^{13}C NMR Studies of Photoinitiated Cross-Linking of Low-Density Polyethylene

Baojun Qu,* Xin Qu, and Yunhua Xu

Structure Research Laboratory, University of Science and Technology of China,
230026 Hefei, Anhui, P. R. China

Ulla Jacobsson[†] and Bengt Rånby[‡]

Department of Chemistry, Organic Chemistry and Department of Polymer Technology,
Royal Institute of Technology, S-100 44 Stockholm, Sweden

K. E. Russell and W. E. Baker

Department of Chemistry, Queen's University, Kingston, Ontario, Canada K7L 3N6

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ABSTRACT: Structures of cross-links produced in benzophenone-photoinitiated cross-linking of low-density polyethylene (LDPE) and a model compound n-$C_{24}H_{50}$ have been studied for the first time by solution-state ^{13}C NMR spectroscopy. Well-resolved resonance lines, assigned to CH_H, α-CH_2, and β-CH_2 groups related to H-cross-links, have been observed for the photo-cross-linked samples below the gel dose. At the same time, the resonance lines associated with Y-type long branches are also found to be significantly formed during the photoinitiated cross-linking of LDPE. The concentrations of H-links and Y-branches are estimated to be 5.7−16.9 and 7.6−21.6 per 10 000 carbon atoms, respectively, for the samples UV-irradiated for 5−10 s in the melt, indicating that Y-links also are effectively produced in the photoinitiated LDPE samples. These results are slightly but significantly different from those reported for high-energy radiation-induced cross-linking of high-density polyethylene.

Introduction

Photoinitiated cross-linking of polyethylene (PE) has been studied extensively for many years[1−11] and has led to recent industrial applications for manufacturing of cross-linked PE-insulated wire and cable.[12−14] However, many basic problems still remain unsolved. The chemical structure and nature of the cross-links is not known although the H-cross-links produced by photoinitiated cross-linking of LDPE have been proposed to be dominant, as shown by the spin-trapping ESR technique in preceding papers.[15,16] Therefore, there is considerable interest in direct observation and identification of the cross-links formed in photo-cross-linked polyethylene (XLPE).

High-resolution ^{13}C NMR spectroscopy in solution has been successfully used to measure the type and number of cross-links produced by high-energy radiation (γ or electron beam) of PE.[17−24] The ^{13}C NMR technique possesses the required sensitivity to detect concentrations of long-chain branches (Y-type) and H-type cross-links as low as approximately 0.5 structural units per 10 000 carbon atoms. However, previous ^{13}C NMR studies of irradiated PE with appreciable gel content have failed to show structural features associated with the radiation of PE, while corresponding studies on n-alkanes as model compounds of PE have been more successful for the identification of cross-links.[17−21] The problems involved in obtaining resonance signals from gelled PE are that NMR dipolar interactions in the gel phase are not effectively averaged through the available polymer molecular motions. Under such circumstances, the resonance lines would become too broad to be seen in solution-state ^{13}C NMR spectra. The approach of examining PE samples irradiated with absorbed doses less than the gel dose has led to identification of the structures formed in γ-irradiated PE prior to gelation. Bennett et al.[17] determined ^{13}C chemical shifts of the methine CH carbons and the neighboring CH_2 carbons for the H-type cross-links, using a model compound in solution. Bovey et al.[18] used this technique to identify both radiation-induced H-cross-links and long chain branches (Y-links) in n-alkanes irradiated in the molten state. Randall et al.[19−21] first observed radiation-induced long-chain branches (Y-links) in HDPE irradiated below the gel dose using ^{13}C NMR in solution. Such long branches, named Y-branches or Y-links, are not distinguished from the long branches usually involved in unirradiated PE samples. These Y-links were believed to result from reaction of terminal C=C bonds in polymer molecules with main-chain radicals. However, Randall et al. could not observe resonance lines associated with H-links for irradiated PE of high molecular weights. By using solution-state ^{13}C NMR, Horii et al.[22,23] have reported the observation of both Y- and H-links in γ-irradiated HDPE of relatively low molecular weight obtained by fractionation of the samples. They found that G values for formation of Y-links were higher at low irradiation temperatures, whereas H-links were formed more efficiently at high irradiation temperatures and in the melt. Recently, O'Donnell et al.[24,25] have reported new peaks at 42.2 ppm assigned to H-cross-links in γ-irradiated ethylene−propylene (EP) copolymers and reported the quantitative observation of H-links in γ-irradiated linear LDPE (LLDPE) from solid-state ^{13}C NMR spectra.

All the previous ^{13}C NMR work has been focused on high-energy radiation cross-linking of polymers. There is no report on the ^{13}C NMR study of photo-cross-linking of PE. In the present work, we have used the solution ^{13}C NMR method to study cross-link structures in photoinitiated cross-linking of LDPE and model com-

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* To whom correspondence should be addressed.

[†] Department of Chemistry, Organic Chemistry.

[‡] Department of Polymer Technology.

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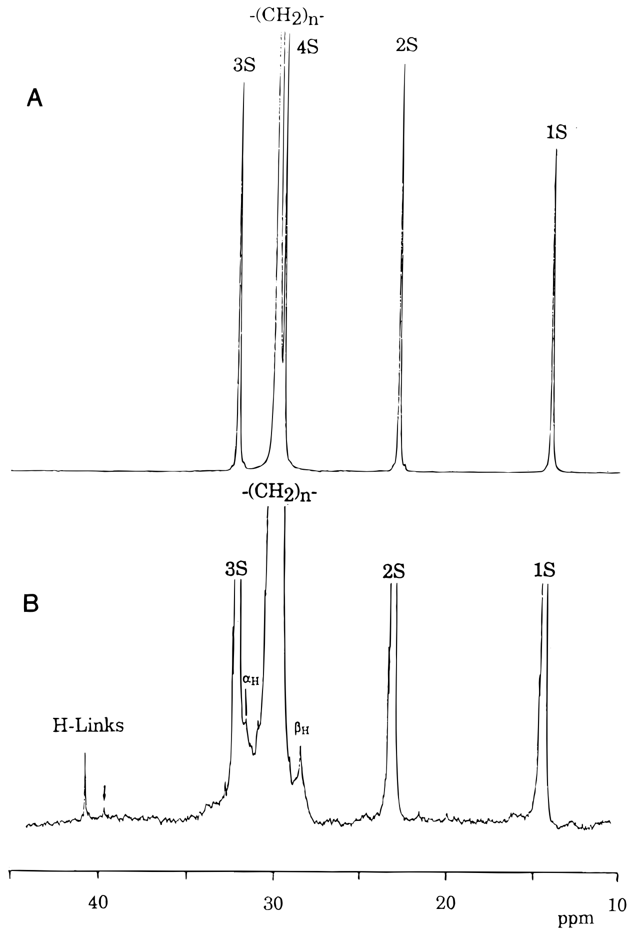


Figure 1. ^{13}C NMR spectra of n-$C_{24}H_{50}$ samples in solution: (A) unirradiated (50.3 MHz); (B) UV-irradiated at 70 °C in vacuum for 5 min (100 MHz).

pound $C_{24}H_{50}$ in the presence of benzophenone (BP) as photoinitiator. Our purpose is to detect and identify the type of cross-links as introduced by UV-photoinitiated cross-linking and to assess the number of cross-links by a direct and quantitative ^{13}C NMR method, in order to elucidate the cross-linking mechanism of LDPE initiated by UV irradiation.

Experimental Section

Materials. Tetracosane (n-$C_{24}H_{50}$, purity >99%, mp 49−52 °C, bp 391 °C) from Aldrich was used as a model compound. LDPE resin (NCPE 6600, MI = 0.3, density 922 kg/m^3, MW 140 000; M_w/M_n = 9) was supplied by Neste Polyeten AB, Sweden. Benzophenone (BP, purity >99%, mp 47−49 °C) from Merck was used as a photoinitiator. 1,2,4-Trichlorobenzene ($C_6H_3Cl_3$, 99+%, mp 16 °C, bp 214 °C) and benzene-d_6 (99.5 atom % D) from Aldrich were used as solvents in the ^{13}C NMR measurements. All the above chemicals are commercial products used as received.

Sample Preparation. $C_{24}H_{50}$ Samples. The photoinitiator (BP, 3 wt %) was dissolved in the liquid model compound $C_{24}H_{50}$ (1.0−1.5 g) at 60 °C in 10 mm o.d. quartz tubes to prepare samples for UV irradiation. The sample tube was evacuated by the freeze−thaw method to a vacuum of 1×10^{-5} Torr and sealed after degassing for 24 h. The samples in vacuum and at 70 °C were then irradiated with UV light (high-presure mercury lamp, Philips HPM 15 of 2 kW at 10 cm distance from the sample) for 3−5 min in a UV-CURE device in our laboratory.

LDPE Samples. Four LDPE samples with different UV irradiation times or prepared by different mixing methods were used in this work. Samples 1, 2, and 4 were prepared in a vacuum system with the following procedures. The photoinitiator (BP, 1%) was mixed in the LDPE resin (0.8−1.0 g) in a 10 mm o.d. NMR tube. The sample tube was evacuated and then sealed, as described above. Sample 1 was not irradiated by UV light. Samples 2 and 4 were irradiated for 5 and 10 s at 140 °C, respectively. After UV irradiation the samples were left in the tube at room temperature for 72 h to reduce the concentration of long-lived radicals.

For comparison with the sample preparation in vacuum, sample 3 was prepared in the normal way reported in our previous work.[6,11] The sample containing 50 g of LDPE and 0.5 g of BP (1%) was mixed for 10 min at 160 °C using a Brabender Plasticorder. After mixing, the sample was hot-pressed to sheets of 1 mm thickness for 5 min at 160 °C using a Schwabenthan-Polystat 400 S press. The sample was then UV-irradiated for 10 s under a nitrogen atmosphere. The other procedures are the same as those described above.

^{13}C NMR Measurements. ^{13}C NMR spectra were measured by using proton broad band decoupling on either a Bruker AM 400 spectrometer in Stockholm or a Bruker CXP-200 in Kingston, operating at 100.6 and 50.3 MHz and at 80 °C for $C_{24}H_{50}$ and 125 °C for the LDPE samples, respectively. The samples were dissolved in 1,2,4-trichlorobenzene/benzene-d_6 (TCB/C_6D_6 = 80/20 v/v) at about 20 wt % and sealed in NMR tubes (10 mm o.d.) after degassing. Deuterated chloroform ($CDCl_3$) was used as reference in the experiments.

The NMR experimental conditions used for the Bruker AM400 and CXP-200, respectively, are as follows: spectral width, 25 000 Hz (250 ppm) and 15 000 Hz (150 ppm); pulse delay (PD) after free induction decay (FID), 6.5 and 8 s; flip angle, 60 and 45° ; acquisition time, 0.655 and 0.541 s; data points, 32 and 16 k; accumulated FID's from 3000 to 11 000. The Bruker AM 400 was employed for the quantitative measurements of LDPE samples, whereas the Bruker CXP-200 was used for the error analysis of model compound $C_{24}H_{50}$. No correction was performed for the relative integral intensities of the resonance lines in question in the present study, because the nuclear Overhauser enhancement (NOE) was reported to be of almost the same order of magnitude for these lines in the high-energy radiation cross-linking of PE and its model compounds.[22]

Results and Discussion

Structural Changes in Photoinitiated Cross-Linking of $C_{24}H_{50}$. The structural changes of two $C_{24}H_{50}$ samples with and without UV irradiation have been studied by solution ^{13}C NMR spectroscopy, as shown in Figure 1. The 50.3 MHz ^{13}C NMR spectrum of the $C_{24}H_{50}$ sample before UV irradiation (shown in Figure 1A) consists of five clearly resolved resonances, as expected for a normal long-chain paraffin.[17−21] Figure 1B shows the 100.6 MHz ^{13}C NMR spectrum of the $C_{24}H_{50}$ sample after irradiation with UV light in vacuum in the melt (70 °C) for 5 min. Apparently, a new weak resonance line appears at 40.83 ppm. The new peak originates from the methine carbon atoms associated with the H-type cross-link structures, as reported for γ-irradiation of n-paraffins[17−21] and PE.[18−24] The resonance lines α-CH_2 and β-CH_2 associated with H-links overlapped on those of the 3S structural units and the $-(CH_2)_n-$, respectively. There appears a weak peak at 39.7 ppm, as indicated by the arrow in Figure 1B, which may be due to the branches called Y-cross-links, as reported in the literature.[20]

Photoinitiated Cross-Links of UV Irradiated LDPE Samples. The 100.6 MHz ^{13}C NMR spectrum of the unirradiated LDPE sample (no. 1) is shown in Figure 2A. It can be seen that the spectrum is well-resolved and very complicated. The spectral assignments for the main components are given in Table 1 by comparison with chemical shift data reported in the literature.[17−26] The spectrum of the unirradiated LDPE sample in Figure 2A is very similar to that reported for

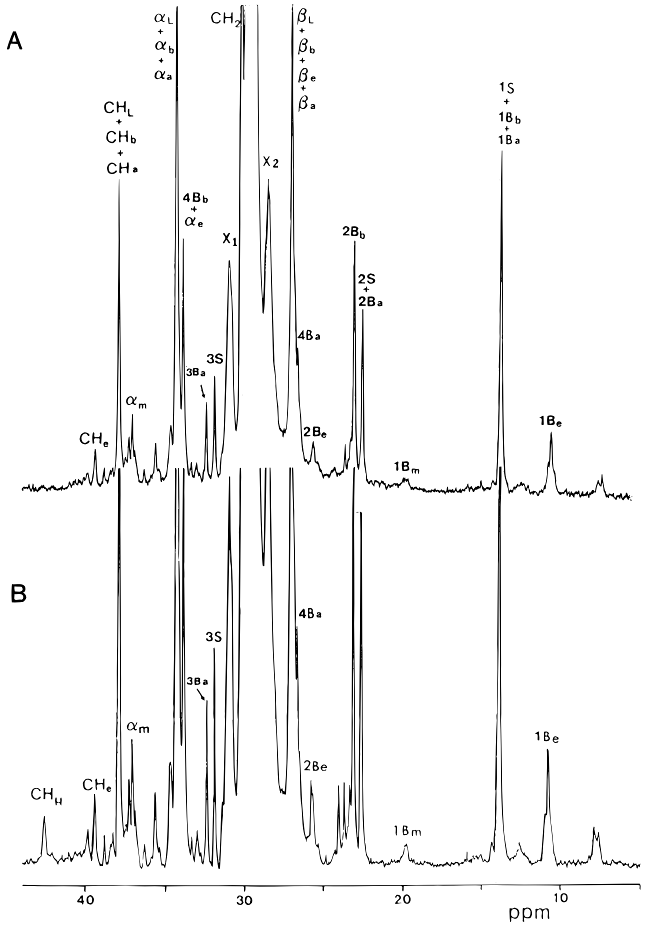


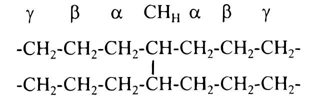
Figure 2. 100.6 MHz ^{13}C NMR spectra of LDPE samples measured in 20% TCB/C_6D_6 solution and at 125 °C: (A) unirradiated; (B) UV-irradiated for 10 s under a nitrogen atmosphere.

LDPE by Bovey et al.,[18,26] but it has much better resolution because of using a high-resolution 100.6 MHz ^{13}C NMR spectrometer. The resonance lines at 39.38 and 37.86 ppm are assigned to ethylene branches CH_e and butyl, amyl, and long branches ($CH_b + CH_a + CH_L$), respectively. The corresponding α and β positions of the various branches are assigned to the signals at 34.24 and 26.98 ppm, respectively. The signal X_1 at 30.78 ppm could be from the γ-CH_2 groups of various branches and the signal X_2 at 28.30 ppm from the overlapping of ($4S + 3B_b + 3B_a$) components, as given in Table 1.

Table 1. ^{13}C NMR Spectral Assignments for the Main Component of Unirradiated and Irradiated LDPE Samples

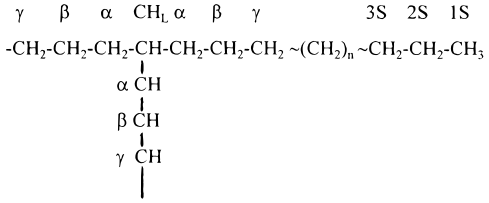
chemical shifts for unirradiated sample 1, ppm	assignment[a]	chemical shifts for irradiated sample 3, ppm
	CH_H[b]	42.50
39.38	CH_e	39.33
37.86	CH_L[c] + $CH_b + CH_a$ (+ CH_Y)	37.90
37.04	α_m	36.98
34.24	$\alpha_L + \alpha_b + \alpha_a$ (+α_Y)	34.24
33.86	$4B_b + \alpha_e$	33.74
32.39	$3B_a$	32.36
31.82	3S	31.82
30.78	$\gamma_L + \gamma_b + \gamma_a + \gamma_e$ (+γ_Y)	30.76
29.69	$-(CH_2)_n-$	29.68
28.30	$4S + 3B_b + 3\ B_a$	28.17
26.98	$\beta_L + \beta_b + \beta_e + \beta_a$ (+β_Y)	26.98
26.53	$4B_a$	26.46
25.56	$2B_e$	25.69
22.85	$2B_b$	22.78
22.47	2S	22.33
19.86	$1B_m$	19.73
13.79	$1S + 1B_b$	13.78
10.63	$1B_e$	10.62
7.78	$1B_{ee}$	7.78
7.50	$1B_{be}$	7.50

[a] L, S, and B refer to long branches, saturated end groups, and short branches; m, e, b, and a represent methyl, ethyl, butyl, and amyl groups, respectively; the Greek letter describes the position along the chain of the nearest substituent; CH_H and CH_Y represent the H-links and Y-type branches produced by UV irradiation, respectively. [b] Abbreviations according to the following structure:



$$\begin{array}{c} \gamma\quad\beta\quad\alpha\quad CH_H\quad\alpha\quad\beta\quad\gamma \\ -CH_2-CH_2-CH_2-CH-CH_2-CH_2-CH_2- \\ | \\ -CH_2-CH_2-CH_2-CH-CH_2-CH_2-CH_2- \end{array}$$

[c] Abbreviations according to the following structure:



$$\begin{array}{l} \gamma\quad\beta\quad\alpha\quad CH_L\quad\alpha\quad\beta\quad\gamma \qquad\qquad 3S\quad 2S\quad 1S \\ -CH_2-CH_2-CH_2-CH-CH_2-CH_2-CH_2\sim(CH_2)_n\sim CH_2-CH_2-CH_3 \\ \qquad\qquad\qquad\quad | \\ \qquad\qquad\qquad\ \alpha\ CH \\ \qquad\qquad\qquad\quad | \\ \qquad\qquad\qquad\ \beta\ CH \\ \qquad\qquad\qquad\quad | \\ \qquad\qquad\qquad\ \gamma\ CH \\ \qquad\qquad\qquad\quad | \end{array}$$

The 100.6 MHz ^{13}C NMR spectra of the LDPE samples 2 and 3 irradiated by UV light at 140 °C for 5 s in vacuum and 10 s in nitrogen atmosphere, respectively, are almost identical except for having different relative intensities. The ^{13}C NMR spectrum of sample 3 UV-irradiated in N_2 is shown in Figure 2B. A new resonance line at 42.50 ppm produced by the irradiation (CH_H; cf. Figure 2B) has been assigned to the H-links reported early in the model compound,[17] *n*-alkanes,[18−21] and polyethylene.[18−24] Compared with the value obtained from $C_{24}H_{50}$, the chemical shift of H-links from the XLPE sample has moved toward the low field, which is probably caused by hindered molecular movements from the polymer chain and higher gel contents. O'Donnell et al.[24,25] have reported the resonance line at 42.2 ppm assigned to H-links. Detection of α- and β-CH_2 carbons associated with the H-links in sample 3 was not possible due to overlapping resonances, i.e. γ-CH_2 (marked by X_1) at 30.76 ppm and ($4S + 3B_b + 3B_a$) components (marked by X_2) at 28.17 ppm (cf. Table 1).

For sample 4, prepared in vacuum and UV-irradiated for 10 s at 140 °C , the α- and β-CH_2 carbons associated with the H-links at 42.48 ppm were visible, as shown in Figure 3. The corresponding chemical shifts are listed in Table 2, together with the data reported in the literature.[18−23]

The chemical shifts of the long branches and Y-branches, which are referred to as CH_L, α_L, and β_L, are listed in Table 3. The corresponding data reported by Randall et al.[19−21] and Horii et al.[22,23] are presented in the same table. The relative intensities of the resonance lines associated with long branches are significantly increased in the UV-irradiated samples (nos. 2, 3, and 4) in comparison to those of the unirradiated sample 1. This indicates that the long branches produced by UV irradiation, which are called Y-branches or Y-links (CH_Y), are also formed in the photo-cross-linked samples. Randall et al.[19−21] have suggested that the production of the Y-branches could be a main cause of the gelation in high-energy radiation of HDPE.

Quantitative Determinations of the H-Links and Y-Branches in XLPE. The yield of H-links is obtained by dividing the integral intensity of the CH_H line at about 42.50 ppm (cf. Figure 2B) with the total intensity

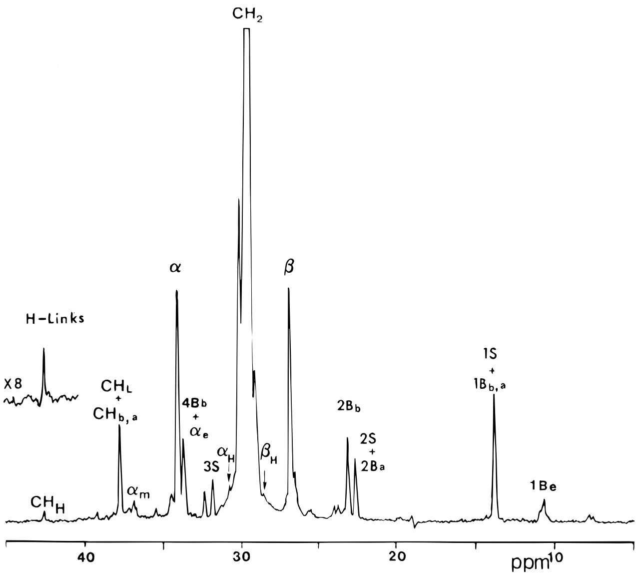


Figure 3. 50.3 MHz ^{13}C NMR spectrum of LDPE sample UV-irradiated for 10 s and measured in 20% TCB/C_6 D_6 solution at 125 °C in vacuum.

Table 2. Comparison of Chemical Shifts Associated with the H-Link

	chemical shifts, ppm			
H-link	sample 4 in this work	Bovey et al.[18]	Randall et al.[19−21]	Horii et al.[22,23]
CH$_H$	42.48	40.5	41.01	41.10
α$_H$	30.71	31.9	30.47	31.88
β$_H$	28.50	28.6	28.61	28.66
γ$_H$	30.17		30.60	30.20

Table 3. Chemical Shifts of the Long Branches in the LDPE and XLPE Samples

	chemical shifts, ppm					
	this work					
long branches	no. 1	no. 2	no. 3	no. 4	Randall et al.[19]	Horii et al.[22,23]
CH$_L$	37.86	37.71	37.90	37.70	38.19	38.23
α$_L$	34.24	34.10	34.24	34.06	34.55	34.62
β$_L$	26.98	26.84	26.98	26.89	27.30	27.33
γ$_L$	30.17	30.04	30.76	30.13		30.49

of the spectrum. However, the Y-branches (CH$_Y$) detected in the ^{13}C NMR are indistinguishable from the long branches (CH$_L$) in the unirradiated sample. In order to estimate the yield of Y-branches, we refer to the method described by Horii et al.[22] Under the assumption that there is no change by irradiation of the concentration of the original long branches, the yield of the Y-branches formed can be calculated as an increase in concentration of the long branches. However, the lines assigned to the CH, α- and β-CH$_2$ carbons of the long-chain (CH$_L$) and Y-type branches (CH$_Y$) are overlapping with those of the butyl, ethyl, and amyl branches. Therefore, in the present study the contributions from the original short branches should be removed from the integral intensities of the corresponding resonances associated with the Y-branches using the integrated intensities of the isolated lines, 2B$_b$, 2B$_e$, and 3B$_a$. For instance, the resonance lines of the CH carbons (CH$_L$) and α-CH$_2$ carbons (α$_L$) of the long branches (cf. Figure 2) are completely superimposed on the lines of the corresponding carbons, (CH$_b$ + CH$_a$) and (α$_b$ + α$_a$) for the butyl and amyl branches, respectively. By subtracting the integral intensities of the lines 2B$_b$ (butyl branch) at 22.78 ppm and 3B$_a$ (amyl branch) at 32.36 ppm from the integral intensities of CH$_L$ and α$_L$ resonances, the differences in concentration for the CH$_L$ and α$_L$ carbons between the irradiated and unirradiated samples are obtained. These results are assumed to be the yields of the CH$_Y$ and α$_Y$ carbons, respectively, of Y-branches produced by the UV irradiation. On the other hand, the line assignable to the β$_L$ carbon also contains contributions from the β$_b$, β$_e$, and β$_a$ carbons. Therefore, those additional contributions should be removed from the total integral intensities using the integral intensities of the resonance lines (2B$_b$, 2B$_e$, and 3B$_a$) of the CH$_2$ carbons in the butyl, ethyl, and amyl branches, respectively. Then, the yield of β$_Y$ is determined in the same manner as for the CH$_Y$ and α$_Y$ carbons. The number-averaged values of the CH$_Y$, α$_Y$, and β$_Y$ carbons (1:3:3) are assumed to be the yield of the Y-branches.

Table 4. Photoinitiated Cross-Linking Yields of H-Links and Y-Branches for Different Irradiated LDPE Samples

		no. of units per 10 000 carbon atoms	
sample no.	irradiation conditions	H-links	Y-links
2	5 s in vacuum	5.7 ± 0.5	7.6 ± 0.5
3	10 s in N$_2$	12.6 ± 0.5	14.7 ± 0.5
4	10 s in vacuum	16.9 ± 0.5	21.6 ± 0.5

Table 4 shows the yields of H-links and Y-branches thus determined for the three differently irradiated LDPE samples. As we can see, the H-links and Y-branches are of the same order of magnitude in the XLPE samples. For the 5 and 10 s irradiation times in vacuum or N$_2$, the number of H-links and Y-branches are 5.7−16.9 and 7.6−21.6 per 10 000 carbon atoms, respectively. Thus, in the photoinitiated cross-linking of LDPE in the melt, the Y-branches are also formed as efficiently as the H-links. These results are somewhat different from those reported for γ-radiation-induced cross-linking of HDPE having a relatively low MW fraction.[22,23]

Error Analysis of H-Cross-Link Concentration in $C_{24}H_{50}$ Samples. The ^{13}C NMR basic requirements for quantitative analyses of various PE structural units, such as correct choice of solvent, consideration of concentration effects on line width and of satisfying the "nuclear Overhauser effects" (NOE), and the spin−lattice relaxation times (T_1) requirements, etc., have been reviewed.[27] It was reported[22,23] that 0.5 structural units per 10 000 C atoms in PE can be identified by high-resolution ^{13}C NMR measurements in solution at a sample concentration of 15−20% and at 398−405 K. In the present work, the sample preparation and the ^{13}C NMR experimental conditions are basically the same as those in the work reported by Horii et al.[22,23] However, the pulse delay (PD) after FID is shorter and the accumulation of FID is less than those in their literature. Horii et al.[22] have studied the ^{13}C spin−lattice relaxation times of the various carbons in γ-irradiated HDPE. The T_1 values they obtained are as follows: $-(CH_2)_n-$, 3.30 s; 1S, 12.4 s; 2S, 11.2 s; 3S, 7.6 s; CH$_H$, 0.30 s; α-CH$_2$, 0.7 s; and β-CH$_2$, 1.0 s. Apparently, the pulse delay (PD) of 8 s after FID used in this work is not sufficient for the rf excited carbon nuclei of $-(CH_2)_n-$, 1S, 2S, and 3S to be fully relaxed between pulses, although the signal intensity of H-links $-(CH_H)-$ is not affected because of its very short T_1 (0.3 s). Normally, the pulse delay requires a pulse spacing of 5T_1 for 90° flip angles in the ^{13}C NMR quantitative measurement.[28] Therefore, it is nessary to estimate the

Table 5. Relative Integrated Intensities of Various Structural Units and Yields of H-Links Formed in Photoinitiated Cross-Linking of $C_{24}H_{50}$

structural units	relative integrated intensities of irradiated samples 0 min	3 min	5 min	mean errors,[a] %
$-(CH_2)_n-$	45.82	44.06	43.31	+0.7
1S	4.75	4.49	4.64	−5.4
2S	4.92	4.78	4.72	−2.2
3S	5.23	4.79	4.86	+1.2
H-links		0.10	0.13	
TCI[b]	60.73	58.12	57.53	1.3
no. of H-links per 10 000 carbon atoms		8.5	11.0	

[a] The mean errors are calculated according to the ratio of carbon atoms in the various units of $C_{24}H_{50}$ before UV irradiation: 1S:2S:3S:$-(CH_2)_n-$ = 1:1:1:9. [b] The total carbon intensities (TCI) for a ^{13}C NMR spectrum are given by[20] TCI = $A + 3S$, where S is the average intensity observed for the 1S, 2S, and 3S carbons and the A term is the average intensity of the repeating methylene units.

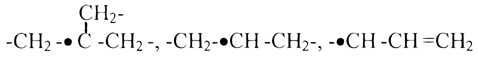
error of quantitative analysis by using the simple model $C_{24}H_{50}$ in this work.

The relative integrated intensities of various structural units from 50.3 MHz ^{13}C NMR spectra of the photo-cross-linked $C_{24}H_{50}$ samples are given in Table 5. Based on the quantitative analysis of 50.3 MHz ^{13}C NMR spectra, the yield of H-links is 8.5 and 11.0 H-links per 10 000 carbon atoms obtained for the $C_{24}H_{50}$ samples UV-irradiated for 3 and 5 min, respectively. The mean error of the amount of the various structural units and the weighted mean error of the total integrated intensity are estimated according to the ratio of carbon atoms in various units of $C_{24}H_{50}$ before UV irradiation, as shown in Table 5. It appears that the weighted mean error 1.3% is within the error range of ^{13}C NMR measurements.

In ^{13}C NMR spectroscopy, the signal intensity of the various carbons is not always proportional to the chemical composition even if equilibrium magnetizations are used for each acquisition of the FID. This is due to the nuclear Overhauser enhancement (NOE), which induces an increase in signal intensity by a factor of 1.2−3.0 depending on the molecular mobility of the various carbon atoms. However, it was found that the correcting factors are small in γ-irradiated PE.[22] In addition, the lower flip angle 45° was used in our experiments. Therefore, the numbers of H-links estimated in this work are reliable results.

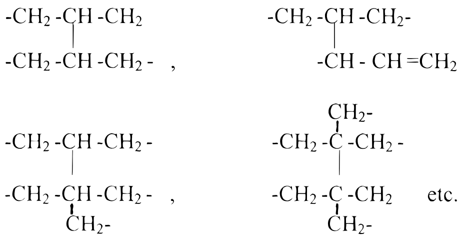
Mechanism of Photoinitiated Cross-Linking. In our previous studies,[15,16] we have identified by the ESR spin-trapping method the main radical intermediates in the presence of internal unsaturated double bonds. We did not detect end group radical intermediates in the photoinitiated XLPE. Therefore, we proposed that the H-links would be dominant by the combination of the above identified radical intermediates. However, in the present study we have determined not only H-links, but also Y-branches by ^{13}C NMR. This gives evidence that there must exist another mechanism forming Y-branches, which is not a recombination of two alkyl radicals which gives H-links. It is well-known that LDPE contains the structural units of paraffin, branches, and unsaturated double bonds, such as vinyl groups. They can react with the alkyl radicals produced by radiation to form Y-branches, as reported by Randall et al.[19]

According to the previous studies of radical intermediates[15,16] and the above analysis of cross-link structures in this work, a mechanism of photoinitiated cross-linking of LDPE can be proposed as follows. The triplet state ^{3}(BP)* abstracts hydrogen from the LDPE chain to form alkyl radicals, mainly tertiary and secondary carbon radicals, including allylic carbon radicals:[15,16]

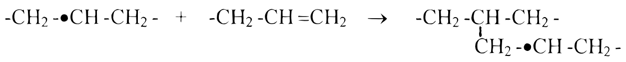


$-CH_2-\bullet\overset{CH_2-}{C}-CH_2-,\ -CH_2-\bullet CH-CH_2-,\ -\bullet CH-CH=CH_2$

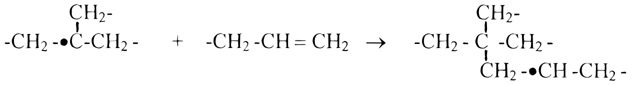
When the above radicals undergo recombination with each other, the H-links are formed as follows:



The Y-links can be produced by addition of the above radicals to vinyl end groups:



$-CH_2-\bullet CH-CH_2- + -CH_2-CH=CH_2 \rightarrow -CH_2-\underset{CH_2-\bullet CH-CH_2-}{CH}-CH_2-$



$-CH_2-\bullet\overset{CH_2-}{C}-CH_2- + -CH_2-CH=CH_2 \rightarrow -CH_2-\underset{CH_2-\bullet CH-CH_2-}{\overset{CH_2-}{C}}-CH_2-$

The vinyl end groups could be formed by β scission during the photoinitiated free-radical process except the original ones in the LDPE sample.

Conclusions

1. Both H- and Y-type cross-links produced during the BP-photoinitiated cross-linking of LDPE and model compound n-$C_{24}H_{50}$ in the melt have been detected and identified by the solution-state ^{13}C NMR method.

2. A new resonance line at 42.48 ppm for LDPE is assigned to methine carbons in H-links. The two corresponding resonance lines at 30.71 and 28.50 ppm can be assigned to α-CH_2 and β-CH_2 carbons (see Table 2). The corresponding data of H-cross-links from n-$C_{24}H_{50}$ are 40.83, 31.57, and 28.37 ppm, respectively.

3. The resonance lines associated with Y-branches or Y-links in LDPE overlap with those of the long branches CH_L at 37.90 ppm, α_L at 34.24 ppm, and β_L at 26.98 ppm (cf. sample 3 in Table 3). The intensities of resonance lines associated with the long branches increase with the UV irradiation time below the gel dose, showing that the Y-branches are also effectively formed in the photoinitiated cross-linking of LDPE in the melt.

4. The quantitative studies from the ^{13}C NMR measurements show that the concentrations of H-links and Y-branches are estimated to be 5.7−16.9 and 7.6−21.6 per 10 000 carbon atoms with the XLPE samples UV-irradiated for 5 and 10 s in the melt, respectively.

5. The estimate of mean errors from the experimental and theoretical calculations of model $C_{24}H_{50}$ shows that the quantitative measurements of cross-link structures in this work are reliable results within the normal error range in ^{13}C NMR.

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