

Review

**REACTION MECHANISM OF BENZOPHENONE-PHOTOINITIATED
CROSSLINKING OF POLYETHYLENE***

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Abstract The radical intermediates, the crosslink microstructures, and the reaction mechanism of benzophenone (BP)-photoinitiated crosslinking of low-density polyethylene (LDPE) and model compounds (MD) have been reviewed in detail. The spin-trapping electron spin resonance (ESR) spectra obtained from the LDPE/BP systems with spin-trap agents show that two kinds of polymer radical intermediates are mainly formed: tertiary carbon and secondary carbon radicals. The spin-trapping ESR studies of MD/BP systems give further evidence that photocrosslinking reactions of PE predominantly take place at sites of tertiary carbon, secondary carbon, and especially allylic carbon when available. The high resolution ^{13}C -NMR spectra obtained from LDPE and MD systems show that the crosslink microstructures have H- and Y-type links and that their concentrations are of the same order. The fluorescence, ESR, ^{13}C and ^1H -NMR spectra from the PE and MD systems demonstrate that the main photoreduction product of BP (PPB) is benzpinacol formed by the recombination of two diphenylhydroxymethyl ($\text{K}^\bullet$) radical intermediates. Two new PPB products: an isomer of benzpinacol with quinoid structure, 1-phenylhydroxymethylene-4-diphenylhydroxymethyl-2,5-cyclohexadiene and three kinds of α -alkyl-benzhydrols have been detected and identified. These results provide new experimental evidence for elucidating the reaction mechanism in the BP-photoinitiated crosslinking of polyethylene.

Keywords Photocrosslinking mechanism, Polymer radical intermediates, Crosslink microstructures, Photolytic products of benzophenone, Polyethylene, Model compound

INTRODUCTION

Photoinitiated cross-linking of bulk polyethylene (PE) in its melt form has been studied extensively for many years^[1–11] and has led to recent industrial applications for manufacturing cross-linked PE-insulated wire and cable^[12–16]. Benzophenone (BP) and its derivatives as photoinitiators can efficiently initiate photocrosslinking of high-density polyethylene (HDPE), branched low-density polyethylene (LDPE), and linear low-density polyethylene (LLDPE). Photoinitiated crosslinks in the PE samples are experimentally proved by gel formation and swelling in good solvents, such as xylene. However, many basic problems, such as the chemistry of photoinitiated crosslinking, including identification of chemical species responsible for the crosslinks as well as the nature of the reactions leading to the crosslinks, remained unclear for a long time before the following publications appeared. The polymeric alkyl radical intermediates and microstructures of cross-links produced in the photocrosslinking of LDPE and its model compounds have been studied by spin-trap electron spin resonance (ESR)^[7, 8] and ^{13}C -NMR^[9]. The photolytic products and photoreduction mechanism of BP as a photoinitiator in the photoinitiated cross-linking of polyethylene have been investigated by means of fluorescence methods, ESR, ^{13}C and ^1H -NMR spectroscopy^[10].

The purpose of this article is to summarize our previous work and to further systematically clarify the

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mechanism of photoinitiated crosslinking of PE and the nature of the reactions leading to crosslinks.

DETECTION AND IDENTIFICATION OF LDPE RADICAL INTERMEDIATES

The spin-trapping electron spin resonance (ESR) technique has been successfully used to detect and identify the polymer radical intermediates ($P\cdot$) produced by photoinitiated reactions of LDPE in the melt^[7, 8]. 2,3,5,6-Tetramethylnitroso-benzene (ND) and 2,4,6-tri-*tert*-butylnitrosobenzene (BNB) are efficient spin traps for C-, N- and O-centered short-lived radicals, which are resistant to UV radiation and do not form new species detectable by ESR spectroscopy.

Spin-Trapping Reactions of the Radical Intermediates from the LDPE/BP/ND System

A typical nine-line ESR spectrum observed for the LDPE/BP/ND system above its melting point after UV irradiation for 5 min is shown in Fig. 1(a). The corresponding simulated spectra are shown in b, I_A and II_A of Fig. 1. The ESR spectra are quite stable even at high temperature (403 K), which is indicative of the spectra of spin-adducts formed by reactions of the spin trap ND with radical intermediates produced in the BP-photoinitiated crosslinking of LDPE. Spectrum b is formed by the addition of I_A and II_A (Fig. 1).

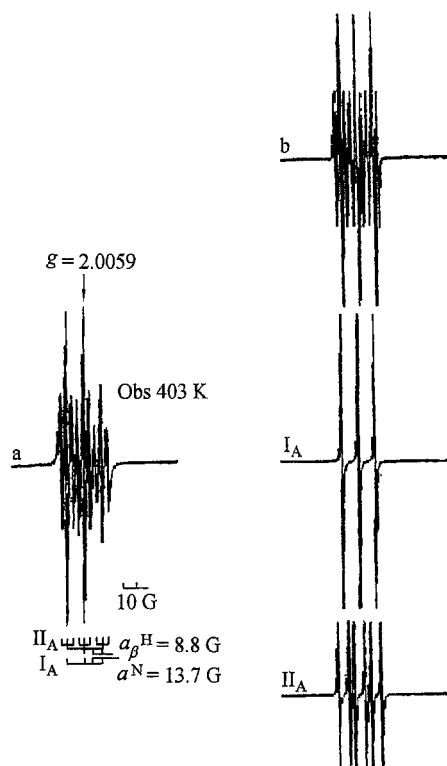


Fig. 1 (a) ESR spectrum observed at 403 K after UV-irradiation (5 min) of an LDPE/BP/ND sample at room temperature
(b) Simulated spectrum corresponding to the observed spectrum: simulated spectrum (I_A) of spin-adduct I_A of tertiary carbon radical and (II_A) of spin-adduct II_A of secondary carbon radical

The triplet and doublet-triplet peaks can be assigned to the spin-adducts I_A and II_A in the formulas (1) and (2). These adducts were formed by the reactions of the spin trap ND or BNB with the $P\cdot$ radical intermediates produced by hydrogen abstraction of the excited triplet state $^3(BP)^*$ from the PE chains. Therefore, the $P\cdot$ radical intermediates and the spin-trapping reactions with the trap ND are proposed to be the following:

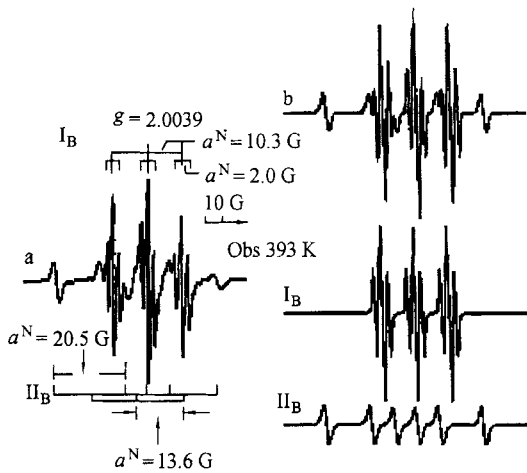
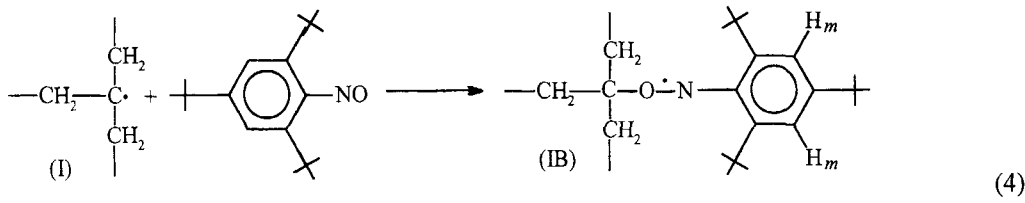


Fig. 2 (a) ESR spectrum observed at 393 K after UV irradiation (5 min) of an LDPE/BP/BNB sample at room temperature
(b) Simulated spectrum corresponding to the observed spectrum: simulated spectra (I_B , II_B) of the spin-adducts I_B and II_B .



Another component, II_B , which appears as a double triplet, is attributed to a nitroxide-type spin-adduct II_B , as shown in formula (5), because its splitting constant with β -H ($a^H\beta = 20.5$ G) and its g factor ($g = 2.0063$), show characteristic values for the nitroxide adduct. The spin-adduct II_B is assigned to the secondary carbon radical II:

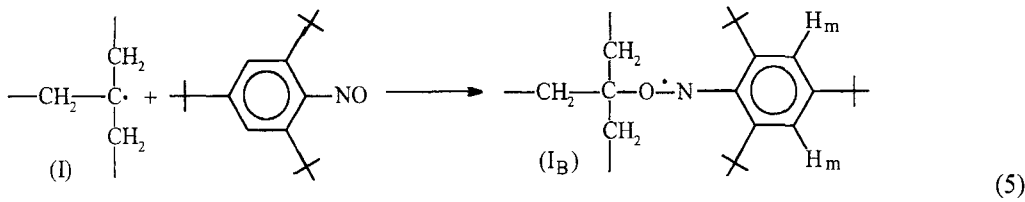


Table 1. Comparison of ESR parameters for the BNB spin-adducts formed by UV-irradiation of LDPE^[7] and γ -irradiation of *n*-eicosane^[17]

Trapped radical	Present results ^[7]				Obtained by Tabata <i>et al.</i> ^[17]			
	g value	a^N	splitting const, G		g value	a^N	splitting const, G	
			a^H_m	a^H_β			a^H_m	a^H_β
$\begin{array}{c} \text{CH}_2\text{---} \\ \\ \text{---CH}_2\text{---}\dot{\text{C}}\text{---CH}_2\text{---} \end{array}$	2.0039	10.3	2.0	—	2.0039	10.36	1.99	—
$\begin{array}{c} \text{CH}_2\text{---} \\ \\ \text{---CH}_2\text{---}\dot{\text{C}}\text{---CH}_3 \end{array}$	—	—	—	—	2.0046	10.5	1.93	—
$\text{---CH}_2\text{---}\dot{\text{C}}\text{H---CH}_2\text{---}$	2.0063	13.6	—	20.5	2.0063	13.1	—	20.6

Table 1 lists the ESR parameters for the BNB adducts of I_B and II_B . Apparently, the results in this work are in good agreement with those reported on the γ -irradiation of *n*-eicosane as a model compound for LDPE^[19]. The agreement between the observed (Fig. 2a) and the simulated spectrum (Fig. 2b) is quite satisfactory, which

further verifies the interpretations.

Spin-Trapping Reactions of LDPE Model Compounds

Commercial LDPE polymers usually contain small amounts of unsaturated C=C bonds (either as end groups or as inner groups) in addition to branch points and paraffin chain segments. Therefore, the following three kinds of model compounds for LDPE have been studied^[8]: *n*-paraffins, branched hydrocarbons, and unsaturated hydrocarbons containing allylic hydrogen.

n-Paraffins

The two *n*-paraffins C₂₄H₅₀ and C₁₂H₂₆ were used as models for long chain segments of LDPE. The ESR spectrum for the *n*-C₂₄H₅₀/BP/BNB obtained at 325 K after UV irradiation for 4 min at room temperature in vacuum (10⁻⁴ Torr) is shown in Fig. 3. The spectrum contains four components A–D represented by the stick diagrams in Fig. 3. These components are assigned to the anilino- and nitroxide spin-adducts A–D, respectively, as shown in Fig. 4.

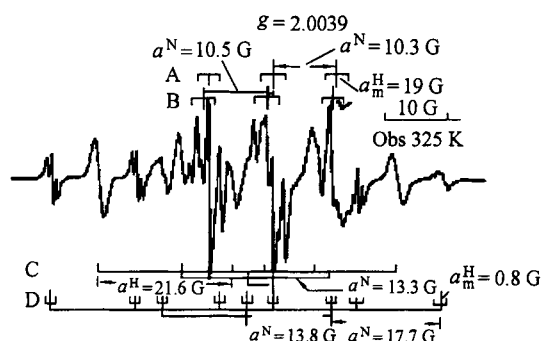


Fig. 3 ESR spectrum recorded at 325 K from the *n*-C₂₄H₅₀/BP/BNB system UV-irradiated and measured at 1 × 10⁻⁴ Torr and room temperature

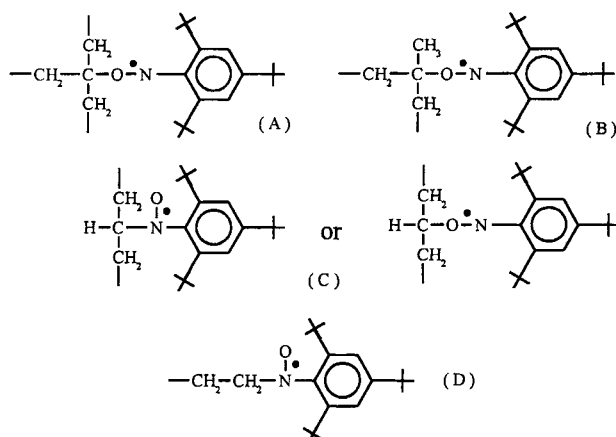


Fig. 4 Spin-adducts assigned as present in the *n*-C₂₄H₅₀/BP/BNB system irradiated with UV light

The spin-adducts A and B represent two types of tertiary carbon radicals, which form H-type and Y-type crosslinks in Silverman's nomenclature^[19]. We will discuss them in the following section. Originally, there is no tertiary bonded hydrogen in the *n*-paraffin model molecule. Therefore, the tertiary carbon radical formed by hydrogen abstraction originates from crosslinked dimers of two C₂₄H₅₀ molecules. The spin-adduct C is assigned to the secondary carbon radical generated by hydrogen abstraction from the CH₂ segments of the model molecule. The spin-adduct has either anilino- or nitroxide-type structure. The spin-adduct D is assigned to the small amount of chain end methylene radicals formed by hydrogen abstraction from methyl end groups. The ESR parameters and the assignments of the spectra to the radicals are in good agreement with those reported by Tabata et al. for crosslinking of *n*-eicosane by γ -irradiation^[17, 18]. The difference is that the chain end radical ($-H_2C\cdot$) was also detected in our experiment^[8].

The spin-adducts B and D (Fig. 4) were not detected in the ESR spectra of LDPE spin-adducts with spin traps ND and BNB. This is reasonable because LDPE macromolecules contain fewer end groups ($-CH_3$) compared with the model compounds.

The ESR spectrum of the spin-adduct from *n*-C₁₂H₂₆/BP/BNB at room temperature, recorded after UV irradiation under nitrogen for 5 min is almost the same as that of *n*-C₂₄H₅₀/BP/BNB and assigned to radicals of the same structure. The detailed ESR data of the spin-adducts A–D for the two *n*-paraffins and the assigned radical (A) to (D) are listed in Table 2.

The ESR data for the *n*-paraffins model compounds are interpreted as two main photoinitiated reactions: (i) The excited ³(BP)^{*} first abstracts hydrogen from methylene groups to form $-HC\cdot-$ radicals; (ii) After

combination of these radicals, the excited $^3(\text{BP})^*$ further abstracts labile tertiary hydrogen to form tertiary carbon radicals.

Table 2. ESR parameters of spin-adduct radicals $[\text{R-BNB}]^{\cdot}$ from *n*-paraffins^[8]

Paraffin	R ·	[R-BNB] · spin-adducts		
		<i>g</i> value	a^{N}_{m} G	a^{N}_{B} G
A: <i>n</i> -C ₂₄ H ₅₀ (at 1×10^{-4} Torr)	$\text{CH}_2\text{—}$	2.0039	A:10.3	1.9
	$\text{—CH}_2\text{—}\dot{\text{C}}\text{—CH}_2\text{—}$		B:10.4	1.9
	(A)			
	$\text{CH}_2\text{—}$	2.0045	A:10.5	1.9
B: <i>n</i> -C ₁₂ H ₂₆ (N ₂)	$\text{—CH}_2\text{—}\dot{\text{C}}\text{—CH}_3$		B:10.5	1.9
	(B)			
	$\text{—CH}_2\text{—}\dot{\text{C}}\text{H—CH}_2\text{—}$	2.0061	A:13.3	21.6
	(C)		B:13.3	21.7
	$\text{—CH}_2\text{—}\dot{\text{C}}\text{H}_2$	2.0062	A:13.8	17.9
			B:13.9	17.8

^a Not resolved

Branched hydrocarbons

Isooctane and 3-ethylhexane are model compounds for the branching units of LDPE chains, each of them only contains one tertiary bonded hydrogen but of different structures. The isooctane/BP/BNB (A) and 3-ethylhexane/BP/BNB (B) samples were UV-irradiated at room temperature for 3 min under N₂ atmosphere and for 5 min in vacuum, respectively. Their ESR spectra are shown in Figs. 5(a) and 5(b).

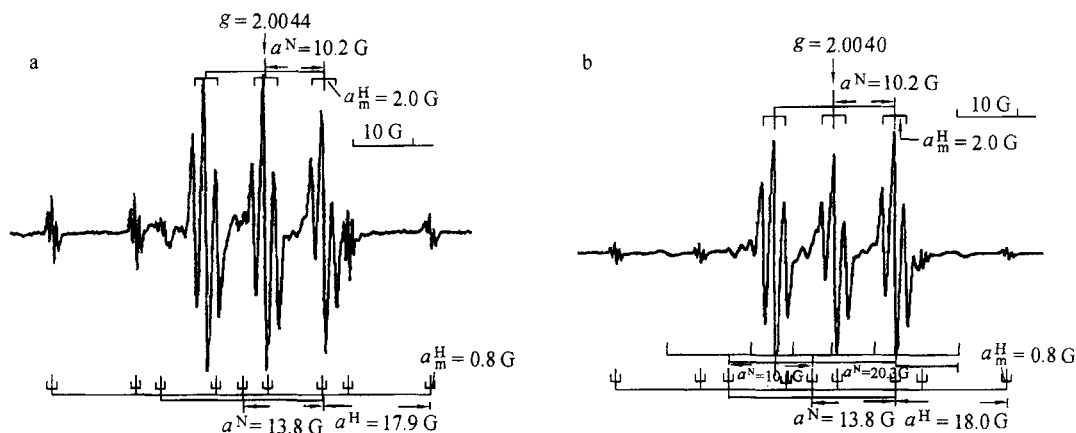


Fig. 5 (a) ESR spectrum of the 2,2,4-trimethylpentane (isooctane) /BP/BNB irradiated with UV light under nitrogen atmosphere; (b) spin-adduct radicals recorded for the 3-ethylhexane/BP/BNB UV-irradiated at 5×10^{-5} Torr

Two spectral components are identified in Figs. 5(a) and 5(b), which have been assigned to the radicals given in Table 3. The main component is a triplet of triplets due to the nitrogen (10.2 G) and the two meta hydrogen (2.0 G) of the phenyl group in the anilino-type spin-adduct as previously described. The weaker spectral component was assigned to a primary radical $\cdot\text{CH}_2\text{—}$ formed by hydrogen abstraction from one of the five methyl groups of isooctane (Table 3). The spectral component is a triplet of triplets of small triplets assigned to nitrogen (13.8 G), the two-methylene hydrogen (17.9 G) and the two-*meta* hydrogen (0.8 G) of the phenyl groups in BNB with the spin trap in nitroxide form. Hydrogen abstraction from methyl groups would occur in measurable amounts due to the high concentration of methyl groups in isooctane. There is no evidence of hydrogen abstraction from methyl groups in LDPE, and from CH₂ group in isooctane, probably due to the steric hindrance of the five methyl groups.

Table 3. ESR parameters of spin-adduct radicals [R-BNB][•] from tertiary hydrocarbons^[8]

	R•	[R-BNB] [•] spin-adducts			
		<i>g</i> value	<i>a</i> ^{N_α} , G	<i>a</i> ^{N_β} , G	<i>a</i> ^{N_m} , G
Isooctane (N ₂)	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{C}-\text{CH}_2-\dot{\text{C}}-\text{CH}_2 \\ \quad \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$	2.0044	10.2	-	2.0
	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{C}-\text{CH}_2-\text{CH}-\dot{\text{C}}\text{H}_2 \\ \quad \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$	2.0063	13.8	17.9	0.8
3-Ethyl-hexane (at 1×10 ⁻⁵ Torr)	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_2 \\ \\ \text{CH}_3\text{CH}_2\text{CH}_2-\text{C}-\text{CH}_2\text{CH}_3 \\ \\ \cdot \end{array}$	2.0040	9.9	-	1.9
	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_2 \\ \\ \text{CH}_3\text{CH}_2\dot{\text{C}}\text{H}-\text{CH}-\text{CH}_2\text{CH}_3 \\ \\ \cdot \end{array}$	2.0061	10.1	20.3	a
	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_2 \\ \\ \dot{\text{C}}\text{H}_2\text{CH}_2\text{CH}_2-\text{CH}-\text{CH}_2\text{CH}_3 \\ \\ \cdot \end{array}$	2.0062	13.6	18.0	0.8

^a Not resolved

The ESR spectrum of spin-adducts from UV-irradiated samples of 3-ethylhexane/BP/BNB contains three components (Fig. 5b). The main component is identical with that of isooctane (Fig. 5a) and is assigned to the tertiary radical (Table 3). The second component is also the same as that of isooctane with nearly the same hyperfine coupling constants. The third component is very weak, a triplet (*a*^N = 10.1 G) of doublets (*a*^{N_β} = 20.3 G), assigned to a radical formed by hydrogen abstraction from a CH₂ group of which there are four in the 3-ethylhexane molecule having less steric hindrance than isooctane.

The results for hydrogen abstraction from isooctane and 3-ethylhexane show that tertiary bonded hydrogen (>CH—) is easier to be abstracted in photocrosslinking with BP than are secondary (—CH₂—) and primary bonded hydrogen (—CH₃). This is well in line with the known bond dissociation energies (Table 4) for the three types of hydrogen^[20]. It was also reported^[21] that the relative rate constants for hydrogen abstraction from primary, secondary, and tertiary hydrocarbons of low molecular weight are 1:40:300. For a model compound with steric hindrance, the abstraction of hydrogen at primary and secondary carbons to form the corresponding radicals may still be favored by the high concentrations of CH₂ and CH₃. Tertiary hydrogen and end groups (CH₃) in LDPE are fewer in numbers compared with the secondary hydrogen in CH₂ groups.

Table 4. C—H bond dissociation energies^[8, 20]

Compounds	C—H (kcal/mol)
CH ₃ —CH ₂ —H	98
(CH ₃) ₂ CH—H	95
(CH ₃) ₃ C—H	91
H ₂ C=CHCH ₂ —H	88
H ₂ C=CH—H	104

Unsaturated hydrocarbons

Three kinds of unsaturated compounds, 1-hexene with a double bond as the end group and two with an inner double bond, *cis*- and *trans*-3-hexene, were used as model compounds. It was reported^[22, 23] that the small amounts of double bonds in commercial LDPE samples are important during the crosslinking of the polymer by

γ -irradiation.

The ESR spectrum of a 1-hexene/BP/BNB sample, UV-irradiated for 3 min under nitrogen atmosphere is shown in Fig. 6. Only one spectral component was detected, a triplet of doublets with coupling constants 21.6 G and 13.4 G with the g value 2.0061. This component was assigned to the spin-trapped allyl radicals. The broad lines of this spectrum (Fig. 6) may be due to the overlap of spin-trapped allyl and secondary carbon radicals, which have similar g values and hyperfine coupling constants. These two ESR spectra would be difficult to resolve and differentiate^[24].

Figure 7 shows the ESR spectra recorded for *trans*-3-hexene sample after UV irradiation in vacuum (1×10^{-5} Torr) but otherwise under the same conditions as used for 1-hexene. In Fig. 7, the dominant spectral component is assigned to a spin-trapped allyl radical, a triplet ($a^N = 10.2$ G) of doublets ($a^H_\beta = 20.4$ G) of small triplets ($a^H_m = 0.8$ G), due to coupling with the two-meta hydrogen of the phenyl group in the spin trap. There are also small amounts of two other components. One is a triplet ($a^N = 10.9$ G) of triplets ($a^H_m = 1.9$ G) which is tentatively assigned to a spin-trapped tertiary carbon radical. The other component is a triplet ($a^N = 13.5$ G) of triplets ($a^H_\beta = 18.0$ G) of small triplets ($a^H_m = 0.8$ G) assigned to a spin-trapped $\bullet\text{CH}_2-$ radical formed by hydrogen abstraction from a CH_3 group.

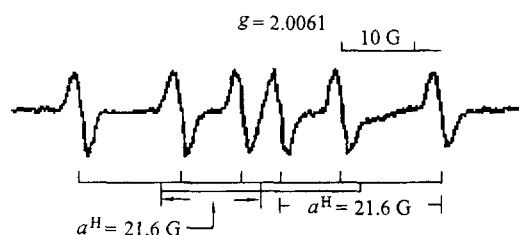


Fig. 6 ESR spectrum recorded at room temperature for 1-hexene/BP/BNB UV-irradiated under nitrogen atmosphere

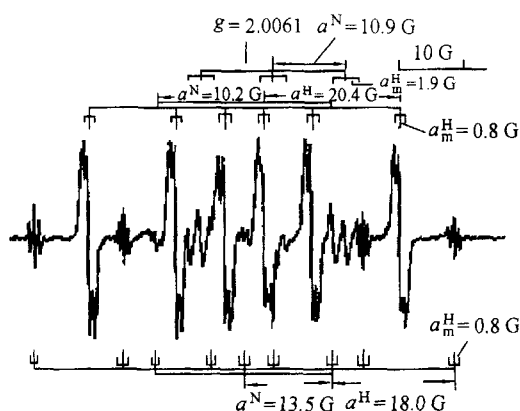


Figure 7 Spin-adduct radicals observed for *trans*-3-hexene /BP/BNB UV-irradiated at 5×10^{-5} Torr

The ESR spectrum of the *cis*-3-hexene is analogous to that of *trans*-3-hexene (Fig. 7). The assigned radicals from 1-hexene, *cis*- and *trans*-3-hexene are given in Table 5. There is good evidence for the assignment of the main radical components to allyl radicals.

¹³C-NMR STUDIES OF CROSSLINK MICROSTRUCTURES

The crosslink microstructures produced in BP-photoinitiated crosslinking of LDPE and a model compound $n\text{-C}_{24}\text{H}_{50}$ have been studied for the first time by solution-state ¹³C-NMR spectroscopy^[9]. Well-resolved resonance lines, assigned to CH_H , $\alpha\text{-CH}_2$, and $\beta\text{-CH}_2$ groups related to H-crosslinks, have been observed for the photocrosslinked samples below the gel dose. A new resonance line at $\delta = 40.83$ for $\text{C}_{24}\text{H}_{50}$ or at $\delta = 42.48$ for LDPE is attributed to the methine carbons in H-links. Two other resonance lines at $\delta = 31.57$ and $\delta = 28.37$ for $\text{C}_{24}\text{H}_{50}$ or at $\delta = 30.71$ and $\delta = 28.50$ for LDPE are assigned to $\alpha\text{-CH}_2$ and $\beta\text{-CH}_2$, respectively. At the same time, the resonance lines associated with Y-type long branches, which are referred to as CH_L at $\delta = 37.70$, α_L at $\delta = 34.43$, and β_L at $\delta = 26.89$, also appear to a significant extent during the photoinitiated crosslinking 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.

Table 5. ESR parameters of spin-adduct radicals [R-BNB] $\cdot$ from unsaturated compounds^[8]

R $\cdot$	[R-BNB] $\cdot$ spin-adducts			
	<i>g</i> value	a_{α}^N , G	a_{β}^N , G	a_{ms}^N , G
1-Hexene (N ₂) <chem>CH2=CH-CH(CH2)2CH3</chem>	2.0061	13.4	21.6	
<i>cis</i> -3-Hexene (at 1×10^{-5} Torr) <chem>CH3CH=C(CH2)2CH3</chem>	2.0061	10.1	20.3	0.8
	2.0062	13.3	17.6	0.8
	2.0036	10.9		1.9
<i>trans</i> -3-Hexene (at 1×10^{-5} Torr) <chem>CH3CH=C(H)CH2CH3</chem>	2.0061	10.2	20.4	0.8
	2.0062	13.5	18.0	0.8
	2.0036	10.9		1.9

H- and Y-Type Crosslinks in the Photoinitiated XLPE Samples

The 100.6 MHz ^{13}C -NMR spectra of the unirradiated and UV-irradiated LDPE samples are shown in Fig. 8. It can be seen that the spectrum of unirradiated sample (No.1) in Fig. 8(a) is well resolved and very complicated.

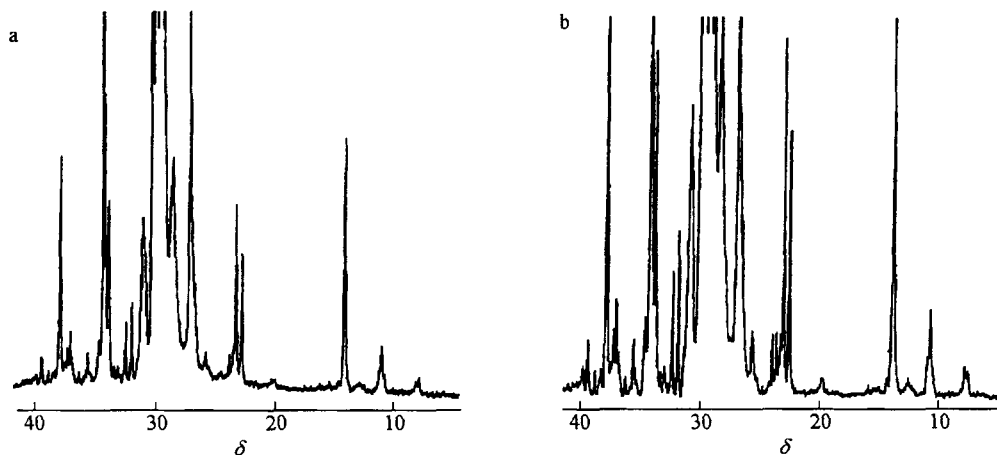


Fig. 8 100.6 MHz ^{13}C -NMR spectra of LDPE samples measured in 20% TCB/ C_6D_6 solution and 125 $^{\circ}\text{C}$
(a) Unirradiated; (b) UV irradiated for 10 s in N₂

The spectral assignments for the main components are given in Table 6 by comparison with chemical shift data reported in the literature^[25-34]. The spectrum of the unirradiated LDPE sample (Fig. 8a) is very similar to that reported for LDPE by Bovey *et al.*^[26, 34], but it has much better resolution. The resonance lines at $\delta = 39.38$ and 37.86 are assigned to ethylene branches CH_e and butyl, amyl, and long branches ($\text{CH}_b + \text{CH}_a + \text{CH}_l$), respectively. The corresponding α and β positions of the various branches are assigned to the signals at $\delta = 34.24$ and 26.98, respectively. The signal X_1 at $\delta = 30.78$ could come from the $\gamma\text{-CH}_2$ groups of various branches and

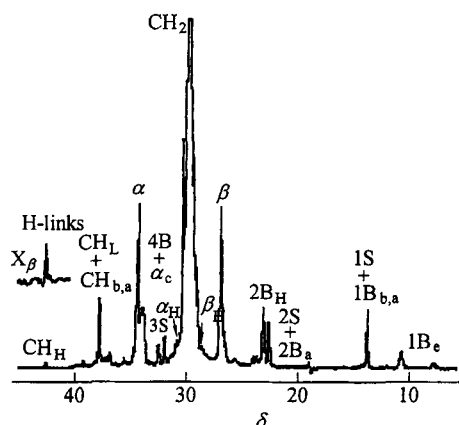


Fig. 9 50.3 MHz ^{13}C -NMR spectrum of LDPE sample UV-irradiated for 10 s and measured in 20% $\text{TCB}/\text{C}_6\text{D}_6$ solution and at 125°C in vacuum

Table 7. Comparison of chemical shifts associated with the H-Links^[9]

H-link	Chemical shifts, δ			
	Sample no.4 in this work ^[9]	Bovey <i>et al.</i> ^[26]	Randall <i>et al.</i> ^[27-29]	Horii <i>et al.</i> ^[30, 31]
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

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 8. The corresponding data reported by Randall *et al.*^[27-29] and Horii *et al.*^[30, 31] 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 (No. 2, No. 3, and No. 4) in comparison to those of the unirradiated sample No. 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 photocrosslinked samples. Randall *et al.*^[27-29] has suggested that the production of the Y-branches could be a main cause of the gelation in high-energy radiation of HDPE.

Table 8. Chemical shifts of the long branches in the LDPE and XLPE samples^[9]

Long branches	Chemical shifts, δ				
	This work ^[9]				Horii <i>et al.</i> ^[30, 31]
	no.1	no.2	no.3	no.4	
CH_L	37.86	37.71	37.90	37.70	38.19
α_L	34.24	34.10	34.24	34.06	34.55
β_L	26.98	26.84	26.98	26.89	27.30
γ_L	30.17	30.04	30.76	30.13	—
					0.49

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 $\delta = 42.50$ (cf. Fig. 8b) with the total intensity 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, the method described by Horii *et al.*^[29] was adapted. 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) overlap with those of the butyl, ethyl and amyl branches. Therefore, the contributions from the original short branches should be removed from the integral

intensities of the corresponding resonance 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 -CH₂ carbons (α_L) of the long branches (cf. Fig. 8) are completely superimposed on the lines of the corresponding carbons, ($CH_b + CH_a$) and ($\alpha_b + \alpha_a$) for the butyl and amyl branches, respectively. By subtracting the integral intensities of the lines $2B_b$ (butyl branch) at $\delta = 22.78$ and $3B_a$ (amyl branch) at $\delta = 32.36$ from the integral intensities of CH_L and α_L resonance, 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 the contributions from the β_b , β_e and β_a carbons. Therefore, these 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 CH₂ 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 9 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 N₂, 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 the relatively low MW fraction^[30, 31].

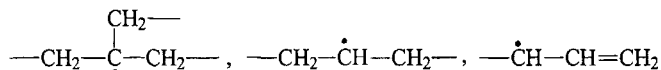
Table 9. Photoinitiated cross-linking yields of H-links and Y-branches for different irradiation samples^[9]

Sample no.	Irradiation conditions	No. of units per 10 000 carbon atoms	
		H-links	Y-links
No.2	5 s in vacuum	5.7 ± 0.57	6 ± 0.5
No.3	10 s in N ₂	12.6 ± 0.5	14.7 ± 0.5
No.4	10 s in vacuum	16.9 ± 0.5	21.6 ± 0.5

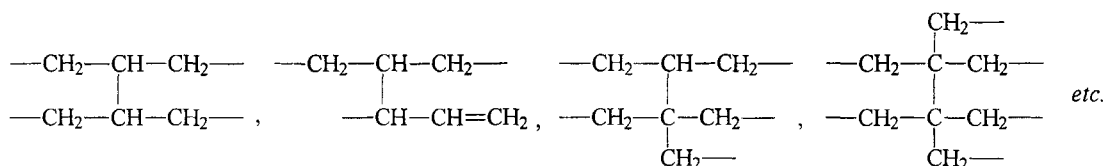
Formation Mechanism of Photoinitiated Crosslinks

The main radical intermediates in the presence of internal unsaturated double bonds of the MD compounds have been identified by the ESR spin-trapping method^[8]. We have not detected 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. Yet, we have determined not only H-links, but also Y-branches by ¹³C-NMR. This indicates that there must exist another mechanism of forming Y-branches, which is not a recombination of two alkyl radicals that gives H-links. It is well known that LDPE contains the structural units of paraffin, branches, and 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.*^[27–29].

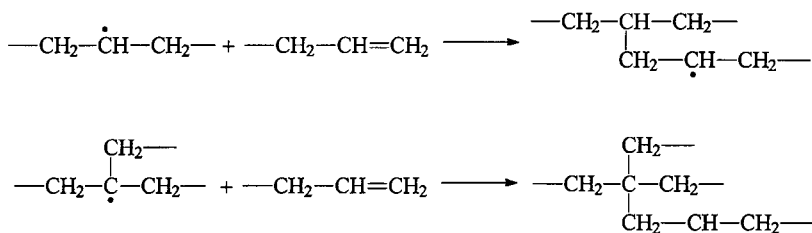
According to the studies in the last section, the polymer alkyl radical intermediates are mainly tertiary and secondary carbon radicals, including allylic carbon radicals:



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



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



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

DETECTION AND IDENTIFICATION OF BP PHOTOREDUCTION PRODUCTS

The photolytic products and a new photoreduction mechanism of BP as a photoinitiator in the photocrosslinking of PE and its model compounds have been studied by means of fluorescence, ESR, ^{13}C and ^1H -NMR spectroscopy^[10]. The fluorescence spectra of the PE and MD systems demonstrate that the main photoreduction product of BP (PPB) is benzpinacol formed by the recombination of two diphenylhydroxymethyl ($\text{K}\cdot$) radical intermediates. The ESR spectrum obtained from the UV irradiation of the MD/BP system gives positive evidence of $\text{K}\cdot$ radicals. Two new PPB products: an isomer of benzpinacol with quinoid structure, 1-phenylhydroxymethylene-4-diphenylhydroxymethyl-2,5-cyclohexadiene and three kinds of α -alkylbenzhydrols have been detected and identified for the first time by ^{13}C and ^1H -NMR spectroscopy from the MD systems. The latter could be formed by the reactions of $\text{K}\cdot$ radicals with alkyl radicals produced by hydrogen abstraction of the excited triplet state $^3(\text{BP})^*$ from polyethylene or its model compounds. These results provide new experimental evidence for elucidating the photoreduction mechanism of BP in the photoinitiated crosslinking of polyethylene.

Benzpinacol

Figure 10 shows the fluorescence spectra of pure benzpinacol, the PPB products obtained from different sample systems, and pure benzophenone. It can be seen that pure benzpinacol [Fig.10(A-a)] has an emission spectrum with a maximum at wavelengths between 290 and 310 nm, whereas no such emission spectrum was observed for pure benzophenone [Fig. 10(A-d)] under the same measuring conditions. Figure 10(A-b, c) shows the fluorescence spectra of PPB obtained from $n\text{-C}_{12}\text{H}_{26}$ /BP and isooctane/BP systems, respectively. Apparently, these two fluorescence spectra with a maximum peak between the wavelength 300 and 310 nm are similar to that from pure benzpinacol [Fig. 10(A-a)]. Therefore, the peaks shown in Fig. 10(A-b, c) should be associated with benzpinacol. However, the difference between the PPB and pure benzpinacol in the shape and shift of fluorescence peaks indicates the existence of other possible PPB products.

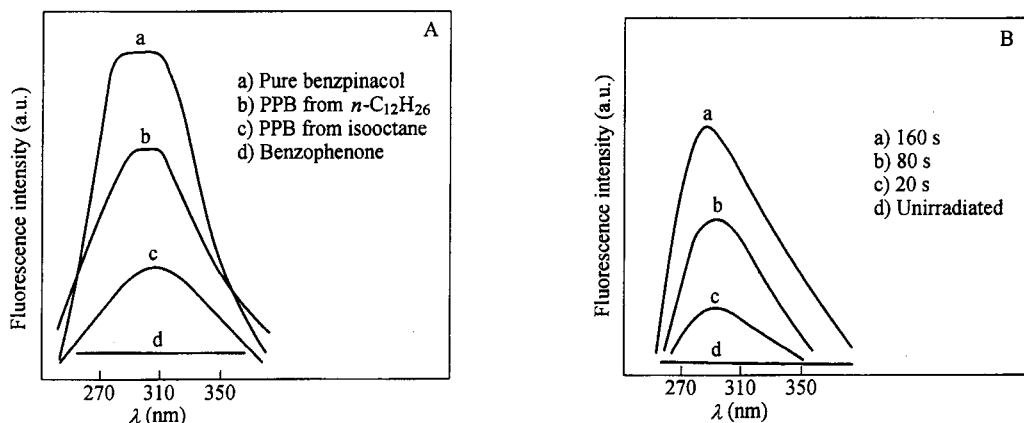


Fig. 10 Fluorescence spectra (A) several related compounds; (B) different UV-irradiated HDPE/1% BP films

Figure 10(B) shows the typical fluorescence spectra of HDPE/1%BP films with different UV irradiation times. For the unirradiated film, no emission spectrum was observed [Fig. 10(B-d)]. With shorter irradiation time (20 s), a peak with a maximum at about 290 nm began to emerge [Fig. 10(B-c)]; for longer irradiation times such as 80 s and 160 s, the fluorescence intensity at 290 nm increased rapidly [Fig. 10(B-a, b)]. All the data from the LDPE/BP and LLDPE/BP systems^[10] show the same results, that is, relative fluorescence intensities at 290 nm increase with the irradiation time and concentrations of BP in the samples, which means the increase of benzpinacol products. The above fluorescence spectroscopic results indicate that benzpinacol has been formed in the photoinitiated cross-linking of PE samples.

Ketyl Radical Intermediates

A well-resolved ESR spectrum recorded *in situ* at room temperature for *n*-C₁₂H₂₆/BP solution after UV-irradiation for several minutes is shown in Fig. 11(a). The spectrum with $g = 2.00326$ can be assigned to the BP ketyl radical intermediate (also called diphenylhydroxymethyl radical or semipinacol radical) produced by hydrogen abstraction of ³(BP)* from the *n*-C₁₂H₂₆ molecules. The hyperfine structure (hfs) coupling constants of the ketyl radicals determined from Fig. 11(a) are 3.30, 1.25, 3.68, and 2.03 G for the four *ortho*-, four *meta*-, two *para*-position protons of the phenyl rings, and one proton of the hydroxy group, respectively. The line width of the simulated spectrum was 0.1 G. Based on the above ESR parameters, the corresponding simulated spectrum is shown in Fig. 11(b). Apparently, the agreement between the observed (Fig. 11a) and the simulated spectrum (Fig. 11b) is quite satisfactory, which further verifies the assignment of the ketyl radicals. However, the counterpart alkyl radicals produced from *n*-C₁₂H₂₆ were not detected in Fig. 11. It can be explained that the life times of the transient alkyl radicals at room temperature are too short to be detected by ESR.

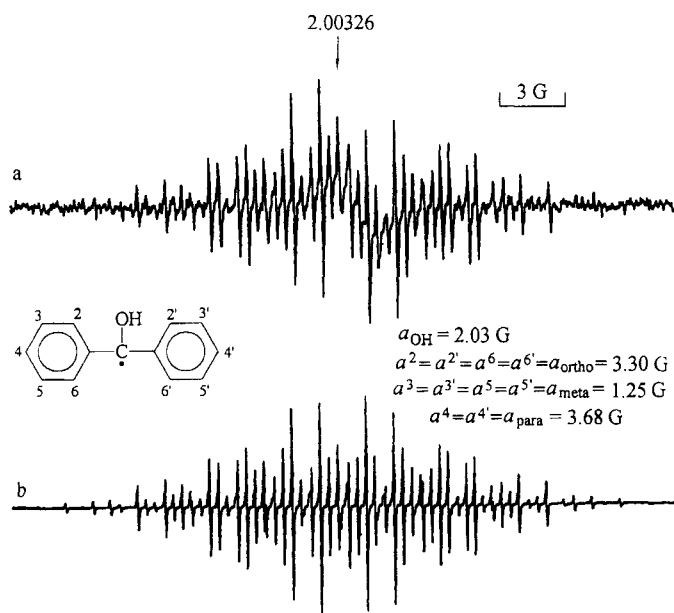


Fig. 11 (a) ESR spectrum observed *in situ* at room temperature after UV irradiation (5 min) of a *n*-C₁₂H₂₆/BP sample in the ESR cavity, (b) simulated spectrum corresponding to the observed spectrum. The line width parameter of the simulated spectrum was 0.1 G. The hfs parameters used for the simulated spectrum of ketyl radicals were $a_{\text{ortho}} = 3.30$ G, $a_{\text{meta}} = 1.25$ G, $a_{\text{para}} = 3.68$ G, and $a_{\text{OH}} = 2.03$ G

Isobenzpinacol as Benzpinacol Derivatives

In order to further detect and identify the other possible PPB products beside for benzpinacol, we have studied the structures of PPB in detail using ¹³C and ¹H-NMR methods. Figure 12 shows the 22.49 MHz ¹³C-NMR

spectrum of PPB obtained from the $C_{24}H_{50}/BP$ system^[10]. The resonance line at $\delta = 83.1$ can be assigned to the carbons associated with the $-OH$ group of benzpinacol. The peaks at $\delta = 144.3$, 127.4, 128.7, and 127.0 are assigned to the *substituted*-, *o*-, *m*- and *p*- carbons of the benzene ring in benzpinacol, respectively. The above assignments and symbols are also shown in Fig. 12. The peaks of the solvent $CDCl_3$ appear at $\delta = 75.7$, 77.1 and 78.5. These data are in good agreement with those of pure benzpinacol^[10].

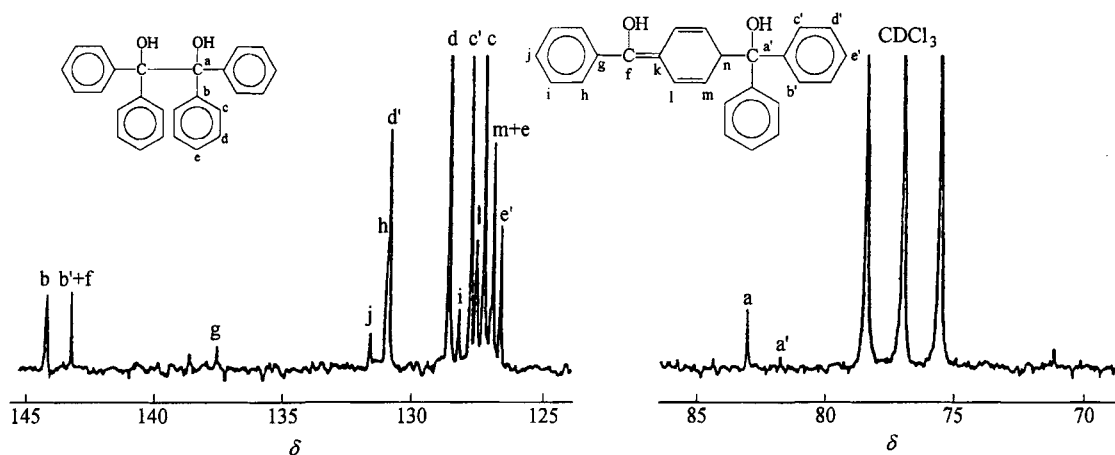


Fig. 12 ^{13}C -NMR spectrum of PPB from the n - $C_{24}H_{50}/BP$ sample

However, many other peaks in Fig. 12 still remain unknown, which indicate the existence of other PPB products. We have tentatively assigned these resonance lines to the isomer of benzpinacol with quinoid structure, 1-phenylhydroxymethylene-4-diphenyl-hydroxymethyl-2,5-cyclohexadiene. The peak a' at $\delta = 81.8$ has been assigned to the carbon bonded to the OH group and the peaks b' , c' , d' , and e' at $\delta = 143.3$, 127.9, 131.0, and 126.7 assigned to the corresponding carbon atoms of phenyl rings in the semipinacol part of the isomer. The peak n at about $\delta = 43.0$ may be due to the sp^3 hybridized carbon in the quinoid structure bonded with the semipinacol part. Because the quinoid isobenzpinacol product is much less than that of benzpinacol and unstable in the photoreduction of BP, their quantitative analysis is therefore impossible. The remained peaks between $\delta = 124$ and 138 originate from the corresponding carbon atoms of the aromatic rings and hydroxymethylene-2,5-cyclohexadiene in the part of the quinoid structural isomer. The above ^{13}C -NMR assignments and corresponding symbols of isobenzpinacol structures are also shown in Fig. 12. The yellowish samples obtained from the n - $C_{24}H_{50}/BP$ and n - $C_{12}H_{26}/BP$ systems also indicate the existence of quinoid structural isomers of benzpinacol, as reported in the literature^[35].

α -Alkylbenzhydrols

Figure 13 displays the 500.13 MHz ^1H -NMR spectrum of PPB from the n - $C_{24}H_{50}/BP$ sample^[10]. The stronger line at $\delta = 3.02$ and those between $\delta = 7.0$ and 7.3 can be assigned to the ^1H atoms in the OH group and the phenyl group of benzpinacol, respectively. We found that the peak at $\delta = 3.02$ disappeared completely when D_2O was added to the system to exchange the active ^1H atoms of the OH group. This indicated that the peak at $\delta = 3.02$ originates from ^1H of the OH group. The peaks marked a and b in Fig. 13 are characteristic of benzpinacol, as reported in the literature^[10].

In the previous studies^[8], we have identified the radical intermediates produced from the photoinitiated crosslinking of model compounds by spin trapping ESR spectroscopy. The ESR results confirm that there exist three kinds of radical intermediates in the photoinitiated reactions of two n -paraffins $C_{24}H_{50}$ and $C_{12}H_{26}$: (i) secondary carbon radicals $-CH_2-\dot{C}H-CH_2-$; (ii) tertiary carbon radicals $\dot{C}(CH_2-)_3$ or $CH_3-\dot{C}(CH_2-)_2$, and chain end methylene radicals $-CH_2-\dot{C}H_2$. Therefore, these radical intermediates could react with the BP ketyl radical intermediates to form various α -alkylbenzhydrols, except for forming the crosslinks by their

combination with each other.

The weaker peaks between $\delta = 0.88$ and 2.62 in the figure have been assigned to ^1H atoms from the α -alkylbenzhydrols (I), (II), and (III), as shown in Fig. 13. The small peaks at $\delta = 7.5\text{--}7.8$ indicate the existence of a small amount of isobenzpinacol. These results show that the secondary carbon radicals as the precursors of tertiary carbon radicals are the dominant intermediates. Figure 13 indicates that the corresponding peak intensities of α -alkylbenzhydrols (II) are dominant comparing with those of α -alkylbenzhydrols (I) or (III).

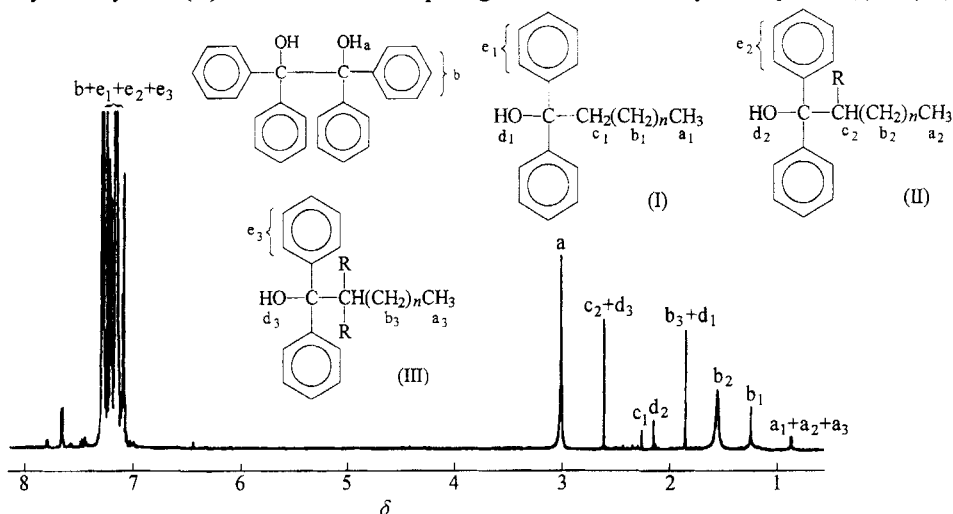


Fig. 13 ^1H -NMR spectrum of PPB from the $n\text{-C}_{24}\text{H}_{50}/\text{BP}$ sample

The corresponding analyses and tentative assignments of ^1H -NMR spectra of α -alkylbenzhydrols (I), (II), and (III) obtained from two n -paraffins $\text{C}_{24}\text{H}_{50}$ and $\text{C}_{12}\text{H}_{26}$ were reported in the literature^[10], and the chemical shifts of α -alkylbenzhydrol (I) fit well with those reported in the literature^[37].

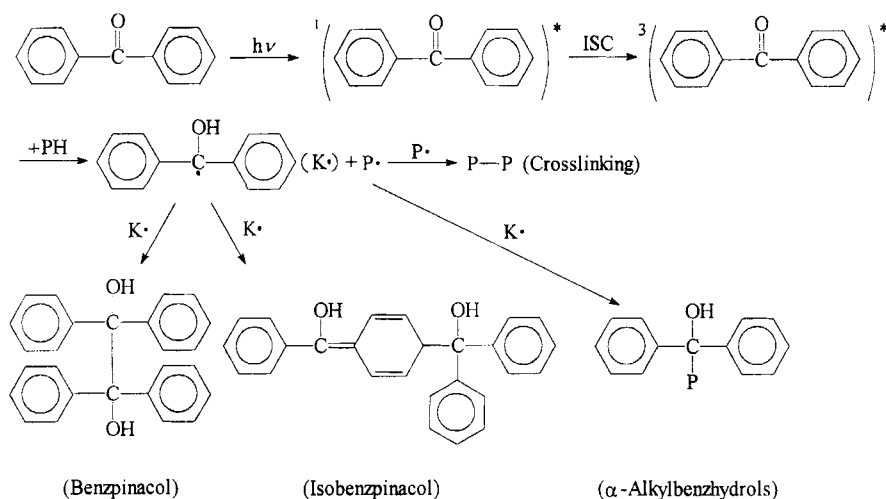


Fig. 14 A new mechanism of benzophenone photo-reduction in photoinitiated crosslinking of polyethylene and its model compounds

Reaction Mechanism of BP in the Photoinitiated Crosslinking of PE

When the photoinitiator BP absorbs a UV quantum, it is excited to the singlet state and then rapidly relaxes to the more stable triplet state $^3(\text{BP})^*$ through intersystem crossing (ISC). $^3(\text{BP})^*$ can abstract hydrogen from the PE

chains to form the ketyl ($K \cdot$) and polymer alkyl ($P \cdot$) radicals which are described in the previous section. The two $P \cdot$ radicals combine with each other to produce crosslinks. Based on the above studies of PPB products and photoinitiated crosslinking of PE^[7, 8], a new mechanism of BP photoreduction in the photoinitiated crosslinking of PE and model compounds can be proposed as described in Fig. 14.

REFERENCES

- 1 Rånby, B., "Photoinitiated reactions of organic polymers", in: "Polymer Science in the Next Decade", ed. by Vogl, O. and Immergut, E.H., J. Wiley, New York, 1987, p.121-133
- 2 Rånby, B., Chen, Y.L., Qu, B.J. and Shi, W.F., "Photoinitiated crosslinking of polyethylenes and unsaturated polyesters", in: "Polymers For Advanced Technology", ed. by Lewin, M., VCH Publ., New York, 1988, p.162-181
- 3 Qu, B.J., Shi, W.F. and Rånby, B., J. Photopolym. Sci. Technol., 1989, 2: 269
- 4 Chen, Y.L. and Rånby, B., J. Polym. Sci. Part A: Polym. Chem., 1989, 27: 4051, 4077; 1990, 28: 1847
- 5 Yan, Q., Xu, W.Y. and Rånby, B., Polym. Eng. Sci., 1991, 31: 1561, 1567; 1992, 32: 831, 1433
- 6 Qu, B.J. and Rånby, B., J. Appl. Polym. Sci., 1993, 48: 701, 711; 49: 1799
- 7 Qu, B.J., Xu, Y.H., Shi, W.F. and Rånby, B., Macromolecules, 1992, 25: 5215
- 8 Qu, B.J., Xu, Y.H., Shi, W.F. and Rånby, B., Macromolecules, 1992, 25: 5220
- 9 Qu, B.J., Qu, X., Xu, Y.H., Jacobsson, U. and Rånby, B., Macromolecules, 1997, 30: 1408
- 10 Qu, B.J., Xu, Y.H., Ding, L.H. and Rånby, B., J. Polym. Sci.: Part A: Polym. Chem., 2000, 38: 999
- 11 Wu, Q.H., Qu, B.J., Xu, Y.H. and Wu, Q., Polym. Degrad. Stab., 2000, 68: 97
- 12 Qu, B.J., Shi, W.F., Liang, R.Y., Jin, S.Z., Xu, Y.H., Wang, Z.H. and Rånby, B., Polym. Eng. Sci., 1995, 35: 1005
- 13 Rånby, B., 1992, Eur. Pat., 490854
- 14 Qu, B.J., Liang, R.Y., Shi, W.F., Jin, S.Z. and Xu, Y.H., 1991, Chinese Pat., 91 208158.9
- 15 Qu, B.J., Liang, R.Y., Xu, Y.H. and Shi, W.F., 1998, Chinese Pat., 98 250180.3
- 16 Qu, B.J., Xu, Y.H., Liang, R.Y. and Shi, W.F., 1998, Chinese Pat., 98 111722.8
- 17 Tabata, M., Sohma, J., Yamaoka, H. and Matsuyama, T., Chem. Phys. Lett., 1985, 119: 256
- 18 Tabata, M., Sohma, J., Yamaoka, H. and Matsuyama, T., Radiat. Phys. Chem., 1986, 27: 35
- 19 Randall, J.C., Zoepfl, F.J. and Silverman, J., Radiat. Phys. Chem., 1983, 22: 183
- 20 Morrison, R.T. and Boyd, R.N., "Organic Chemistry (5th Ed.)", Allyn and Bacon, Boston, 1987, p.21
- 21 Giering, L., Berger, M. and Steel, C., J. Am. Chem. Soc., 1974, 96: 953
- 22 Torikai, A., Asada, S. and Fueki, K., Polym. Photochem., 1986, 7: 1
- 23 Amin, M.U., Scott, G. and Tillekeratne, L.M.K., Eur. Polym. J., 1975, 11: 85
- 24 Hilborn, J. and Rånby, B., Macromolecules, 1989, 22: 1154
- 25 Bennett, R.L., Keller, A. and Stejny, J., J. Polym. Sci. Polym. Chem. Ed., 1976, 14: 3021, 3027
- 26 Bovey, F.A., Schilling, F.C. and Cheng, H.N., "Stabilization and degradation of polymers", in: "Advances in Chemistry Series 169", ed. by Allara, D.L. and Hawkins, W.L., American Chemical Society, Washington, DC, 1978, p.133
- 27 Randall, J.C., Zoepfl, F.J. and Silverman, J.J., Radiat. Phys. Chem., 1983, 22: 183
- 28 Randall, J.C., Zoepfl, F.J. and Silverman, J.J., Makromol. Chem., Rapid Commun., 1983, 4: 149
- 29 Randall, J.C., Zoepfl, F.J. and Silverman, J.J., "NMR and macromolecules: sequence, dynamic, and domain structure", in: "ACS Symposium Series 247", ed. by Randall, J.C., American Chemical Society, Washington, DC, 1984, p.245
- 30 Horii, F., Zhu, Q.R., Kitamara, R. and Yamaoka, H., Macromolecules, 1990, 23: 977
- 31 Zhu, Q.R., Horii, F., Kitamara, R. and Yamaoka, H., J. Polym. Sci., Polym. Chem. Ed., 1990, 28: 2741
- 32 O'Donnell, J.H. and Whittaker, A.K., Radiat. Phys. Chem., 1992, 39: 209
- 33 O'Donnell, J.H. and Whittaker, A.K., Polymer, 1992, 33: 62
- 34 Bovey, F.A., Schilling, F.C., McCrackin, F.L. and Wagner, H.L., Macromolecules, 1976, 9: 76
- 35 Rabek, J.F., "Mechanisms of Photophysical Processes and Photochemical Reactions in Polymers", John Wiley & Sons, Chichester, 1987, p.272