Photoinitiated Cross-Linking of Low-Density Polyethylene.[†] 6. Spin-Trapping ESR Studies on Radical Intermediates[‡]

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ABSTRACT: Radical intermediates formed by UV irradiation of low-density polyethylene (LDPE) in the presence of benzophenone (BP) as a photoinitiator have been trapped by using 2,3,5,6-tetramethylnitrosobenzene (ND) and 2,4,6-tri-*tert*-butylnitrosobenzene (BNB) as spin-trapping reagents. The resulting spin-adduct radicals have been characterized in situ by ESR spectroscopy. Two kinds of spin-adducts are detected and identified: a tertiary carbon radical and a secondary carbon radical which are formed by addition of the spin traps (ND or BNB) to two polymer radicals. These intermediates are produced by hydrogen abstraction of the BP excited triplet state from branch points and methylene groups of the LDPE chain, respectively. This is the evidence that the photo-cross-linking of LDPE mainly takes place at both tertiary carbons (branch points) and secondary carbons along the chains and that H-shaped links dominate. Secondary bonded hydrogens are less reactive but occur in a much larger number than tertiary bonded hydrogens in LDPE.

Introduction

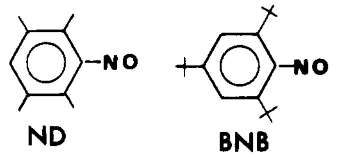
Recently, there has been some significant breakthroughs in the photoinitiated cross-linking of thick samples of polyethylene.[1-3] It is well established that both high-density (HDPE) and low-density polyethylene (LDPE) are readily photo-crosslinked by UV light in the presence of benzophenone (BP) or its derivatives as photoinitiators and cross-linkers.[4] Photoinitiated cross-links in the PE samples are experimentally proved by gel formation and swelling in good solvents. However, the chemistry of photoinitiated cross-linking, including identification of chemical species responsible for the cross-links as well as the nature of the reactions leading to the cross-links, has not been elucidated yet.

Conventional ESR techniques have been widely used to detect radicals generated by UV irradiation of polyethylene[5-10] in vacuum at liquid nitrogen temperature. Under these conditions, it is very difficult to obtain detailed information of the structure of the radicals produced because of the short lifetime of the initial radicals and the poor resolution of the ESR spectra from the macromolecular radicals in the solid state. The spin-trapping technique is a very efficient method for stabilizing short-lived radical intermediates[11-16] using nitroso compounds as spin traps. The short-lived free radicals formed in the system react with the traps and form stable nitroxide (or anilino-type) radicals. Well-resolved ESR spectra are obtained from the stabilized radicals (spin-adducts) in the liquid state or in the melt. In this way it is possible to identify various radical species present in a system. 2,3,5,6-Tetramethylnitrosobenzene (ND) and 2,4,6-tri-*tert*-butylnitrosobenzene (BNB) are efficient traps for C-, N-, and O-centered short-lived radicals,[17-21] which can be resistant to UV radiation and not form new species detectable by ESR spectroscopy. Therefore, spin traps are successfully applied in the investigation of photochemical processes.

The object of this work is to detect and identify the radical intermediates formed by the BP-photoinitiated cross-linking of LDPE, using spin-trapping reagents ND and BNB in order to clarify the mechanism of photoinitiated cross-linking reaction of LDPE.

Experimental Section

Materials. LDPE resin (1I2A-1, MI = 2.0) supplied by Yan Shan Petrochemical Co., Ltd., Beijing, was purified by reprecipitation twice from xylene solution into methanol. Benzophenone (BP) as photoinitiator from Shanghai Reagent Factory No. 1 (chemically pure) was used as received. The spin trap ND (mp 168–169 °C) was prepared in this laboratory according to the method reported by Smith et al.[22] The structure was checked by NMR and elemental analysis. Another spin trap BNB (mp 172–173 °C) from Aldrich was used as received. The formulas of the spin traps are as follows:



Sample Preparation. Photoinitiator BP (2 wt %) and spin trap ND or BNB (4 wt %) were dissolved in the LDPE resin melt to produce two kinds of sample systems designated LDPE/BP/ND and LDPE/BP/BNB. The LDPE/BP/ND or LDPE/BP/BNB mixture was put in a specially designed quartz ESR tube[23] and irradiated in vacuum by UV light (GGU-500 W, a high-pressure mercury lamp, made in Shanghai, with the main peaks of its emission spectrum located near 350 nm) in situ for 3–5 minutes at room temperature.

ESR Measurements. In control experiments, pure LDPE, containing spin traps, BP/ND, BP/BNB, LDPE/BP, LDPE/ND, and LDPE/BNB systems were irradiated with UV light under the same conditions as the corresponding LDPE sample system. ESR spectra of spin-adduct radicals were observed in irradiated LDPE/BP/ND and LDPE/BP/BNB systems in the molten state

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[†] A first report on rapid photo-crosslinking of polyethylene was given by Bengt Rånby at the International Symposium Honoring Herman F. Mark on his 90th Birthday, May 1985: *Polymer Science in the Next Decade*; Vogl, O., Immergut, E. H., Eds.; J. Wiley: New York, 1987; pp 121–133.

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using a Bruker ER 200 D X-band spectrometer equipped with a temperature controller and employing 100 kilocycle (kc)/s modulation. The g values were determined by comparison with the spectrum of DPPH (g = 2.0037). Hyperfine splitting constants were measured, using a Hall unit for calibration of the magnetic field. The microwave power incident on the cavity was of the order of 2 mW (20 dB), a level at which saturation of the resonance did not occur. The simulation spectra were carried out on an Aspect 3000 computer of the Bruker ER 200 D spectrometer.

Results and Discussion

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

Control experiments show that no detectable ESR signal is observed for the pure LDPE, the spin trap itself, and the BP/ND and LDPE/BP systems under the same irradiation conditions. However, in the LDPE/ND system, a very weak nine-line ESR spectrum can be detected after prolonged UV irradiation of 30 min, but the intensity was less than $^1/_{16}$th of that for the LDPE/BP/ND system.

Changes of the ESR Spectra with Temperature. To interpret the nine-line spectrum in Figure 1A, the changes with temperature of the ESR spectra of ND spin-adducts are observed, as shown in Figure 2. Below 325 K, the asymmetric triplet peaks are characteristic of the solid-state spectrum of a nitroxide spin-adduct. Above 325 K, the double triplet peaks begin to be resolved and the triplet peaks appear at 373 K, which is close to the melting temperature of LDPE. When the temperature is further increased, the intensity of the double triplet peaks begins to decrease, whereas the intensity of the triplet peaks first increases below 383 K and then decreases above 383 K (Figure 3). The relative intensities of the two groups of peaks (measured by comparing the relative amplitude of the first spectral line in each component at low field) have different decay rates with increasing temperature, as shown in Figure 3. Apparently, the nine-line spectrum consists of one triplet and another double triplet as shown in Figure 1 I_A and II_A. They arise from two different nitroxide species: in one species the unpaired electron interacts with the tertiary carbon groups and in the other species with the secondary carbon groups with a proton adjacent to the N atom. This indicates that the spin trap scavenges the radicals formed by hydrogen abstraction from LDPE chains.

Spin-Trapping Reactions of Radical Intermediates. According to the detailed analysis of the hyperfine structure (hfs) and the intensity distribution of the two nitroxide spin-adducts in Figure 1, the triplet and doublet–triplet peaks can be assigned to the spin-adducts I_A and II_A in formulas 3 and 4. These adducts are formed by the reactions of the spin trap ND with the radical intermediates (formula 2) produced by hydrogen abstraction of the excited triplet state $^3(BP)^*$ (formula 1). Therefore, the mechanism of photoinitiated cross-linking and the spin trapping are proposed to be following initial radical formation and spin-trapping reactions.

1. **Initial Radical Formation.** When the photoinitiator BP absorbs a UV quantum, it is excited to the singlet state and then rapidly (10^{-10} s) relaxes to the more stable triplet state $^3(BP)^*$ through intersystem crossing

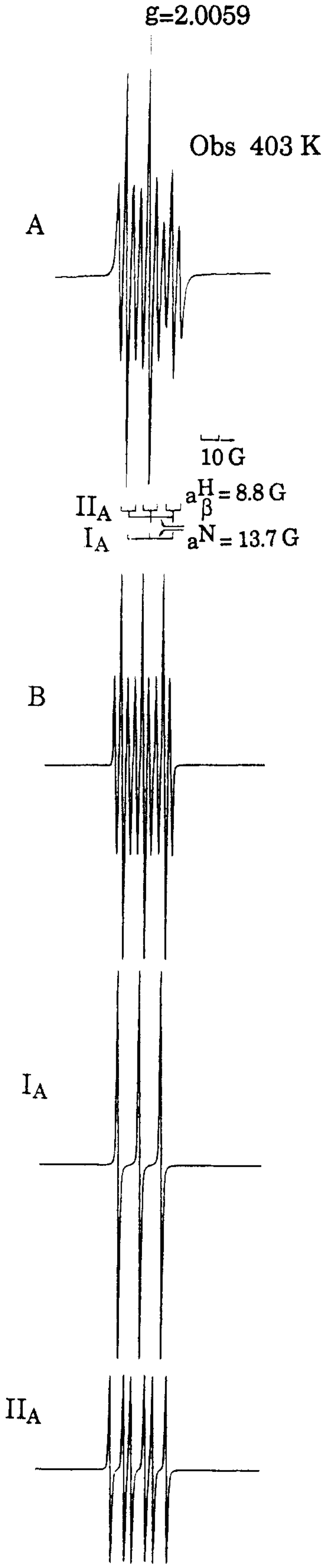


Figure 1. (A) ESR spectrum observed at 403 K after UV irradiation (5 min) of an LDPE/BP/ND sample at room temperature. The stick diagrams, I_A and II_A, are the spectra of spin-adducts of the tertiary carbon and the secondary carbon radicals, respectively. (B) Simulated spectrum corresponding to the 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, respectively. The line width (LW) parameters of the simulated spectra of I_A and II_A were 1.5 G for both. The other parameters used for the simulated spectra of the corresponding spin-adducts are given in Table I.

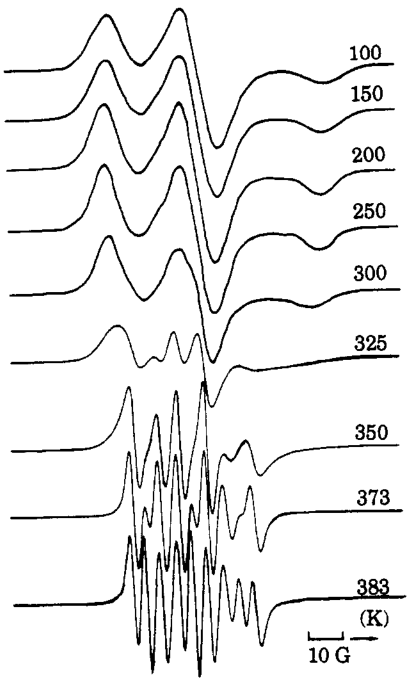
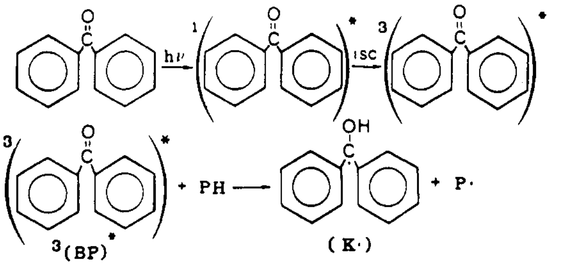


Figure 2. ESR spectra of ND/LDPE spin-adducts observed at various temperatures.

(ISC).[24] ^{3}(BP)* can abstract hydrogen from the LDPE chain (PH)

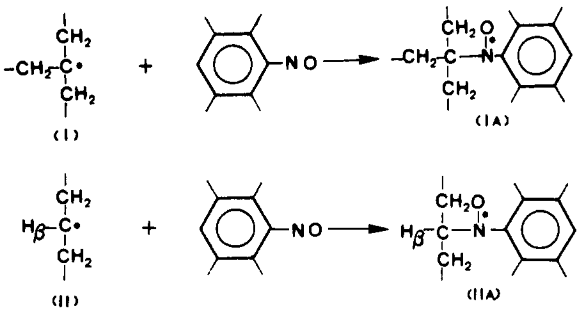


(1)

(2)

where P• represents alkyl radicals: tertiary and secondary carbon radicals I and II formed by hydrogen abstraction of the excited triplet state ^{3}(BP)* from LDPE chain. Two polymer radicals P• combine to form a cross-link.

2. Spin-Trapping Reactions. The spin-adducts I_A and II_A are obtained by the reactions of radicals I and II with the spin trap ND:



(3)

(4)

The triplet is attributed to the tertiary carbon radical I_A. The triplet of doublets are assigned to a spin-adduct radical (II_A) where the original triplet is further split by the β-H of the secondary carbon radical adduct (II_A).

The hfs splitting constants and the g values of the spin adducts I_A and II_A are listed in Table I. In the same table are presented corresponding data for spin-adducts produced by hydrogen abstraction from small organic molecules by the spin trap pentamethylnitrosobenzene (PMNB) which has a structure similar to ND. The data in Table I show good agreement of our ESR spectra with those reported by Doba et al.[13] The simulated spectrum (Figure 1B) obtained by an Aspect 3000 computer of the Bruker ER 200 D spectrometer, based on the coupling constants of this work, fits well with the observed spectrum (Figure 1A). This gives further evidence that the radicals which have reacted with ND are the tertiary carbon radical I and secondary carbon radical II.

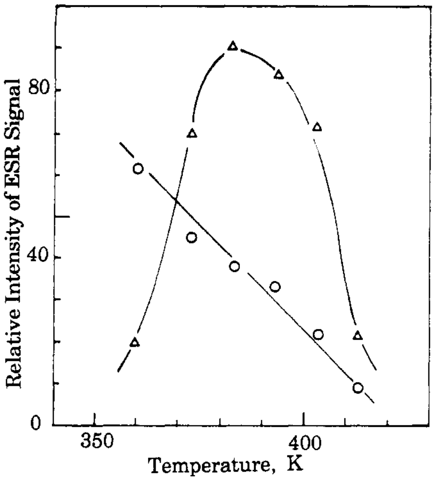
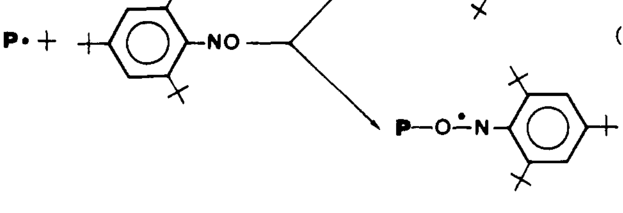


Figure 3. Variation in the relative intensities of triplet (△) and double triplet (○) spectra with increasing temperatures.

Table I
Comparison of ESR Parameters for the Spin-Adduct Radicals Formed from Nitrosobenzene (ND) and Pentamethylnitrosobenzene (PMNB)

	ND, present results			PMNB, by Doba et al.[13]		
		splitting constant, G			splitting constant, G	
trapped radical	g	a^N	a^{H_β}	g	a^N	a^{H_β}
$-CH_2-\dot{C}H-CH_2-$	2.0059	13.7	8.8			
$-CH_2-\dot{C}(CH_2-)-CH_2-$	2.0060	13.7				
$-CH_3-\dot{C}H-CH_2-CH_3$				2.0058	13.7	7.8
$\dot{C}(CH_3)_3$				2.0060	13.6	

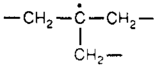
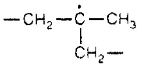
BNB Spin-Trapping Reactions. The photoinitiated radical reactions of PE have been further studied with another spin-trapping reagent 2,4,6-tri-*tert*-butylnitrosobenzene (BNB). BNB has two trapping sites, one on the nitrogen to attach a nonbulky radical to form a nitroxide spin-adduct and another on the oxygen atom of the nitroso group to attach a bulky group to form an anilino spin-adduct[25,26] (formula 5). It is possible to distinguish between the anilino and the nitroxide radicals from the differences in the g values and the nitrogen splitting constants.



(5)

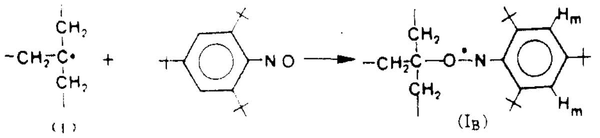
The ESR spectrum observed for the LDPE/BP/BNB system in the melt after UV irradiation for 5 min at room

Table II
Comparison of ESR Parameters for the BNB Spin-Adducts Formed by UV Irradiation of LDPE and γ-Irradiation of *n*-Eicosane

	present results				obtained by Tabata et al.[26]			
		splitting const, G				splitting const, G		
trapped radical	*g*	a^{N}	$a^{H}{}_{m}$	$a^{H}{}_{\beta}$	*g*	a^{N}	$a^{H}{}_{m}$	$a^{H}{}_{\beta}$
 $-CH_2-\dot{C}(-CH_2-)-CH_2-$	2.0039	10.3	2.0		2.0039	10.36	1.99	
 $-CH_2-\dot{C}(-CH_2-)-CH_3$					2.0046	10.50	1.93	
$-CH_2-\dot{C}H-CH_2-$	2.0063	13.6		20.5	2.0063	13.1		20.6

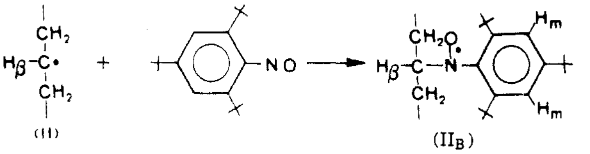
temperature is shown in Figure 4A, while no ESR signal can be detected from the various control experiments. The spectrum consists of two different components, marked I_B and II_B in Figure 4.

Component I_B, which is a triplet of triplets originating from couplings with the single nitrogen (a^{N} = 10.3 G) and with two meta protons ($a^{H}{}_{m}$ = 2.0 G) of the phenyl group in BNB, is assigned to an anilino-type spin-adduct (I_B), as shown in formula 6, because the observed *g* factor (*g* = 2.0039, see Table II) is close to the value of the anilino radical reported in the literature.[21] The spin-adduct I_B is positive evidence for the presence of the tertiary carbon radical I in the UV-irradiated LDPE which contains a tertiary hydrogen at every branch point.



(6)

Another component, II_B, which appears as a double triplet, is attributed to a nitroxide-type spin-adduct (II_B), as shown in formula 7, because its splitting constant with β-H ($a^{H}{}_{\beta}$ = 20.5 G) and its *g* factor (*g* = 2.0063) are the characteristic values for the nitroxide adduct. The spin-adduct II_B is assigned to the secondary carbon radical II. These assignments are supported by the characteristic behavior of BNB as a spin trap: a bulky radical is trapped by BNB to form an anilino-type spin-adduct but a non-bulky group is trapped as a nitroxide-type spin-adduct.[25,26]



(7)

Table II lists the ESR parameters of the BNB adducts 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 PE by Tabata et al.[26] The agreement between the observed (Figure 4A) and the simulated spectrum (Figure 4B) is quite satisfactory, which further verifies the interpretations.

Randall, Zoepfl, and Silverman[27] studied γ-radiation-induced structural changes in polyethylene by ^{13}C NMR spectroscopy. They successfully identified the chemical species corresponding to cross-links of both the H-type (H-link) and the long-chain branches (Y-links) in the irradiated PE. Tabata and Sohma et al.[25,26] studied the cross-links induced by γ-irradiation and neutron irradiation of *n*-eicosane as the polyethylene model compound

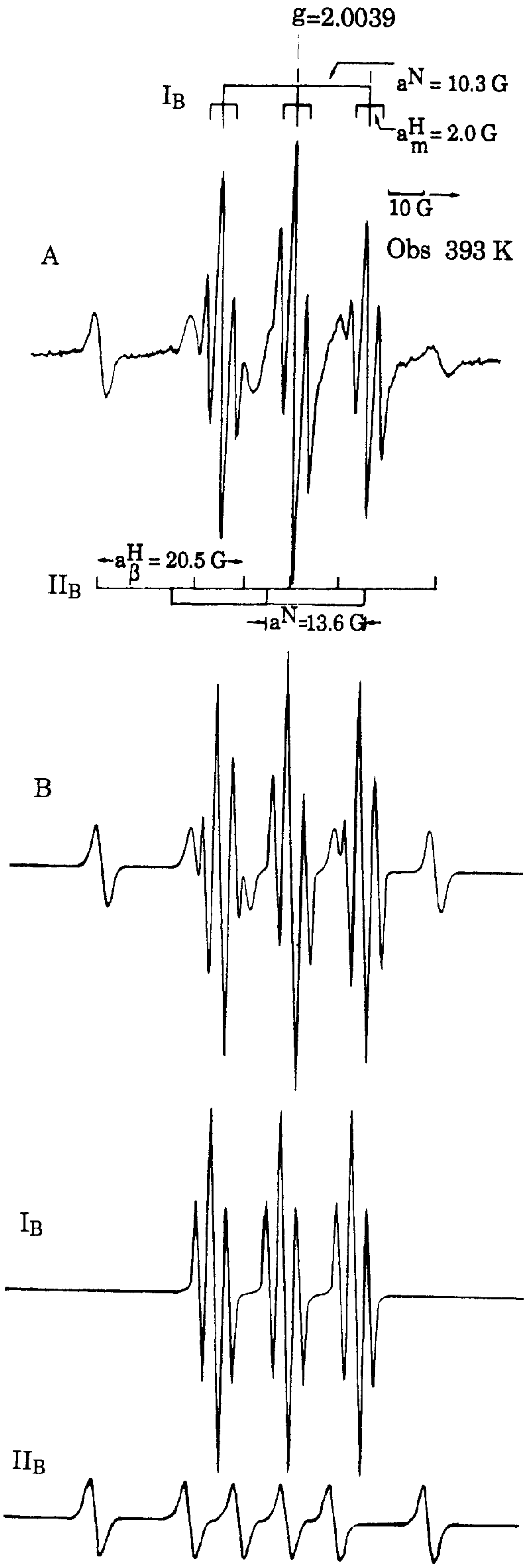


Figure 4. (A) ESR spectrum observed at 393 K after UV irradiation (5 min) of an LDPE/BP/BNB sample at room temperature. The stick diagrams, I_B and II_B, are spectra of the spin-adducts of tertiary carbon and secondary carbon radicals, respectively. (B) Simulated spectrum corresponding to the observed spectrum: (I_B, II_B) simulated spectra of the spin-adducts I_B and II_B, respectively. The line width (LW) parameters of the simulated spectra of I_B and II_B were 0.8 and 1.6 G, respectively. The other parameters used for the simulated spectra of the corresponding spin-adducts are given in Table II.

by spin-trapping ESR spectroscopy. As listed in Table II, they detected two kinds of cross-links arising from tertiary carbon radicals, one having an end methyl group attached (the E-type) and another with no methyl group (the C-type). They suggested that the links of the dimers of the E-type and C-type radicals are of the same type as Y-links and H-links in Silverman's nomenclature, respectively. However, in this work we did not detect the ESR signal from an E-type tertiary spin-adduct (see Table II), which might be due to the low concentration of end methyl groups in LDPE compared with *n*-eicosane. But we did detect the C-type tertiary spin-adduct I_A or I_B having no end methyl group, which forms a dimer with an H-link. Therefore, detection of only the C-type radicals suggests that the H-links are predominant in photo-cross-linking of LDPE.

Conclusions

(1) The radical intermediates produced during the BP-photoinitiated cross-linking of LDPE can be stabilized by the spin-trapping technique using ND and BNB as spin traps.

(2) The precursors for cross-links are identified as tertiary (I) and secondary (II) carbon radicals.

(3) Photo-cross-links mainly form by combination of tertiary and secondary carbon radicals.

(4) H-links are predominant in the photo-cross-linked LDPE.

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