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Trevor N. Bowmer^{ab}; Sook-Ying Ho^a; James H. O'donnell^a; Paul W. O'Sullivan^a

^a Polymer and Radiation Group Department of Chemistry, University of Queensland, Brisbane, Australia ^b AT & T Bell Laboratories, Murray Hill, New Jersey

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Scission Efficiencies of Short Chain Branches in the γ -Radiolysis of Ethylene- α -Olefin Copolymers

TREVOR N. BOWMER,* SOOK-YING HO, JAMES H. O'DONNELL,†
and PAUL W. O'SULLIVAN

Polymer and Radiation Group
Department of Chemistry
University of Queensland
Brisbane 4067, Australia

ABSTRACT

γ -Irradiation of copolymers of ethylene with propene, 1-butene, and 1-hexene, containing from 1 to 6 alkyl short chain branches per 1000 carbon atoms, at 25°C in vacuum, produced small amounts of n-alkanes with a maximum yield for the alkane corresponding to the alkyl branch of the α -olefin unit. A multilinear regression analysis showed a highly significant dependence of $G(C_n \text{ alkane})$ on the frequency of alkyl branches containing n carbon atoms, determined by ^{13}C -NMR. The corrections to the $G(C_n \text{ alkane})$ yields from other fragmentation processes were substantial but no dependence for $G(C_n \text{ alkane})$ on fragmentation of chain ends or fragmentation

*Present address: AT&T Bell Laboratories, Murray Hill, New Jersey 07974.

†To whom correspondence should be addressed.

of the chain following branch elimination could be deduced from the data. The scission efficiencies = $G(\text{alkane})$ divided by the branch frequency per 1000 carbon atoms \pm 95% confidence limits were $(0.7 \pm 0.7) \times 10^{-3}$, $(2.7 \pm 0.8) \times 10^{-3}$, and $(1.5 \pm 0.3) \times 10^{-3}$, for methyl, ethyl, and butyl branches, respectively. These factors can be used to determine the short-chain branch frequencies in similar polymers from n-alkane yields on γ -irradiation.

INTRODUCTION

γ -Irradiation of polymers in the solid state produces chain scission and/or cross-linking, modification of the structure of the polymer, and evolution of molecules of low molecular weight.

Hydrogen is the major volatile product from hydrocarbon polymers; this is attributed to the high proportion of C-H bonds and the ease of diffusion of H atoms away from the site of bond scission. Several investigations have shown that minor amounts of volatile alkanes and alkenes are also formed, and the yields of alkanes have been correlated with the nature and frequency of alkyl short-chain branches.

Radiolysis studies of low-density polyethylene by Harlen et al. [1], Willbourn [2], Boyle et al. [3], and Kamath and Barlow [4] have all found that ethane and butane are the main alkanes formed, with ethane predominating. This appeared to confirm the IR studies of Willbourn, who obtained a ratio of ethyl:butyl branches of 2:1.

More recent ^{13}C -NMR determinations of branch frequencies by Dorman et al. [5], Randall [6], Bovey et al. [7], and Axelson et al. [9] have indicated that the branches are predominantly butyl, although the butyl:ethyl ratio varies with the polymerization conditions.

Boyle et al. [3] deduced from a study of the volatile hydrocarbon products from branched polymethylenes and ethylene- α -olefin copolymers that ethyl branches were eliminated approximately twice as efficiently as butyl branches, but Kamath and Barlow [4] obtained the same scission efficiencies for all short branches.

We have previously investigated the apparent contradiction between the radiolysis and ^{13}C -NMR results by studying the same low-density polyethylene samples by both methods [9]. The ethane and butane yields were similar, but the ^{13}C -NMR spectra gave a ratio of ethyl:butyl branches of 1:2. These results could be rationalized with the different scission efficiencies reported by Boyle et al., but contradicted by Kamath and Barlow.

The present work reports determinations of the scission efficiencies for methyl, ethyl, and butyl branches from measurements of alkane yields after γ -irradiation, and of branch frequencies, by ^{13}C -NMR, for a series of copolymers of ethylene with small amounts of propene, 1-butene, and 1-hexene.

EXPERIMENTAL

Copolymers of ethylene with 0.5 to 2% of propene (Z-N), 1-butene (Z-N), and 1-hexene (P) prepared using Ziegler-Natta (Z-N) or Phillips (P) catalysts were kindly provided by Mr O. Delatycki and Dr F. C. Schilling. Molecular weight distributions were determined by GPC; \overline{M}_n and $\overline{M}_w/\overline{M}_n$ are given in Table 1.

^{13}C -NMR spectra were obtained with a JEOL JNM-FX100 spectrometer using 1,2,4-trichlorobenzene as solvent at 120°C and an internal 2 mm capillary containing DMSO- d_6 for locking. Pulse intervals of 20 and 30 s were used to ensure effective nuclear relaxation [8].

Samples (40 mg) of the copolymers were evacuated at 25°C for 24 h at 10^{-2} Pa and sealed in thin-walled glass ampules (50 mm \times 4 mm diam). The ampules were irradiated with ^{60}Co γ -rays to doses of 50 to 200 kGy in a Gammacell 220 unit at ~ 1.5 kGy/h at 25°C.

The volatile products were analyzed by crushing the ampules in a special injection port in a gas chromatograph using a Chromosorb 102 column with temperature programming from 80 to 200°C, after preheating the samples to 150°C for 10 min as described previously [9].

The polymers were also examined by DSC; the values of the melting temperature, T_m (corrected peak maximum), and the enthalpy of melting, ΔH_m , from the melting curves are given in Table 1.

RESULTS AND DISCUSSION

 ^{13}C -NMR Spectra

Random copolymerizations of the α -olefins with ethylene at these low α -olefin contents should result in isolated alkyl branches. This was confirmed from the ^{13}C -NMR spectra; no multiple olefin sequences or other abnormal structures were observed.

Typical ^{13}C -NMR spectra are shown in Fig. 1. Saturated chain ends could be measured readily for the propene and butene copolymers, since these resonances were separated from those due to methyl and ethyl groups, respectively. Thus, Fig. 1(a) shows comparable frequencies of ethyl branches and chain ends in sample EB1. Long branches may also contribute to the chain-end resonances at 14.1 (CH_3), 22.8 (2-CH_2) and 32.4 (3-CH_2) ppm. However, the intensity of the 38.5 ppm resonance (CH branch carbon for C_4 and longer branches) indicates that any long-

TABLE I. Characterization of the Ethylene- α -Olefin Copolymers

Polymer	α -Olefin wt % from feed	\bar{M}_n	\bar{M}_w/\bar{M}_n	T_m ($^{\circ}$ C)	ΔH_m (J/g)	Branches/1000 C		Chain ends/1000 C	
						Feed	13 C-NMR	Feed	13 C-NMR
Propene:									
EP1	0.5	17,200	7.2	132	210	1.7	1.7	1.6	2.0
EP2	0.5	11,950	7.9	130	228	1.7	2.2	2.3	2.1
EP3	0.5	13,900	4.5	130.5	236	1.7	1.9	2.0	3.4
1-Butene:									
EB1	1.0	18,000	15	130.5	214	2.5	2.7	1.6	3.8
EB2	1.0	7,800	25	130.5	210	2.5	2.3	3.6	2.7
EB3	0.25	5,250	26	130.5	223	0.6	0.9	5.3	3.6
1-Hexene:									
EH1	-	11,700	18	128	166	-	4.6	2.4	1.5
EH2	-	14,400	13	128	159	-	5.9	1.9	-
EH3	-	16,000	10.5	131	200	-	2.2	1.8	-

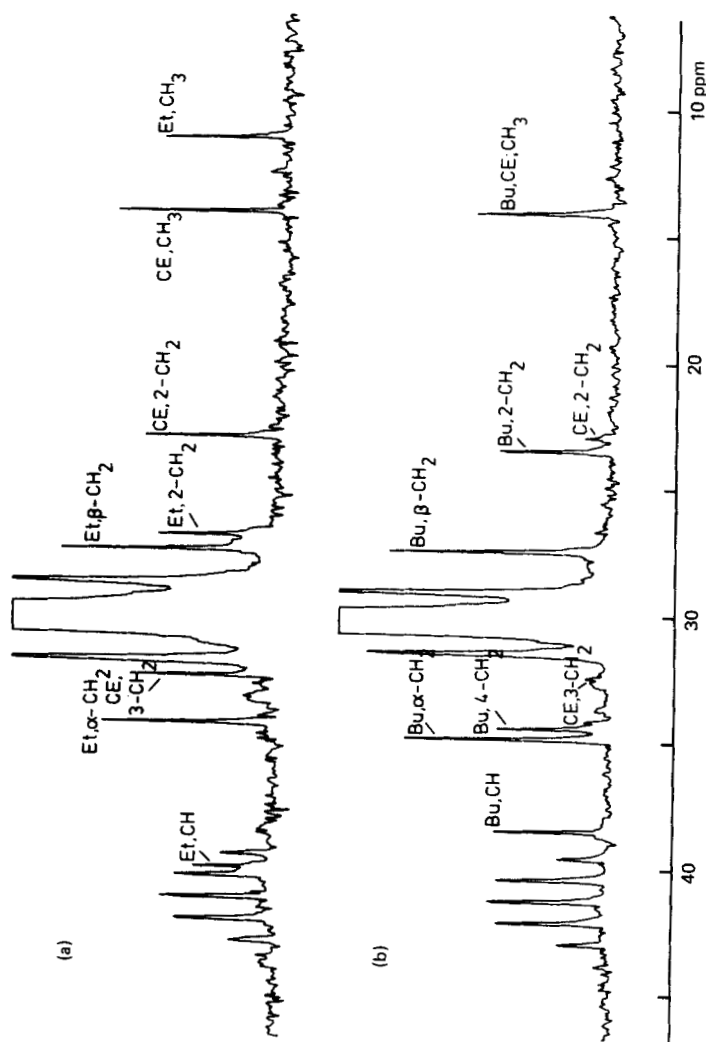


FIG. 1. Typical ^{13}C -NMR spectra of ethylene- α -olefin copolymers showing short-branch carbon resonances and saturated chain ends. (a) Poly(ethylene-co-1-butene), EB1; (b) poly(ethylene-co-1-hexene), EH1. Et = ethyl branch, Bu = butyl branch, CE = chain end.

branch content in these polymers is small compared to short branches and chain ends. The chain ends could also be determined for the hexene copolymers, but less reliably, since the chain-end and butyl-branch CH_3 resonances are superimposed. The numbers of branches and saturated chain ends per 1000 carbon atoms determined from ^{13}C -NMR are given in Table 1. The total number of chain ends calculated from \bar{M}_n values determined by GPC are also given in Table 1.

Volatile Radiolysis Products

The main volatile radiolysis product from all the polymers was H_2 with a G value of about 3. Alkanes from methane to hexane were obtained with G values in the range 10^{-2} to 10^{-4} . Yields of alkenes were negligible at 30°C (but increased with increasing irradiation temperature to be comparable with the alkane yields at 150°C).

The G values for the yields of alkanes from the copolymers and for typical samples of high-density polyethylene (HDPE) and low-density polyethylene (LDPE) are given in Table 2. The product distributions from the copolymers all show maxima corresponding to the alkane formed by H addition to the alkyl branch.

Yields of alkanes other than from the alkyl branches on the polymers are significant. Possible sources of these alkanes include (1) fragmentation of existing chain ends, which would show a dependence on chain-end concentration, i.e., on $1/\bar{M}_n$, (2) fragmentation of new chain ends produced following random chain scission (constant for all copolymers), (3) fragmentation of the chain following branch elimination (dependent on branch frequency), and (4) fragmentation of the branches.

In order to derive the absolute scission efficiency for elimination of each type of branch, the yield of the alkane corresponding to the branch should be corrected for the yield of this alkane resulting from fragmentation Processes 1-4 above. This can be done by using the yields of methane, ethane, and butane from the copolymers which do not contain the selected branch, with allowance for the dependence on the number of chain ends and the total branch frequency. However, the available data can be used more effectively by applying multilinear regression to determine, for all nine copolymers, the dependence of the total yield for each alkane on the frequency of that alkyl branch in the copolymer concurrently with its dependence on additional parameters such as chain-end concentration and branch frequency of any type. Thus, an equation of the following form would result:

$$\begin{aligned} G(\text{C}_n \text{ alkane}) &= G_1(\text{branch elimination}) + G_2(\text{chain-end fragmenta-} \\ &\quad \text{tion}) + G_3(\text{random scission}) + G_4(\text{fragmentation of} \\ &\quad \text{chain after branch elimination}) \\ &= f_0x_n + f_1y + f_2 + f_3z \end{aligned}$$

TABLE 2. Alkane Yields from γ -Irradiation at 25°C^a

Polymer	G-value $\times 10^2$							
	CH ₄	C ₂ H ₆	C ₃ H ₈	i-C ₄ H ₁₀	n-C ₄ H ₁₀	C ₅ H ₁₂	C ₆ H ₁₄	
EP1	0.34 (0.01)	0.20	0.10	0.30	0.08	0.025		
EP2	0.56 (0.23)	0.18	0.08	0.25	0.06	0.03	0.025	
EP3	0.48 (0.15)	0.28	0.18	0.61	0.14	0.03		
EB1	0.41	1.10 (0.86)	0.10	0.70	0.11	0.05		
EB2	0.30	0.68 (0.44)	0.08	0.10	0.08	0.03	0.03	
EB3	0.45	0.54 (0.30)	0.15	0.43	0.21	0.10		
EH1	0.28	0.26	0.14	0.38	0.89 (0.76)	0.05		
EH2	0.32	0.25	0.15	0.35	0.95 (0.82)	0.03	0.03	
EH3	0.26	0.48	0.14	1.2	0.55 (0.42)	0.16	0.07	
HDPE	0.40	0.28	0.08	0.07	0.11	0.03	0.03	
LDPE	0.60	4.2	0.50	0.05	4.0	0.60	0.80	

^aY values in parentheses are G values for alkane corresponding to alkyl short-chain branch after correction for fragmentation.

where the dependent variable $G(C_n \text{ alkane})$ is the yield of alkane of length n and where x_n , y , and z are the independent variables: x_n is the frequency of branches of length n , y is the number of chain ends, and z is the total number of branch points, regardless of branch length. The best values of the factors f_0 , f_1 , and f_3 for each of the alkane yields (C_1 , C_2 , and C_4) result from the three regression analyses.

The dependence of $G(C_n \text{ alkane})$ on the corresponding branch frequency was significant to a level of $>99\%$ for ethane and butane and $>95\%$ for methane. It is possible to test statistically for the dependence of the yields of branch alkane on y and z by extending from a simple linear regression to multilinear regression and observing the improvement in the fit as each of the variables is included in turn.

Using this procedure, we have found that including a term for the dependence of $G(C_n \text{ alkane})$ on the number of chain ends provided no significant improvement in the regression for ethane or butane yields, and for methane the improvement was significant to a level of 80% . It was expected that fragmentation of the existing chain ends would be the main source of the minor alkane yields, and we can only conclude that the range of molecular weights is too small and the error in the $G(\text{alkane})$ values too large for a dependence to be proven. Similarly, no significant dependence of alkane yield on z , the frequency of branches, could be determined from the available data. That is, a significant contribution to $G(C_n \text{ alkane})$ from fragmentation of the chain after branch elimination could not be established.

Consequently, the determination of the scission efficiency for each branch type reverts to a linear regression of $G(C_n \text{ alkane})$ against the frequency of the corresponding branch. For each alkane the correction to the $G(C_n \text{ alkane})$ values is then a constant value, within experimental error, for all copolymers. This suggests that the main source of minor alkanes is Process 2, viz., fragmentation of new chain ends produced by random chain scission, a reaction which is probably enhanced by excess energy at the scission site.

The scission efficiencies and the corrections to the alkane yields from fragmentation processes are shown in Table 3. The multilinear regression results incorporating a term for fragmentation of existing chain ends are included for comparison.

The corrected $G(C_n \text{ alkane})$ values, i.e., $G(C_n \text{ alkane}) - f_2$ from the linear regression, are shown in parentheses in Table 2. Corrections for minor alkane yields from fragmentation are more important for copolymers in this study than for copolymers with higher short-chain branch frequencies, or for low-density polyethylenes.

The C_4 alkane comprised both isobutane and n-butane, with iso-

TABLE 3. Scission Efficiencies (f_0) and Correction Factors (f_1 and f_2) for Alkane Yields Determined from (A) linear regression and (B) multilinear regression^a

C_n	(A) $G(C_n \text{ alkane}) = f_0 x_n + f_2$		
	$10^3 f_0^c$	$10^3 f_2$	
CH ₄	0.70 ± 0.7	3.33 ± 0.8	
C ₂ H ₆ ^b	2.71 ± 0.8	2.37 ± 1.0	
n-C ₄ H ₁₀	1.53 ± 0.25	1.25 ± 0.7	

C_n	(B) $G(C_n \text{ alkane}) = f_0 x_n + f_1 y + f_2$		
	$10^3 f_0^c$	$10^3 f_1^d$	$10^3 f_2$
CH ₄	0.82 ± 0.7	0.34 ± 0.6	2.41 ± 1.0
C ₂ H ₆	2.73 ± 0.9	0.13 ± 0.8	2.68 ± 1.5
n-C ₄ H ₁₀	1.56 ± 0.3	0.20 ± 0.5	0.72 ± 0.8

^a ± Error represents 95% uncertainty.

^b Using 8 data points only; EH3 disregarded.

^c Units for f_0 are $G(C_n)/(\text{no. of branches of length } C_n \text{ per } 1000 \text{ C atoms})$.

^d Units for f_1 are $G(C_n)/(\text{no. of chain ends per } 1000 \text{ C atoms})$.

butane predominating (except for the ethylene-hexene copolymers). The source of the isobutane is uncertain. Evidence from various sources suggests that it is not primarily formed by isomerization of n-butane. Thus, $G(\text{isobutane})$ is small relative to $G(\text{n-butane})$ for low-density polyethylene and for reduced poly(vinyl chloride), especially for samples containing residual tri(n-butyl)tin hydride, which gives enhanced butane yields. The yields of n-butane have been used in the present study for the determination of scission efficiencies.

Scission Efficiencies

The $G(C_n \text{ alkane})$ values have been plotted in Fig. 2 against the frequencies of the short-chain branches in the copolymers, determined by ¹³C-NMR.

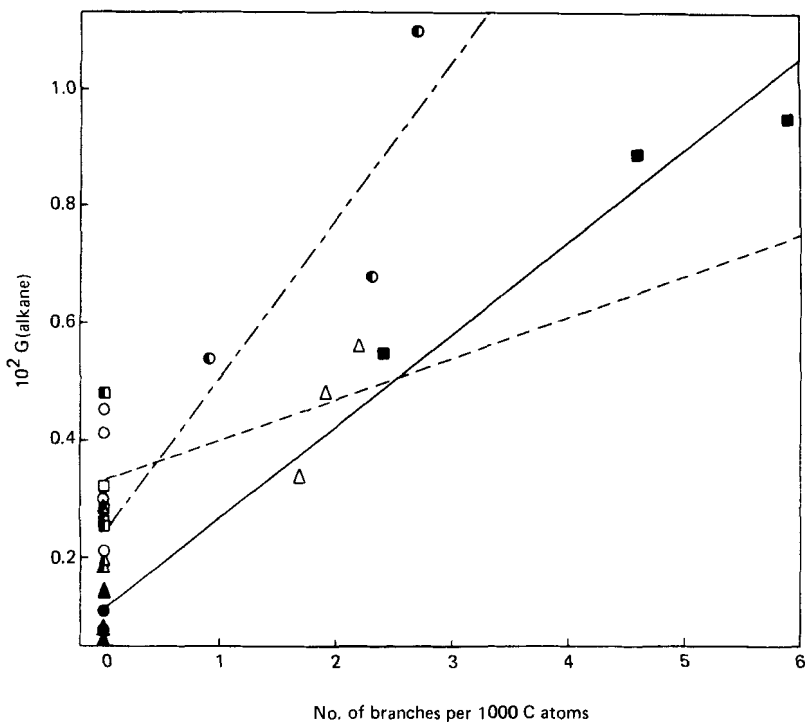


FIG. 2. Correlation of the G value of the alkane corresponding to the alkyl branch with the frequency of methyl, ethyl, and butyl branches in ethylene- α -olefin copolymers. (---) Methane yields (open symbols): (Δ) EP copolymers, (\circ) EB copolymers, (\square) EH copolymers. (-.-) Ethane yields (half symbols): (\blacktriangle) EP copolymers, (\bullet) EB copolymers, (\blacksquare) EH copolymers. (—) Butane yields (filled symbols): (\blacktriangle) EP copolymers, (\bullet) EB copolymers, (\blacksquare) EH copolymers.

Table 4 shows the scission efficiencies obtained in this work and also those calculated from the results of Boyle et al. [3] and Kamath and Barlow [4]. The yields of volatile hydrocarbons were unfortunately only expressed relative to hydrogen by Boyle et al. We have taken $G(\text{H}_2) = 2.9$ from our own work [9] to derive G values for comparison purposes. However, $G(\text{H}_2)$ may vary with molecular weight, nature of end groups, and other factors. We obtain a scission efficiency for ethyl branches which is about twice that of butyl branches and about four times that for methyl branches. An enhanced scission efficiency for ethyl branches was reported by Boyle et al., based on a number of indirect comparisons between different types of polymers,

TABLE 4. Scission Efficiencies of Alkyl Short-Chain Branches^a

α -Olefin	Scission efficiency ^b $\times 10^3$	Reference ^c (catalyst)
Propene	0.30	3 (P)
	0.62	3 (Z-N)
	0.73 (0.57 ^d)	4 (P)
	0.7 ± 0.7^f	e (Z-N)
1-Butene	0.52	3 (P)
	1.82	3 (Z-N)
	0.73 (0.56 ^d)	4 (P)
	2.7 ± 0.8^f	e (Z-N)
1-Hexene	1.53 ^g	3
	0.73 (0.49 ^d)	4 (P)
	1.5 ± 0.3^f	e (P)

^aIrradiation at 20°C.

^bScission efficiency = G value of alkane corresponding to H addition to branch, corrected for yields from fragmentation processes, and divided by the number of branches per 1000 C atoms.

^cP = Phillips and Z-N = Ziegler-Natta catalyst.

^dRecalculated with correction for fragmentation processes.

^eThis work.

^f \pm Error represents 95% uncertainty.

^gData from deuterobutyl branched polymethylenes. However, Boyle et al. [3] have deduced a sensitivity factor ratio of 0.9 for 1-hexene: propene by intercomparisons involving homopolymers.

but this is in disagreement with the results of Kamath and Barlow, who obtained similar radiation sensitivities for branches of all sizes.

The absolute scission efficiencies obtained in the present work (at 25°C) are similar to those derived from the results of Boyle et al. for propene and 1-butene copolymers prepared by Ziegler catalysts and for deuterobutyl branched polymethylene, but higher than those reported by Kamath and Barlow. It should be noted that these previous workers used radiation doses (1 MGy) an order of magnitude greater than the present work, and a decrease in G(volatile products) is frequently observed at high doses.

The propene and butene copolymers used in this work were prepared with Ziegler-Natta catalyst, but the hexene copolymer with Phillips catalyst. It is possible that the difference in scission efficiencies for ethyl and butyl branches reflects the difference in the

polymerization process. The data of Boyle [3] suggest such a possibility. However, no structural differences were apparent in the NMR spectra. Also, the ethyl and methyl branches in Ziegler-Natta copolymers show different scission efficiencies.

Statistical evaluation of a large number of experiments with a greater variety of adequately characterized samples would be necessary to unambiguously determine effects due to all possible parameters.

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