Observation by ^{13}C n.m.r. of H-crosslinks and methyl end groups due to main-chain scission in ethylene–propylene copolymers after γ-irradiation

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High resolution ^{13}C n.m.r. spectra were obtained from two ethylene–propylene copolymers containing 23% (EP23) and 36% (EP36) propylene swollen with $CDCl_3$ after γ-irradiation, although the line widths increased and the intensities of the original resonances decreased with increasing radiation dose. A resonance at 42 ppm after low doses (0.02–0.14 MGy) was attributed to methine carbons in H-crosslinks. New resonances at 11.3, 14.1, 14.5, 22.7 and 23.1 ppm were assigned to methyl and methylene groups on various chain-end structures arising from main chain scission, and yields (G values) were derived for doses up to 2 MGy. G(scission) values of 0.16 and 0.37 for EP23 and EP36, respectively, were in good agreement with values derived previously from soluble fraction measurements and from solid-state n.m.r. spectra after much higher radiation doses. The proportions of different chain-end structures suggested that scission was favoured by a factor of 1.6 at C–C bonds adjacent to the methyl substituents compared with other main-chain C–C bonds.

(Keywords: n.m.r.; radiation; ethylene–propylene; crosslinks; scission)

INTRODUCTION

High-energy radiation, such as γ-rays and electrons, causes crosslinking and scission in polymer molecules and the consequent changes in molecular weight can substantially alter the physical and mechanical properties. Radiation chemical yields, $G(X)$ and $G(S)$, for crosslinking and scission respectively, can be derived indirectly from changes in molecular weight below the gel dose, soluble fractions above the gel dose, swelling ratios, and measurements of several other properties, using various assumptions, including the assumption that there is a random spatial distribution of the crosslinks.

The chemical reactions of crosslinking and scission are not well understood and there is considerable interest in the direct observation and determination of the crosslinks and of the new chain ends resulting from main-chain scission. Randall *et al.*[1] have observed Y-crosslinks in polyethylene below the gel dose by ^{13}C n.m.r. in solution: these Y-links are believed to result from reaction of terminal C=C bonds in the polymer molecules with main-chain radicals[2]. Recently, Horii *et al.*[3,4] reported the observation by solution-state ^{13}C n.m.r. of both Y- and H-links in irradiated polyethylene. G values for formation of Y-links were higher at low temperatures, whereas H-links were formed preferentially at high temperatures and in the melt. O'Donnell and Whittaker[5] have assigned new peaks at 39–47 and 14 ppm in the solid-state ^{13}C n.m.r. spectra of ethylene–propylene (EP) copolymers at high radiation doses to H-crosslinks and methyl chain ends resulting from main-chain scission. $G(X)$ and $G(S)$ values derived from the n.m.r. spectra were in good agreement with values obtained from soluble fractions, indicating that scission and crosslinking occur with random spatial distributions in these amorphous copolymers. Sohma *et al.*[6] have also used solid-state n.m.r. to study irradiated EP copolymer.

In the present paper, we report high-resolution ^{13}C n.m.r. of EP copolymers after γ-irradiation to low doses. The structures and yields of crosslinks and new methyl chain ends have been determined.

EXPERIMENTAL

Polymers

The two EP copolymers were obtained from Japan Synthetic Rubber (EP07P and EP11). Their chemical structures were determined from ^{13}C n.m.r. spectra in solution in trichlorobenzene at 120°C. Assignments were made after comparison with spectra reported by Carman and co-workers[7] and by Randall[8], and confirmed using the INEPT pulse sequence[9]. Quantitative intensities were obtained using a pulse recycle time of 20 s, which was more than five times the longest relaxation time, and with gated decoupling to avoid possible intensity distortions arising from unequal NOE factors. The compositions of EP07P and EP11 were found to be 23 and 36% propylene, respectively, and they contained no termonomer. We have labelled them EP23 and EP36, respectively.

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Irradiation

Samples of the copolymers were evacuated for 24 h and sealed in glass ampoules, which were irradiated at 30°C with ^{60}Co γ-rays in an AECL Gammacell or in the pond facility of the Australian Nuclear Science and Technology Organization.

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

High-resolution ^{13}C n.m.r. spectra were obtained on polymer samples dissolved or swollen in $CDCl_3$ using a Bruker CXP300 spectrometer operating at 75 MHz or a Jeol PS100 spectrometer at 25 MHz.

RESULTS AND DISCUSSION

Characterization of EP copolymers

The structures of the two EP copolymers were determined from their ^{13}C n.m.r. spectra obtained in solution. The ^{13}C n.m.r. spectrum of EP36 is shown in *Figure 1* and the spectral assignments and the distributions of substituents for EP23 and EP36 are given in *Table 1*. (The nomenclature, in which P, S and T refer to methyl, methylene and methine carbons, respectively, and the Greek subscripts to the position along the chain of the nearest substituent, was developed by Carman *et al.*[7,10].)

^{13}C n.m.r. spectra of irradiated polymers

The line widths of the resonances in the ^{13}C n.m.r. spectra increased with radiation dose as shown in *Figure 2* for typical methyl, methylene and methine carbons. This was due mainly to a decrease in the spin–spin relaxation time (T_2) indicating that molecular mobility decreased on irradiation. Charlesby and Folland[11] have observed a decrease in T_2 for ^1H n.m.r. of irradiated polyethylene.

The total intensity of the n.m.r. signal decreased on irradiation as shown in *Figure 3*. This is due to part of the polymer becoming immobilized by crosslinking. The strong dipole–dipole coupling resulting from the decrease in mobility produces line broadening. The scalar decoupling used in obtaining ^{13}C n.m.r. spectra in solution is insufficient to eliminate this dipolar coupling and therefore only the mobile, non-dipolar-coupled parts of the polymer are detected. A decrease in intensity of the n.m.r. spectra of chemically crosslinked polymers has been reported by Ford and co-workers[12,13].

The decrease in intensity was much larger than the number of crosslinks, e.g. after 2 MGy, only 0.5% of the carbons would be involved in crosslinks[5], but the n.m.r. intensity was reduced by 80%. Therefore, strong dipolar coupling must also be experienced by carbons in close proximity to crosslinks. Both the soluble and insoluble portions of the irradiated polymer must contribute to the n.m.r. signal, since the decrease in signal is less than the decrease in solubility. Significant mobility must be experienced in part of the swollen gel, presumably in chain segments distant from crosslinks.

Table 1 N.m.r. spectral assignments and distribution of methylene carbons

Chemical shift (ppm)	Assignment	Distributions EP23	Distributions EP36
45–47	$S_{\alpha\alpha}$	0.017	0.070
37.58	$S_{\alpha\gamma}$	0.031	0.077
37.23	$S_{\alpha\delta^+}$	0.147	0.141
34.53	$S_{\alpha\beta}$	0.020	0.060
32.91	$T_{\delta^+\delta^+}$		
30.48	$T_{\beta\delta^+}$		
30.31	$S_{\gamma\gamma}$	0.065	0.098
30.14	$S_{\gamma\delta^+}$	0.107	0.100
29.77	$S_{\delta^+\delta^+}$	0.443	0.237
27.87	$T_{\beta\beta}$		
27.52	$S_{\beta\gamma}$	0.021	0.033
27.19	$S_{\beta\delta^+}$	0.125	0.141
24.59	$S_{\beta\beta}$	0.024	0.043
21.35	$P_{\beta\beta}$		
20.42	$P_{\beta\gamma^+}$		
19.79	$P_{\gamma^+\gamma^+}$		
		1.000	1.000

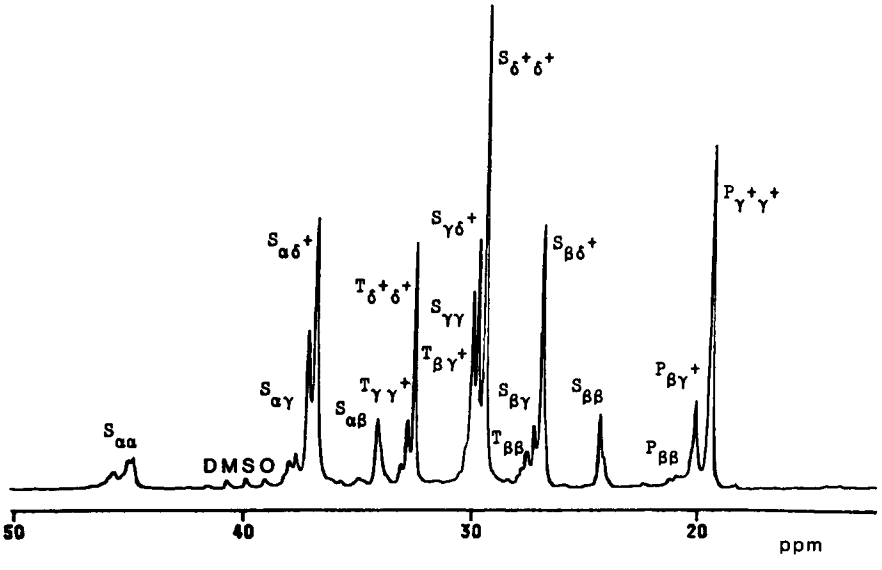

Figure 1 High-resolution ^{13}C n.m.r. spectrum of EP36 in trichlorobenzene (10% w/v) at 120°C and 25 MHz. For symbols, see text

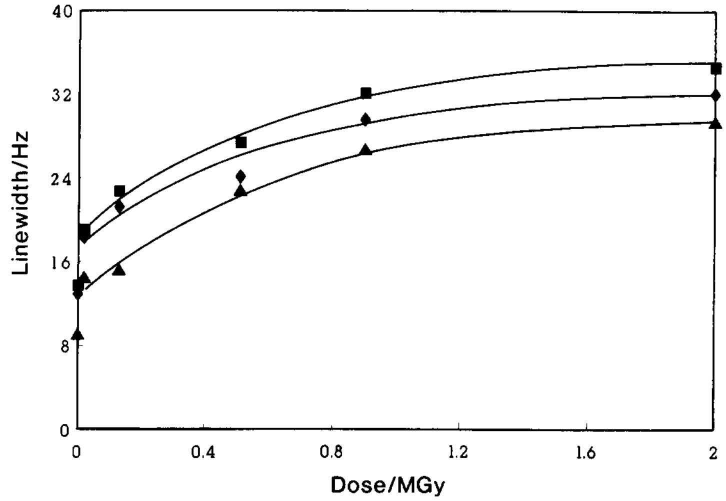

Figure 2 Line widths of peaks due to methyl ($P_{\gamma^+\gamma^+}$, ■), methylene ($S_{\delta^+\delta^+}$, ▲) and methine ($T_{\delta^+\delta^+}$, ◆) carbons in the ^{13}C n.m.r. spectra of EP36 as a function of radiation dose

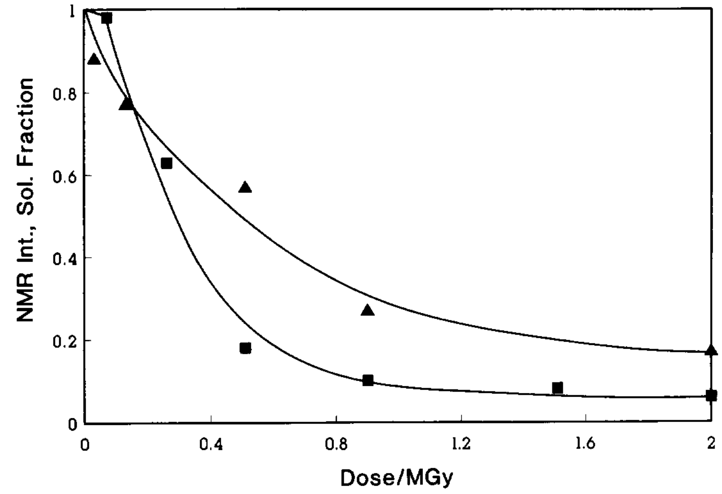

Figure 3 Dependence on radiation dose of (▲) total ^{13}C n.m.r. signal intensity, and (■) soluble fraction, for EP36

Crosslinks

The ^{13}C n.m.r. spectra of EP36 after 0.02, 0.135 and 0.5 MGy (*Figure 4*) show a new peak at 42.2 ppm, which we have assigned to carbons in H-type crosslink structures in agreement with the predicted chemical shift[5]. At low doses there is sufficient molecular mobility for H-links to be observed, but at higher doses dipolar broadening dominates and the signal disappears. The non-linearity of the intensity of this peak with irradiation dose precluded the determination of $G(X)$. The possible detection of Y-links was prevented by overlapping resonances.

H-links have been observed in irradiated liquid n-hexadecane and n-eicosane ($C_{20}H_{42}$) by Bennett *et al.*[14] and in n-$C_{44}H_{90}$ by Bovey *et al.*[15]. Randall *et al.*[1] have identified H-links in high-density polyethylene irradiated in the melt, but observed resonances which they attributed to Y-links after irradiation in the solid state. Horii *et al.*[3,4] were able to quantify the yields of H- and Y-links in polyethylene after irradiation under similar conditions.

These literature reports, and the present results, suggest that either the mechanism of crosslinking is different in rigid, solid hydrocarbons than in the melt or the amorphous state above the glass transition temperature, or that H-links are formed in irradiated rigid hydrocarbons but are not observed by ^{13}C n.m.r. in the liquid phase.

Chain scission

A variety of methyl chain-end structures are possible from main-chain scission in EP, owing to the presence of methyl substituents on the propylene units. The ^{13}C chemical shifts are sensitive to methyl groups up to five carbons away, which should enable the proportions of different chain-end structures resulting from main-chain scission to be determined from the ^{13}C n.m.r. spectra.

The predicted chemical shifts[16–18] of the methyl chain-end carbon and of the carbon α to the methyl for the different possible chain-end structures are given in *Table 2*. (The nomenclature used for the chain-end structures is that developed by Randall[19] for polyethylene.) Peaks at 11.3, 14.1, 14.5, 22.7 and 23.1 ppm are seen clearly in the expanded spectrum (10–25 ppm) in *Figure 5*, and are assigned to structures II–V. The other resonances are obscured by overlapping peaks from

Table 2 Predicted and observed ^{13}C n.m.r. chemical shifts for the possible saturated chain-end structures resulting from main-chain scission of EP copolymers

			Chemical shift (ppm)			
Number	Structure	Designation[a]	PE[b]	G–P[c]	L–A[d]	Observed
I	$-\underset{2}{\overset{\overset{CH_3}{\vert}}{C}H}-\underset{1}{CH_3}$	1, 1B1 2, B1	18.0[e] 29.5[e]	17.0 28.3	22.1 28.0	–[f] –[f]
II	$-\overset{\overset{CH_3}{\vert}}{C}H-\overset{2}{C}H_2-\overset{1}{C}H_3$	1, 1B2 2, 2B2	10.5[e] 29.2[e]	11.3 32.4	10.9 29.6	11.3 –[f]
III	$-\overset{\overset{CH_3}{\vert}}{C}H-CH_2-\overset{2}{C}H_2-\overset{1}{C}H_3$	1, 1B3 2, 2B3	14.5[e] 19.9[e]	14.1 20.3	14.1 20.4	14.5 –[f]
IV	$-\overset{\overset{CH_3}{\vert}}{C}H-(CH_2)_2-\overset{2}{C}H_2-\overset{1}{C}H_3$	1, 1B4 2, 2B4	14.0 23.2[e]	13.9 23.1	13.9 22.9	14.1 23.1
V	$-\overset{\overset{CH_3}{\vert}}{C}H-(CH_2)_{>2}-\overset{2}{C}H_2-\overset{1}{C}H_3$	1, 1B5 2, 2B5	14.0 22.9	13.7 22.9	13.9 22.7	14.1 22.7

[a] Nomenclature of Randall[19]
[b] From Axelson *et al.*[16]
[c] Predicted using the Grant–Paul rule[17]
[d] Predicted using the Lindeman–Adams rule[18]
[e] Corrected using Grant–Paul rule[17]
[f] Not observed owing to overlapping signals

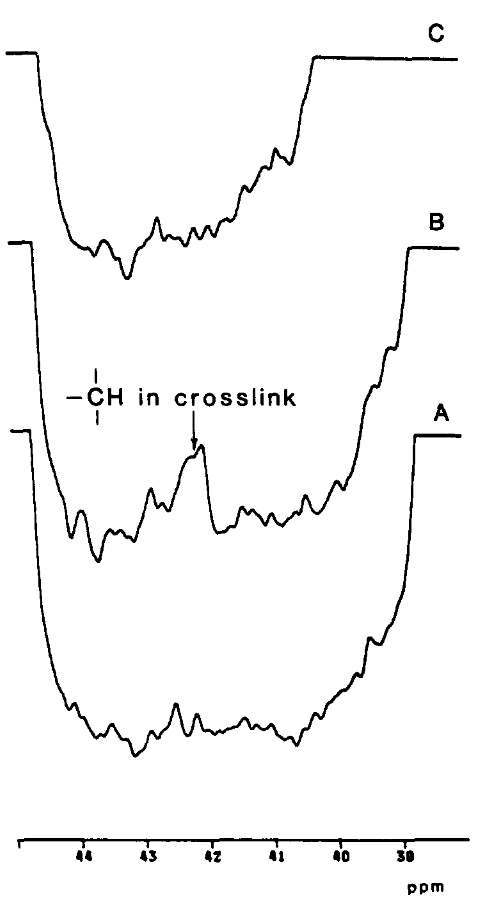

Figure 4 Expanded high-resolution ^{13}C n.m.r. spectra (38–45 ppm) of irradiated EP36 swollen with $CDCl_3$: (A) 0.02 MGy; (B) 0.135 MGy; (C) 0.5 MGy

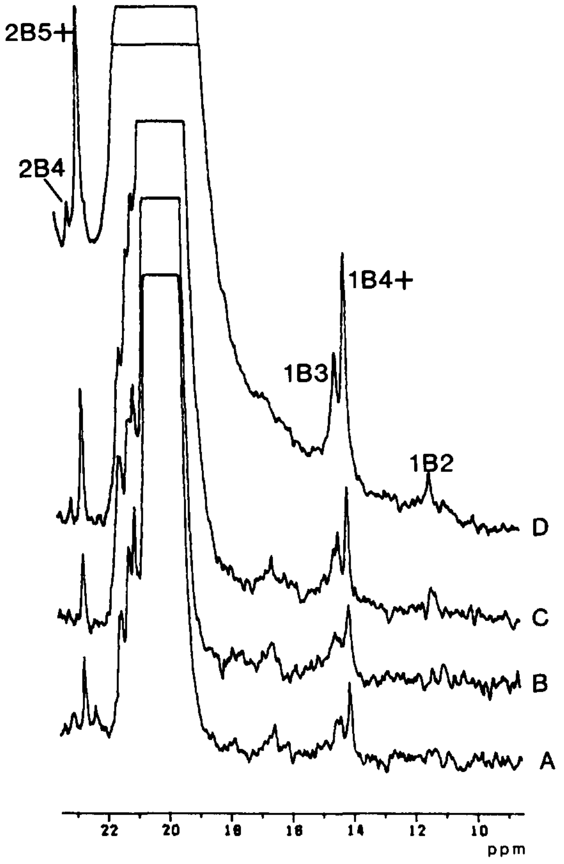

Figure 5 Expanded high-resolution ^{13}C n.m.r. spectra (8.25–23.5 ppm) of irradiated EP36 swollen with $CDCl_3$, showing new methyl (1B) and methylene (2B) chain-end structures: (A) 0.02 MGy; (B) 0.135 MGy; (C) 0.5 MGy; (D) 2 MGy. The peak designations are given in *Table 2*

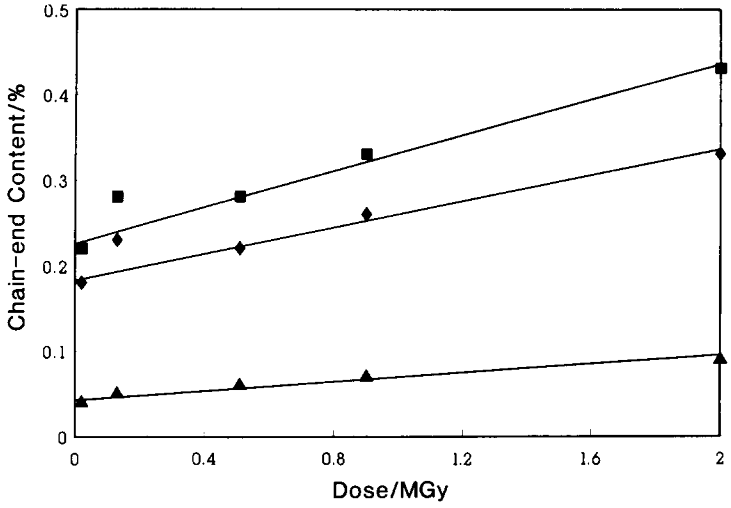

Figure 6 Dependence on radiation dose of the concentrations of new chain-end structures in irradiated EP36 determined by ^{13}C n.m.r.: (▲) propyl; (◆) butyl and longer; (■) total

Table 3 G values for crosslinking and scission in irradiated EP from solid-state ^{13}C n.m.r. spectra, high-resolution solution ^{13}C n.m.r. and soluble fraction analysis

Polymer	$G(X)$	$G(S)$	$G(S)/G(X)$
		Solid-state n.m.r.	
EP23	0.41	0.10	0.24
EP36	0.84	0.31	0.37
		Solution n.m.r.	
EP23	–[a]	0.16	–
EP36	–[a]	0.37	–
		Sol extraction	
EP23	0.45	0.13	0.30
EP36	0.82	0.38	0.46

[a] Not quantitative

methyl carbons on the backbone chain. The concentrations of chain-end structures III, IV and V increased linearly with dose, as shown in *Figure 6*, and G values can be calculated from the slopes of these plots. The total $G(S) = 0.37$ is in good agreement with the G value of 0.38 obtained by soluble fraction extraction and the value of 0.31 obtained previously from solid-state ^{13}C n.m.r. spectra after much higher doses[5]. Good agreement was also obtained for EP23 as shown in *Table 3*.

Proportions of chain-end structures

It is possible to calculate the proportions of different chain-end structures produced by irradiation of the distribution of methyl substituents in the unirradiated polymer if it is assumed that main-chain scission occurs at random. This calculation leads to a prediction for the ratio of (IV + V):III of 3.1 whereas the experimental value was 3.6.

However, C–C bond scission should be favoured by α substitution on account of the relative stabilities of the secondary and tertiary radicals. If it is assumed that scission is 1.6 times more likely at the C–C bond α to a methyl substituent than at other main-chain C–C bonds, then the calculated ratio of (IV + V):III would correspond to the experimental value of 3.6. This is the first spectroscopic evidence that scission in polyolefins is favoured adjacent to the branch point, although it has been inferred from measurements of $G(S)$.

Mechanism of chain scission

Two mechanisms have been suggested for main-chain scission in polyolefins involving either: (1) direct C–C scission[20]; or (2) C–H scission followed by β scission of the main-chain alkyl radical[21].

$$-CH_2-CH_2-CH_2-CH_2- \rightarrow -CH_2-\dot{C}H_2 + \dot{C}H_2-CH_2- + 2H \rightarrow -CH_2-CH_3 + CH_3-CH_2- \quad (1)$$

$$-CH_2-CH_2-CH_2-CH_2- \rightarrow -CH_2-\dot{C}H-CH_2-CH_2- + H \rightarrow -\dot{C}H_2 + CH_2{=}CH-CH_2- + H \rightarrow -CH_3 \quad (2)$$

Reaction 1 results in the formation of two methyl chain ends for every scission, whereas reaction 2 produces one methyl and one vinyl end group. Reaction 1 must occur preferentially in the EP copolymers under the present conditions of irradiation, since no new peaks were observed in the olefinic region of the ^{13}C n.m.r. spectra (new resonances would be expected at 114 and 143 ppm)[22].

CONCLUSIONS

H-crosslinks have been observed in γ-irradiated amorphous EP copolymers, confirming the previous solid-state n.m.r. results[5]. After high radiation doses only part of the crosslinked polymer is detected by solution n.m.r., owing to the presence of strong dipole–dipole interactions. Resonances due to crosslinks, and chain segments in the vicinity of crosslinks, are broadened at higher doses. However, peaks due to new end groups formed by chain scission were observed up to doses of 2 MGy, since these structures maintain their mobility within the crosslinked network. $G(S)$, calculated from the n.m.r. intensities, was in excellent agreement with previous values, demonstrating the quantitative validity of this technique. Furthermore, chain scission was found to occur preferentially at bonds adjacent to the methyl substituents, owing to the greater stability of the secondary radicals formed as intermediates. This mechanism of chain scission, involving cleavage of the main chain and H-atom addition, was further confirmed by the absence of new chain-end structures containing double bonds.

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