent on the relaxation times of the carbon atoms. In the pulsed Fourier transform technique variations in intensity will occur if the pulse cycle time is shorter than the relaxation time of the carbon atoms. The alkyl branch carbons will have different relaxation times than the main

Table 8 Typical product distribution for fragmentation of an alkyl branch — of length n

	n				
	Relative Yield				
Product	2	3	4	5	6
CH_4	0.059	0.052	0.049	0.047	0.046
C_2H_6	0.94	0.13	0.13	0.12	0.12
C_3H_8	–	0.82	0.045	0.043	0.041
C_4H_{10}	–	–	0.78	0.038	0.037
C_5H_{12}	–	–	–	0.75	0.035
C_6H_{14}	–	–	–	–	0.73

chain carbons ($\tau \approx 1.5$ sec[23]); in particular the terminal methyl groups should have the longest relaxation times. These uncertainties in the measured intensities of the resonances of carbon atoms in different environments result in the calculated branch frequency being less reliable than the branch distribution.

There are further uncertainities in the branch frequencies determined by both i.r. and [13]C n.m.r. The values for $CH_3/1000$ carbon atoms from i.r. given in *Table 1* would be expected to include the chain ends and long branches (formed by intermolecular chain transfer) which have terminal CH_3 groups, but not those with other terminal groups. Vinyl and vinylidene groups are known to occur in LDPE, but are unlikely to account for more than ~10% of the chain ends. The branch frequencies from i.r. in *Table 1* have been obtained by subtracting the estimated numbers of main chain ends with terminal CH_3 groups and should include the long branches.

In the [13]C n.m.r. spectra, the terminal CH_3 groups at chain ends will have a chemical shift of 14.3 ppm (equivalent to C_4 and longer branches), the 1-CH_2 groups of 23.0 ppm (equivalent to C_5 and longer branches) and the 3-CH_2, 4-CH_2, will have chemical shifts which will place them under the major CH_2 peak at 30 ppm (see *Figure 1*). The long branches will have resonances at the same positions and also at 38.0 ppm (CH), 34.4 ppm (α), 27.4 ppm (β) and 30.6 ppm (γ). In principle, the number of chain ends can be determined from the relative intensities of these resonances. However, a comparison of the resonances indicates negligible chain ends. Similar results are apparent in the spectra of Bovey *et al.*[24] (cf. sample 5AS5 which should have 2 chain ends per 1000 CH_2). Unfortunately, the resonances at high field give the most unreliable intensities. Randall[22] attributed the decreased intensities to the nuclear Overhauser effect, but we have obtained a substantial increase in intensity on increasing the pulse interval from 1 to 5 sec indicating relaxation time effects. Even for 5 sec pulse intervals, and Bovey has reported no increase in intensity on increasing the pulse interval from 3 to 8 sec, it is apparent that the number of chain ends is considerably underestimated (as also observed by Bovey[23] in $C_{36}H_{74}$). Consequently, the branch frequencies from [13]C n.m.r. in *Table 1* effectively do not include the chain ends, but do include the long branches.

Calculated product distributions

In *Figure 8* the experimentally determined distribution of hydrocarbon products from LDPE-I at 150°C is compared with distributions calculated on the basis that:

(a) Branch fracture occurs exclusively at the tertiary carbon atom with equal efficiencies for all branches and fragmentation of main chain ends is similar to that observed from n-docosane ($x \doteq 0.3$).

(b) Branch fracture occurs exclusively at the tertiary carbon atom with branch detection efficiencies identical to those reported by Boyle *et al.*[17].

(c) Branch fracture occurs as in (b) with fragmentation of the main chain end as in (a).

(d) Branches fragment to give a product distribution as shown in *Table 8* and fragmentation of the main chain end occurs as in (a).

(e) Branches fracture at the tertiary carbon atom with the branch detection efficiencies found by Boyle *et al.*[17], but the branches also fragment as in (d) and main chain end fragmentation occurs as in (a).

In the five mechanisms above no consideration has been

made of the morphology of the polyethylene sample. Therefore comparisons with irradiations of the molten polymer at 150°C should be the most reliable guide to the appropriate mechanism, since the morphological effects will then be absent.

Figure 8 has been calculated using the [13]C n.m.r. determination of total branch frequency. Similar conclusions about the applicability of (a) to (e) are obtained for irradiations at 25°C, from LDPE-II, and by using branch frequencies determined from infra-red spectra. *Figure 8* indicates that fragmentation of the chain ends (mechanism (a)) can supplement the ethane yield from isolated ethyl branches, pairs of ethyl branches and 2-ethyl hexyl branches; but cannot match the experimental distribution. Mechanism (b) utilizing branch detection efficiencies (Boyle *et al.*[17]) without allowance for the main chain end fragmentation is also inadequate. Adding the main chain end fragmentation to mechanism (b) improves the agreement; although the C_1 and C_3 yields are low and the C_4 yield is high, the ethane/butane ratio is close to the experimental value. Mechanism (d) alone is inadequate, but mechanism (e) gives good agreement with the experimental distributions.

High density polyethylene

The hydrocarbon yields from HDPE are expected to come from main chain fracture near the ends of the chains. The product distribution should then be similar to that obtained from linear alkanes[13,17,42,43]. However, we observed much greater methane yields than expected (*Figure 6*). This could be partly due to thermal degradation, but it strongly suggests that the small branch content of this polymer, observed by infra-red spectroscopy, is due to methyl branches, and also a small number of n-butyl branches. This is in agreement with recent infra-red studies by McRae and Williams[46] who inferred from the 1150 cm^{-1} infra-red vibration that 80% of the branches in high density polyethylene were methyl groups.

CONCLUSIONS

An important aspect of our investigation is that [13]C n.m.r. spectra, infra-red spectra and radiolysis product yields have been obtained using the same polymer samples. This enables a direct comparison of the results from the three techniques. The interpretation that we favour is that the [13]C n.m.r. spectra indicate the distribution of branches, i.e. butyl branches predominate in our LDPE samples. The distribution of radiolysis products can then be explained by (a) cleavage at the tertiary carbon atom with the branch detection efficiencies proposed by Boyle *et al.*[17], (b) fragmentation of main chain ends with a product distribution similar to that obtained from linear hydrocarbons, and (c) some fragmentation of the short branches. The discrepancy of a factor of two between [13]C n.m.r. and infra-red spectroscopic determinations of the total number of branches remains unresolved.

LDPE is prepared under a wide variety of conditions and therefore the molecular weight, molecular weight distribution and long and short branch frequencies vary greatly. The nature of the short branches, and hence the branch distributions of different polymers, can also be expected to vary. However, the dominance of n-butyl branches is evident from almost all [13]C n.m.r. studies, indicating the importance of Roedel's back-biting mechanism. We have similarly observed
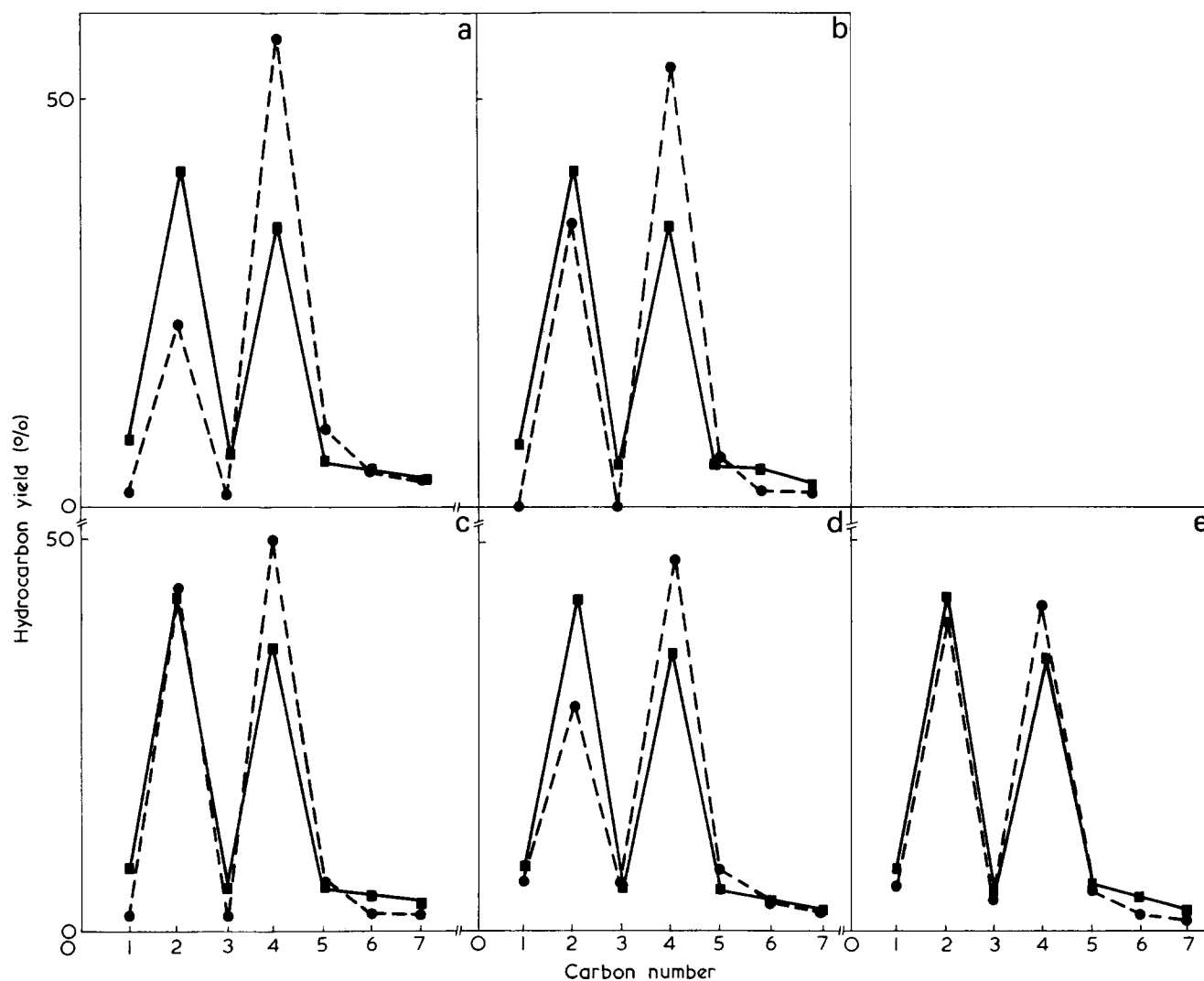
Figure 8 Comparisons between experimental distribution and calculated distributions for LDPE-I irradiations at 150°C. (a)—(e), as defined in text. ■, Experimental; ●, calculated

the presence of ethyl and virtual absence of methyl and propyl branches.

The absence of propyl branches is strong evidence in favour of the Roedel back-biting mechanism and not the reverse as claimed by some authors[47], since a five-membered ring transition state would not permit the $-C-H \ldots C-$ bonds to be colinear, which is necessary for efficient hydrogen atom transfer[48]. Further studies on the efficiency of branch elimination and the fragmentation pattern of the branch as a function of branch length are necessary to establish unequivocally the relationship between radiolysis product and chain branch distributions.

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