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ESR Study of Peroxide-Induced Cross-Linking of High Density Polyethylene

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ABSTRACT: Peroxide-initiated cross-linking of high-density polyethylene (HDPE) was studied using an on-line electron spin resonance (ESR) technique. Peroxides were used to provide primary radicals upon thermal decomposition at elevated temperatures for the generation of polymer backbone radicals. Recording of the ESR spectra during the reaction process verified the free radical mechanisms involved in the modification. The determining variables for the reaction kinetics were the reaction temperature, peroxide type, and concentration level. Cross-linking via the recombination of backbone radicals was the major mechanism for high-density polyethylene modification. It was shown in the ESR spectra that some backbone radicals were trapped into the cross-linked polymer network and were still detectable after several months. The termination of backbone radicals was diffusion controlled. The rate constants were estimated using the measured radical concentration profiles. Significant changes in the signal hyperfine structure were also observed, indicating the formation of allyl radicals and the effects of melting and cross-linking on the mobility of the backbone radicals.

Introduction

Over the past decade, interest has grown in the postreactor modification of polyolefins by controlled degradation and cross-linking to satisfy specific applications.[1−4] Peroxides are economical means for carrying out these reactions. In a recent paper,[5] we reported ESR studies of the controlled peroxide degradation of polypropylene. The aim of the present work is to investigate the peroxide-induced cross-linking of high-density polyethylene (HDPE) using an on-line ESR technique.

Cross-linked polyethylenes have improved physical properties, for example, higher upper temperature use limits, improved dimensional stability, and strength, especially for applications as heavy-duty cable insulating materials.[6] The technology is firmly established using peroxide cross-linking of low-density polyethylene (LDPE) and high-density polyethylene (HDPE) as well as for linear low-density polyethylene (LLDPE).[1,7,8] The cross-linking is believed to be achieved via a free radical mechanism initiated by the decomposition of thermally unstable peroxides. The principal steps in the mechanism are believed to be (1) the generation of primary radicals, (2) the attack of these radicals on the polymer chain via hydrogen abstraction, and (3) the bimolecular recombination of backbone radicals to form carbon−carbon cross-linkages, as shown in Figure 1. However, this sequence of steps in the radical mechanism is based on the analyses of cross-linked polymer end products. Most studies to date have investigated changes in the polymer properties as well as controlling factors of the reaction. The direct experimental study of this radical mechanism is of fundamental importance.

The ESR technique is a microwave transition spectroscopic method based on the interaction between unpaired electron spins with an external magnetic field and with magnetic nuclei as well. It is the technique able to directly detect radical types and concentrations.

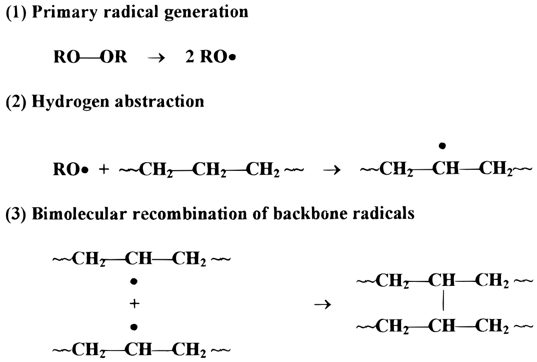

Figure 1. Elementary reactions involved in peroxide modification of high-density polyethylene (HDPE).

The advent of modern ESR methods has provided a powerful tool for polymer free radical studies involving such processes as free-radical polymerization, polymer degradation, and molecular motions.[9−12] However, there is little work reported on polymer melt modifications. In this paper, we present experimental results for the peroxide modification of HDPE.

Experimental Section

HDPE powder (Imperial Oil) was impregnated with peroxides at concentrations of 0.27, 0.22, 0.16, 0.11, 0.054, and 0.027 mol/kg of HDPE. Four types of peroxides (Aldrich Chemicals) were used: *tert*-butyl perbenzoate (TBPB), dicumyl peroxide (DCP), 2,5-dimethyl-2,5-bis(*tert*-butylperoxy)hexyne-3 (L130), and benzoyl peroxide (BPO). Figure 2 shows the peroxide molecular structures. Their decomposition rate constants (provided by the suppliers) are as follows:

$$K_{\mathrm{d,L130}} = 1.9 \times 10^{15} \exp(-150.67/RT)$$

$$K_{\mathrm{d,DCP}} = 9.24 \times 10^{15} \exp(-152.67/RT)$$

$$K_{\mathrm{d,TBPB}} = 9.25 \times 10^{13} \exp(-133.93/RT)$$

$$K_{\mathrm{d,BPO}} = 2.86 \times 10^{12} \exp(-113.22/RT)$$

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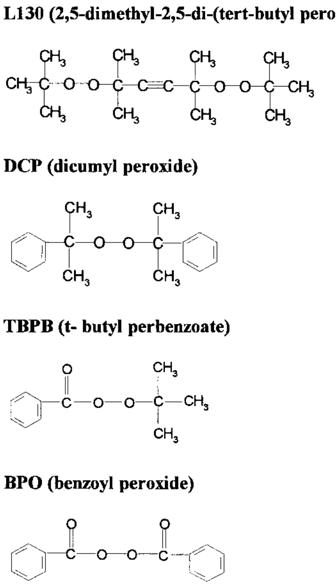


Figure 2. Molecular structure of peroxides used in this work.

where the activation energies are in kJ/(mol K). Details of the sample preparation are found in our recent paper.[5]

The chemical reaction was carried out by inserting glass ampule reactors with a 5 mm outer diameter and a 3 mm inner diameter in the preheated cavity of an ESR spectrometer (Bruker ER 072). Six temperatures (170, 180, and 190 °C; 135, 140, and 150 °C) were used. At these temperatures, ESR spectra having good signal-to-noise ratios were observed for samples with the peroxide concentration levels of 0.054−0.27 mol/kg of HDPE.

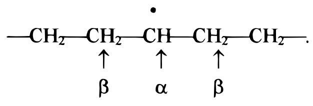
The reaction was initiated by the thermal decomposition of the peroxide at elevated temperatures. To closely monitor the process, the ESR spectra of radicals were recorded frequently using a microwave power of 2.01 mW (20 dB) and a modulation frequency of 100 kHz. The saturation behavior of the radical spectra were also studied, and no power saturation was found at the level of 2.01 mW. Absolute radical concentrations were determined after calibration using a 2,2-diphenyl-1-picrylhydrazyl hydrate (DPPH, Aldrich) standard dissolved in benzene, taking into account the effects of varying temperature.[13]

The ampule reactor in the ESR cavity was heated by thermal conduction through the glass wall. It took a couple of minutes for the HDPE powder to reach the preset temperature. The temperature near the centerline inside ampule reactor was measured using a method developed by Zhu and Hamielec.[14] The time required to melt HDPE sample was obtained from the temperature profile.

The gel contents of the modified polyethylene were determined by xylene extraction using a modified ASTM method 2765. About 0.3 g of each sample obtained from the glass ampule reactors was placed in a pouch made by 400 mesh stainless steel cloth and extracted in boiling xylene for 14 h. The gel contents were calculated from the dried polyethylene residuals.

Results and Discussion

Figure 3 presents some ESR spectra for the four HDPE/peroxide systems, recorded at different reaction times with a peroxide concentration of 0.27 mol/kg HDPE. An examination of the ESR spectra reveals that all the systems show a simple 10-line signal at the beginning of the reactions. This signal can be assigned to the radicals on a polyethylene backbone



$$-\mathrm{CH_2}-\underset{\beta}{\underset{\uparrow}{\mathrm{CH_2}}}-\underset{\alpha}{\underset{\uparrow}{\overset{\bullet}{\mathrm{CH}}}}-\underset{\beta}{\underset{\uparrow}{\mathrm{CH_2}}}-\mathrm{CH_2}-.$$

A

It is expected that the α- and β-protons exert strong effects on the ESR spectrum, resulting in the signal hyperfine structures. The coupling constants are 21.0 and 24.1 G, respectively, comparable to those of radiation-induced polyethylene radicals.[9,15,16]

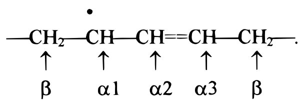
For the first-order splittings, the relative peak intensities are proportional to the coefficients of the binomial expansion.[9] The observed spectra follow this rule very well; the intensity ratios are 1:1:4:4:6:6:4:4:1:1. Using the experimental coupling constants and line widths of HDPE backbone radicals and assuming the spectrum is a superposition of a Gaussian and Lorentian shape, we show both a simulated spectrum and an experimental spectrum in Figure 4A which appear to be in good agreement.

Polyethylene radicals generated by γ and electron beam radiations have been the subject of numerous ESR studies. The irradiation of polyethylene at liquid nitrogen temperature results in the formation of an alkyl backbone radical,[9,16−18] the same as obtained by the peroxide modification. However, at the low temperature, only a broad, not-well-resolved six-line ESR spectrum was reported. In this work, we observed a well-resolved hyperfine structure of polyethylene radicals due to a decrease in the line width which removes the overlapping and the changes in molecular conformation and orientation.[9,12,19,20] The temperature-induced change in relaxation time is responsible for the decreased line width.

Despite the differences in the molecular structures of the peroxides, the four HDPE/peroxide systems exhibit identical 10-line ESR spectra at the beginning of the reactions. It becomes evident that in the peroxide modification processes, peroxide molecules are used only to provide primary radicals for the generation of backbone radicals.[1,21,22] In addition, previous work showed that the primary radicals (i.e., the peroxide fragments) could not be detected in ESR experiments.[20,23,24]

It can also be seen in Figure 3 that there are some characteristic changes in the radical signals during the course of the modification process. Starting with the same 10-line spectrum at the very beginning, the hyperfine structure changes as the reaction proceeds. Let us take the system of HDPE/L130 presented in Figure 3(A) as an example. At the start of the process, no signal is observed; it is followed by the appearance of a 10-line polyethylene backbone radical signal that after a period of time gives way to a second set of narrower 14-line spectra. This developed spectrum finally disappears when the reaction is completed.

Previous ESR investigations on irradiated polyethylenes showed that the following allyl radicals were formed in addition to alkyl radicals.



$$-\underset{\beta}{\underset{\uparrow}{\mathrm{CH_2}}}-\underset{\alpha 1}{\underset{\uparrow}{\overset{\bullet}{\mathrm{CH}}}}-\underset{\alpha 2}{\underset{\uparrow}{\mathrm{CH}}}=\underset{\alpha 3}{\underset{\uparrow}{\mathrm{CH}}}-\underset{\beta}{\underset{\uparrow}{\mathrm{CH_2}}}-.$$

B

At low-temperature irradiation studies, allyl radicals gave a typical septet spectrum with hyperfine splitting constant of 18 G.[25,26] Very recently, Yamamoto et al.[27] observed a narrow 12-line spectrum for allyl type propagating radicals in butadiene polymerization. The spectrum was attributed to five equivalent hydrogen nuclei with hyperfine splitting of approximately 1.4 mT and one hydrogen nucleus with splitting of about 4 mT.

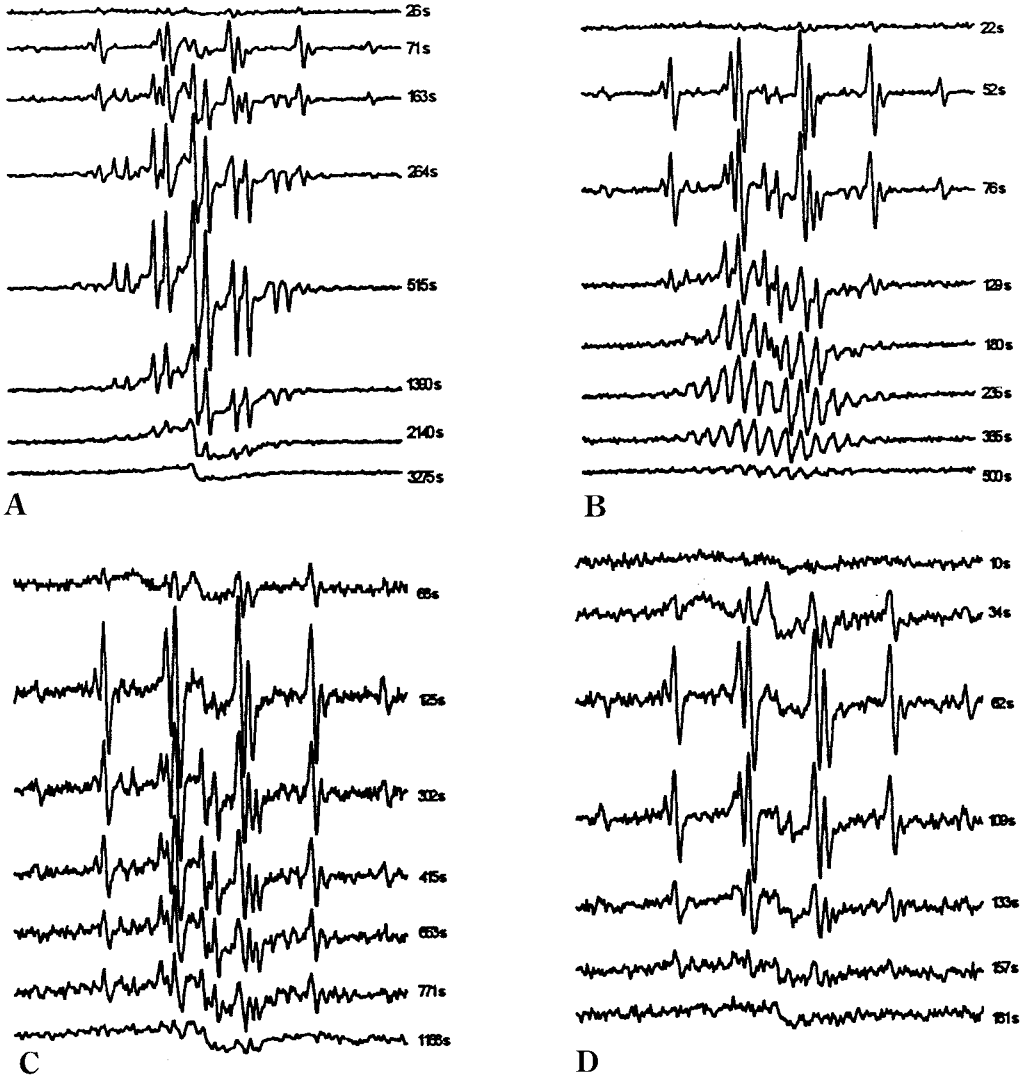


Figure 3. ESR spectra recorded during the peroxide modification of HDPE with (A) 0.27 mol of L130/kg of HDPE at 190 °C, (B) 0.27 mol of DCP/kg of HDPE at 190 °C, (C) 0.27 mol of TBPB/kg of HDPE at 150 °C, and (D) 0.27 mol of BPO/kg of HDPE at 150 °C. The operation conditions are as follows: microwave frequency, 9.39 GHz; modulation frequency, 100 kHz; modulation amplitude, 1.4 G; microwave power, 2.01 mW; sweep time, 10.49 s.

These values are very close to the hyperfine splitting constants, 13.7 and 4.4 G, observed in this work. It is therefore, believed that the second set of ESR signals in Figure 3A is due to allyl radicals. The recent work on chemical cross-linking of polyethylene by Yamazaki and Seguchi [28,29] also confirmed this mechanism.

Figure 4B gives a comparison of the experimental and simulated results for this narrow 14-line spectrum. The calculated spectrum assumed hyperfine splitting values of 13.7 G for six equivalent hydrogen nuclei (α1, α3, and four βs) and 4.4 G for one hydrogen nucleus (α2). The peak at 3331.6 G does not change its position with time, while the peak at 3340.6 G represents the appearance of a new set of hyperfine structures. The intensity ratio of the 3340.6 G peak over that of 3331.6 G increases initially, remains about 1.5 for a long period of time, and is then followed by another increase at the final stage of the reaction process.

Figure 5 shows the changes of intensity for some of the peaks in the 14-line spectrum. The symmetric feature of the second set changes during the reaction. It becomes less symmetrical, as one of the central peaks disappears near the end. It is speculated that this asymmetry in the ESR spectrum is due to an anisotropy of *g* values caused by the formation of cross-linked polymer network.[9,30] Table 1 gives the gel contents for the peroxide modification systems. It is evident that the systems are highly cross-linked. Cross-linking greatly enhances the system viscosity and therefore restricts the tumbling rate of backbone radicals.

On the other hand, the early stage alteration is also believed to be due in part to the melting effect. Figure 6 shows the temperature development inside the glass ampule reactor heated via thermal conduction. The temperature enhances relaxation of polymer chains in the amorphous region, causes the phase transformation in the crystalline domains and consequently induces the mobility and conformation of polyethylene backbone radicals.[12,31] The second set appears when the heat transfer process is completed. Table 2 gives the time when the central peaks of the 14-line spectrum appear and the time required to raise the temperature enough to melt HDPE inside the ampule reactors. These values are reasonably close. A series of experiments below the melting temperature of HDPE (125 °C) were also conducted. There was no noticeable appearance of the central peaks of the second set.

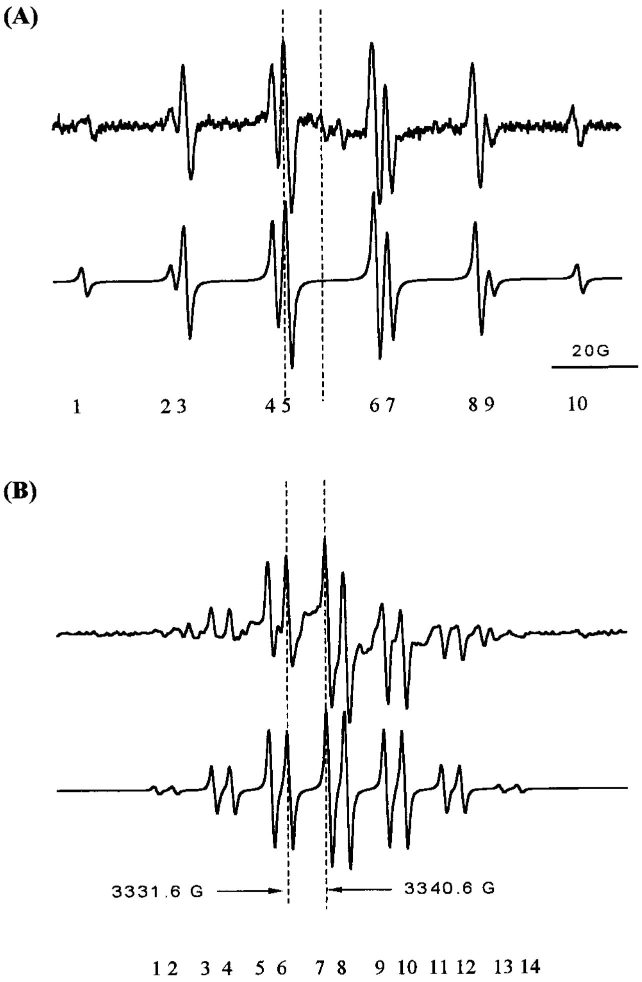


Figure 4. Comparison of the experimental and simulated ESR spectra of polyethylene backbone radicals: (A) initial 10-line spectrum observed at the very beginning of the modification processes; (B) developed 14-line spectrum in the system of HDPE/L130.

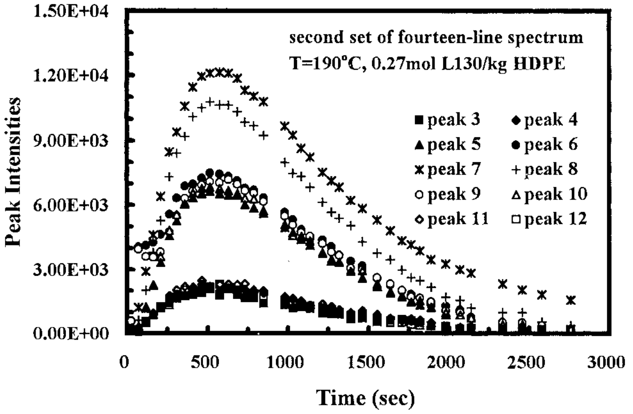


Figure 5. Plots of the intensity vs time for some peaks of the 14-line ESR spectrum observed in the L130/HDPE system at peroxide concentration of 0.27 mol of L130/kg of HDPE at 180 °C.

Other systems such as DCP, TBPB, and BPO also exhibit ESR signal development (refer to Figure 3). Due to the short half-life time of TBPB and BPO peroxides, the reactions of these two peroxide/HDPE systems were conducted at lower temperatures. Similar to L130/HDPE, TBPB/HDPE (Figure 3C) and BPO/HDPE (Figure 3D) show that the second set of peaks appear close to the melting time after the generation of the first 10-line signal. However, these two systems did not show the full development of the 14-line spectrum before the radical signal became too weak to be detected. The ESR spectra of the DCP/HDPE system (Figure 3B) at the same temperatures as L130/HDPE exhibited similar changes at the beginning: no radical at the start, appearance of the first 10-line signal, and display of the new signal with melting of the polymer. However, the spectrum then developed a different pattern. The reason for this remains unknown, and therefore it is left open for discussion.

The generation and termination of radicals are clearly observed in our ESR measurements. The time required to finish the whole process differs depending on the reaction temperature, peroxide type, and concentration. This dependence is manifested in the radical concentration vs time profiles shown in Figures 7 and 8, for the four peroxide/HDPE systems studied. The generation and termination of the backbone radicals are competing reactions. The former is controlled by the abstraction of hydrogen atoms from polyethylene by the primary radicals formed via thermal decomposition of peroxide, while the latter is a bimolecular reaction of backbone radicals. When generation becomes dominant, the radical population increases. When termination becomes dominant, the radical concentration decreases. Considering the short half-life time of the peroxides used, a very long reaction process indicates that the radicals experience difficulty in termination.

There are two possible termination modes of backbone radicals: disproportionation and recombination. The former does not change the molecular weight, while the latter forms a linkage between two polymer chains. The recombination is believed to be the major mechanism for HDPE, evident from the high level of gel formation. The radical concentration profiles during the course of modification can be used to estimate kinetic rate constants. The two fundamental equations used to describe the process are as follows:

$$\frac{\mathrm{d[I]}}{\mathrm{d}t} = -K_{\mathrm{d}}[\mathrm{I}] \qquad (1)$$

$$\frac{\mathrm{d[R^{\bullet}]}}{\mathrm{d}t} = 2fK_{\mathrm{d}}[\mathrm{I}] - K_{\mathrm{t}}[\mathrm{R^{\bullet}}]^2 \qquad (2)$$

Here, t is the reaction time, f is the peroxide efficiency, K_{d} is the peroxide decomposition rate constant, [I] is the peroxide concentration, $[\mathrm{R^{\bullet}}]$ is the radical concentration, and K_{t} is the termination rate constant for the total radical population. The factor 2 accounts for the fact that one peroxide molecule produces two primary radicals (for L130, it is 4). The peroxide decomposition rate constant changes with temperature variation and obeys the Arrhenius law

$$K_{\mathrm{d}} = A \exp(-E/RT) \qquad (3)$$

where A is the frequency factor and E is the activation energy of decomposition.

By solving eqs 1−3 and fitting the radical concentration vs time data, one can obtain the two kinetic parameters: the peroxide efficiency f and the radical termination rate constant K_{t}.[5] However, it was found that a single K_{t} value is not adequate to fit the whole curve of the radical concentration data. Using the radical concentration data in Figures 7 and 8 and

Table 1. Gel Content in Peroxide-Induced Cross-Linking of HDPE

	gel fraction for peroxide type									
	L130			DCP		TBPB			BPO	
mol/kg of HDPE	170 °C	180 °C	190 °C	170 °C	180 °C	135 °C	140 °C	170 °C	140 °C	170 °C
0.27	0.980	0.987	0.993	0.986	0.987	0.937	0.946	0.970	0.602	0.735
0.16	0.970	0.977	0.991	0.974	0.978	0.815	0.871	0.952	0.565	0.688

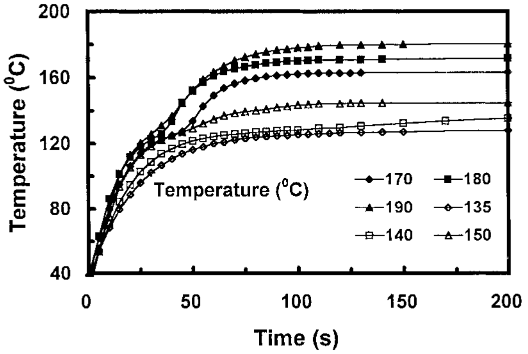


Figure 6. Temperature development at the inner wall and centerline for the HDPE-filled glass ampule reactor inserted into the cavity of Bruker ER 072 spectrometer.

Table 2. Comparison between the Time for the Second Set of 14-Line Spectra to Appear, t_{peak}, and the Time for the Ampule Reactor To Reach the HDPE Melting Temperature, t_{melt}

		t_{peak} (s)			
T (°C)	t_{melt} (s)	L130	DCP	TBPB	BPO
190	32	64	54	38	34
180	36	70	63	43	40
170	45	100	74	60	45
160	50	120	90	75	75

temperature profiles in Figure 6, one can extract K_t data provided the f value is given. Figure 9 shows an example of the development of K_t during the L130 modification of HDPE ($f = 0.5$ is assumed in this example[5,32-34]). The rate constant decreases dramatically at the beginning and levels off as the reaction proceeds. It is believed that radicals on sol polymers have higher termination rate constants than those trapped in gels due to the diffusion constraints imposed by the network structure. The radical information at the final stage of reaction can be used to give an estimate of the rate constant of trapped radicals. When the peroxide molecules are all decomposed, the radical generation term on the right-hand side of eq 2 can be neglected. Integrating eq 2 yields

$$\frac{1}{[R^\bullet]} = K_t t + \frac{1}{[R^\bullet]_0} \tag{4}$$

Plotting $1/[R^\bullet]$ vs t, one can estimate K_t through the slopes.

Figure 10 shows the residue termination rate constants as a function of the temperature and peroxide concentration. These K_t values in the range of 10 to 5×10^3 L/(mol s) are rather small compared to those of polypropylene.[5] It is the cross-linking that results in the low termination rate constants for HDPE. The higher the peroxide level, the higher the cross-linking density, the more rigid the network, and therefore, the smaller the termination rate constant. The log scale K_t shows an approximate linear relationship with the peroxide level. It is also observed that K_t increases with temperature with the apparent activation energies about 20 kcal/(mol K).

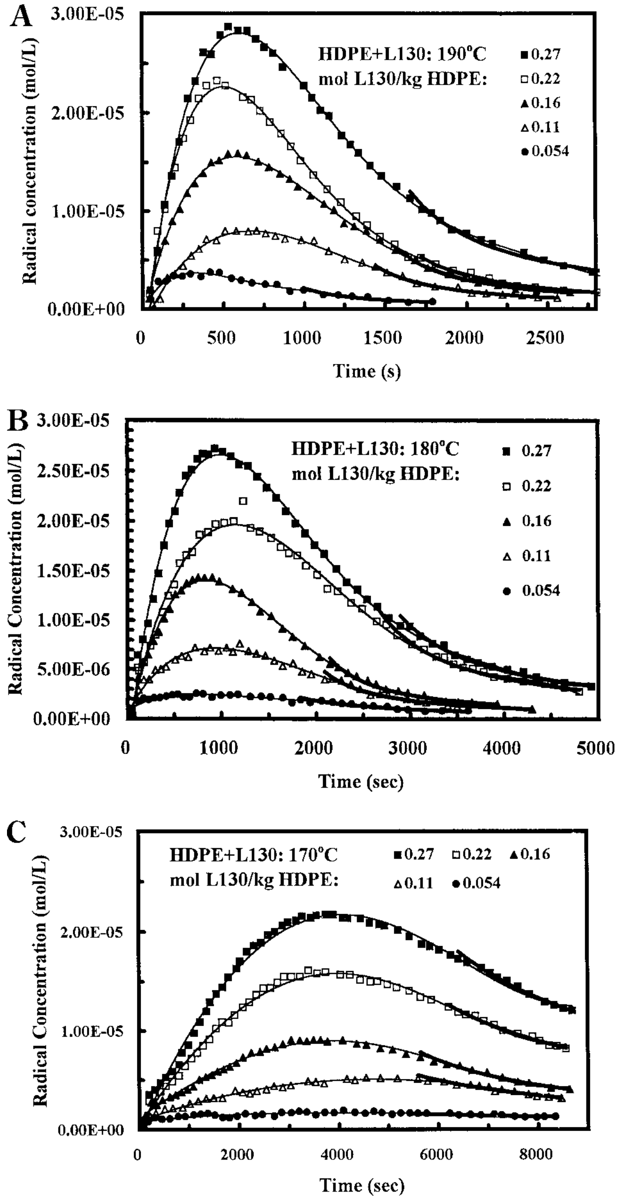


Figure 7. Radical concentration vs reaction time profiles of L130/HDPE system. Temperature: (A) 190, (B) 180, and (C) 170 °C.

Conclusions

The mechanism and kinetics of the peroxide modification of high density polyethylene has been studied using an on-line ESR technique. The successful observation of ESR spectra during the modification elucidated that the reaction process was accomplished via a free radical mechanism. Four types of peroxides (L130, DCP, TBPB, and BPO) were used to provide the primary radicals. An identical 10-line hyperfine structure arising from the secondary carbon radicals was observed, indicating that

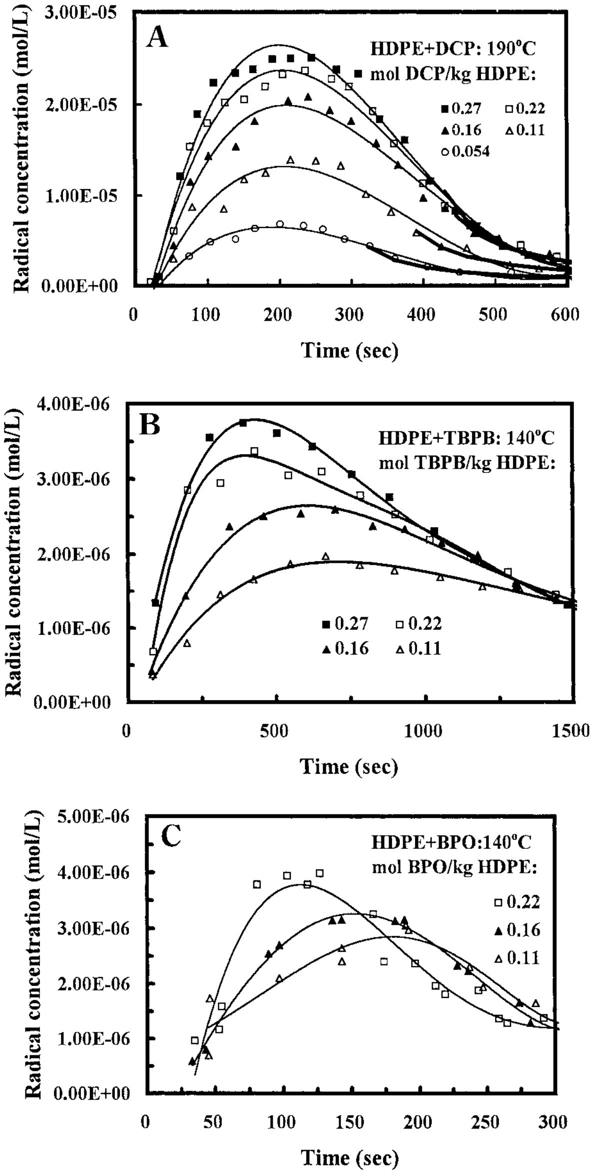


Figure 8. Radical concentration vs reaction time profiles of peroxide/HDPE systems: (A) DCP at 190 °C; (B) TBPB at 140 °C; (C) BPO at 140 °C

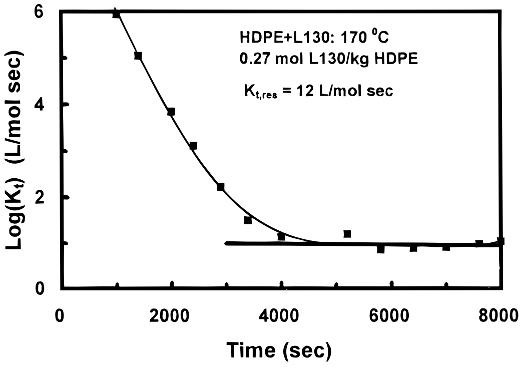


Figure 9. Reduction of termination rate constant during the L130/HDPE reaction at 170 °C.

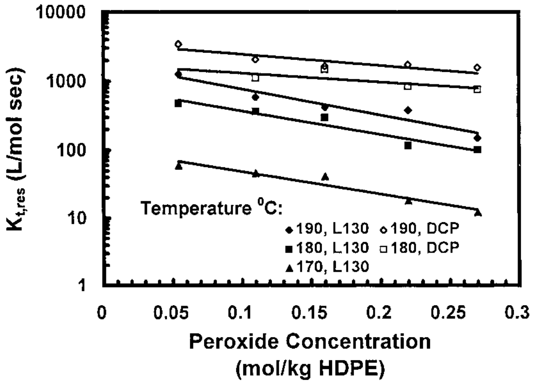


Figure 10. Residue termination rate constant vs peroxide concentration of L130/HDPE and DCP/HDPE reaction systems.

the peroxide was used only for the generation of backbone radicals. The development of the ESR hyperfine structure was simulated and explained with regard to the formation of allyl radicals and the effect of polymer melting and cross-linking on the radical mobility. The distinct radical generation and termination rates were shown directly by the change in the spectrum intensities during the course of the reaction. The determining parameters for the radical concentration included reaction temperature, peroxide type, and concentration level. The recombination appeared to be the major mode of radical termination in the polyethylene modification, yielding a three-dimensional network. The rate constants of radical termination were estimated using the radical concentration profiles. It was shown that the rate constant decreased with time and that the radicals trapped in the polymer network have small termination rates.

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References and Notes

(1) Lazar, M.; Rado, R.; Majek, J. *Adv. Polymer Sci.* **1990**, *95*, 149.
(2) Chodak, I. *Prog. Polym. Sci.* **1995**, *20*, 1165.
(3) Hamielec, A. E.; Gloor, P. E.; Zhu, S. *Can. J. Chem. Eng.* **1991**, *69*, 611.
(4) Lambla, M. *Macromol. Symp.* **1994**, *83*, 37.
(5) Zhou, W.; Zhu, S. *Ind. Eng. Chem. Res.* **1997**, *36*, 1130.
(6) Celina, M.; George, G. A. *Polym. Degrad. Stabliz.* **1995**, *48*, 297.
(7) de Boer, J.; Pennings, A. J. *Polymer* **1982**, *23*, 1944.
(8) Tang, Y.; Tzoganakis, C.; Hamielec, A. E.; Vlachopoulos, J. *Adv. Polym. Technol.* **1989**, *9*, 257.
(9) Ranby, B.; Rabek, J. *ESR Spectroscopy in Polymer Research*; Springer-Verlag: New York, 1977.
(10) Kamachi, M. *Adv. Polym. Sci.* **1987**, *82*, 207.
(11) de Vries, K.; Roylance, D. In *Encyclopedia of Polymer Science and Engineering*; Kroschwitz, J. I., Ed.; Wiley: New York, 1985; Vol. 5, p 687.
(12) Shimada, S. *Prog. Polym. Sci.* **1992**, *17*, 1045.
(13) Poole, C. P. *Electron Spin Resonance: A Comprehensive Treatise on Experimental Techniques,* Interscience Publishers: New York, 1967.
(14) Zhu, S.; Hamielec, A. E. *Polymer* **1991**, *32*, 3021.
(15) Fessenden, R. W.; Schuler, R. H. *J. Chem. Phys.* **1963**, *39*, 2147.
(16) Tamura, N.; Shinohara, K. *Rep. Prog. Polym. Phys. Jpn.* **1963**, *6*, 261.
(17) Tsuji, K. *J. Polym. Sci. A1* **1973**, *11*, 1407.
(18) Waterman, D. C.; Dole, M. *J. Phys. Chem.* **1970**, *74*, 1913.
(19) Shimada, S.; Hori, Y.; Kashiwabara, H. *Polymer* **1978**, *19*, 763.
(20) Gilbert, B. C.; Dobbs, A. J. in *Organic Peroxides*; Swern, D., Ed.; Wiley-Interscience: New York, 1972; Vol. 3, p 271.
(21) Dorn, M. *Adv. Polym. Technol.* **1985**, *5*, 87.
(22) Zhu S.; Hamielec, A. E. *Makromol. Chem., Macromol. Symp.* **1992**, *63*, 135.

(23) Zwolenik, J. J. *J. Phys. Chem.* **1967**, *71*, 2464.
(24) Shida, T. *J. Phys. Chem.* **1968**, *72*, 723.
(25) Ohnishi, S.; Ikeda, Y.; Kashiwagi, M.; Nitta, I. *Polymer* **1961**, *2*, 119.
(26) Ohnishi, S. *Bull. Chem. Soc. Jpn.* **1962**, *35*, 254.
(27) Yamamoto, K.; Shimada, S.; Sakaguchi, M.; Tsujita, Y. *Polym. J.* **1997**, *29*, 370.
(28) Yamazaki, T.; Seguchi, T. *J. Polym. Sci., Part A: Polym. Chem.* **1997**, *35*, 279.
(29) Yamazaki, T.; Seguchi, T. *J. Polym. Sci., Part A: Polym. Chem.* **1997**, *35*, 2431.
(30) Iwasaki, M.; Sakai, Y. *J. Polym. Sci. A2* **1968**, *6*, 265.
(31) Ooi, T.; Shitsubo, M.; Hama, Y.; Shinohara, K. *Polymer* **1975**, *16*, 510.
(32) Bamford, C. H. in *Encyclopedia of Polymer Science and Engineering*; Kroschwitz, J. I., Ed.; Wiley: New York, 1985; Vol. 13, p 789.
(33) Suwanda, D.; Lew, R.; Balke, S. T. *J. Appl. Polym. Sci.* **1988**, *35*, 1033.
(34) Ryu, S. H.; Gogos, C. G.; Xanthos, M. *Adv. Polym. Technol.* **1991/1992**, *11*, 121.

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