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ANALYSIS OF HYDROPEROXIDES IN SOLID POLYETHYLENE BY NMR AND EPR SPECTROSCOPY

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Introduction

Hydroperoxides play a key role in the oxidative degradation of many polyolefins. Hydroperoxides are believed to be the first product formed during oxidative degradation driven by thermal, UV or radiative stresses.[1] As degradation continues, the hydroperoxides react to form a variety of secondary products including alcohols, ketones, acids and esters. Characterization of hydroperoxide formation and their subsequent reaction products has proven to be a valuable tool for understanding the aging mechanism of polymers with and without antioxidants. In this paper we use magic angle spinning (MAS) ^{13}C NMR spectroscopy to study the chemistry of hydroperoxides in ^{13}C-enriched polyethylene. Hydroperoxides were generated by γ-irradiation of polyethylene in air and their subsequent degradation was studied as a function of temperature. The environment of the hydroperoxides generated by γ-irradiation of polyethylene was studied by applying EPR spectroscopy to observe the free-radicals that result from their degradation.

Because of their importance, methods to detect and quantify hydroperoxides in aged polymers have received considerable attention. The study of hydroperoxides is complicated by their low concentration and their ability to react further under relatively mild conditions. A recent review outlined the various methods that have been developed to study hydroperoxide chemistry in polymers.[2] The approaches can be classified as either direct or indirect, where indirect requires that the hydroperoxide be chemically derivatized before detection. The indirect approaches suffer from the disadvantage of disturbing the sample chemically. Direct methods that do not rely on derivatization include infrared and NMR spectroscopies. Although the weak infrared absorption for isolated hydroperoxides has been observed,[3] the detection of hydrogen-bonded hydroperoxide groups is complicated by the overlap of their absorption with that of other hydroxyl groups.[4] Solution state ^{13}C NMR spectroscopy has been used successfully to detect hydroperoxides in dissolved samples of thermally aged polyethylene.[5,6] Hydroperoxides have also been observed by ^{17}O NMR spectroscopy of pentacontane that was thermally aged under ^{17}O enriched molecular oxygen.[7]

We have extended the ^{13}C NMR studies in two ways: first, the use of ^{13}C-enriched polyethylene provides an increase in detection sensitivity of nearly two orders-of-magnitude and second, MAS was employed to eliminate the need to dissolve or swell the sample. In this way we are able to conveniently and directly monitor hydroperoxides and their reaction products in the solid polymer after irradiation and during subsequent annealing experiments. Analysis of the temperature dependence of hydroperoxide decomposition enabled the activation energy of the degradation process to be determined. We have also used electron paramagnetic resonance (EPR) as an indirect method to examine the environment of the hydroperoxide species. EPR cannot directly detect the hydroperoxides in irradiated polymers. It is capable, however, of detecting the radicals that may either be reactants in the formation of hydroperoxides, or products of the degradation of hydroperoxides.[8,9]

Experimental

Materials. Polyethylene, ^{13}C enriched at 99%, was purchased from Isotec Inc. The DSC analysis showed the main crystalline melting point at 125 °C, corresponding to pure high-density polyethylene.

Radiation Aging. Samples were γ-irradiated under flowing air conditions at 25 °C in a ^{60}Co γ-source at a dose rate of approximately 0.74 kGy/h for times ranging from 4 to 20 days. Total doses ranged from 71 to 355 kGy, while substantial embrittlement of this material was encountered at approximately 200 kGy.

Instrumentation. The ^{13}C MAS NMR spectra were recorded on a Bruker AMX-400 spectrometer at 100.6 MHz. Samples of approximately 50 mg were packed into 4 mm rotors and spun at 10 kHz. Direct polarization spectra with high power ^{1}H decoupling were recorded with delay time ranging from 4 to 240 s. X- and K-band EPR was performed using a Bruker ESP300e spectrometer, each cavity being equipped with an Oxford continuous-flow liquid helium cryostat. UV irradiations were carried out using a 200 W mercury vapor lamp from Oriel.

Results and Discussion

Figure 1a shows the ^{13}C MAS NMR spectrum of unaged ^{13}C-enriched polyethylene. The two resonances at 33 and 30 ppm correspond to the crystalline and amorphous components, respectively, of the -CH$_2$- repeat unit in the chain backbone. The resonance at 133 ppm corresponds to a spinning side band of the chain backbone. Small resonances at 14 and 11 ppm are visible on the spectrum that has been vertically expanded by a factor of 50. These resonances, which each comprise less than 0.1% of the total intensity, correspond to methyl end groups and methyl groups on isolated ethyl branches, respectively. The small resonance at 175 ppm corresponds to a high field spinning side band that has been reflected into the spectrum. The spectrum of ^{13}C enriched-polyethylene that was exposed to 7 days of γ-radiation at 25 °C is shown in Figure 1b. The spectrum exhibits the resonances discussed in the preceding paragraph and has resonances at 72, 172-184 and 207 ppm corresponding to secondary alcohols, acid and esters, and ketones, respectively.[5,6] In addition, the spectrum has a distinct resonance at 85 ppm corresponding to hydroperoxides.[5,6] Minor resonances at 81, 99 and 194 ppm have not been positively identified. The relative concentrations of the various chemical species as a function of irradiation time are shown in Figure 2. The concentration of hydroperoxide species formed at 25 °C

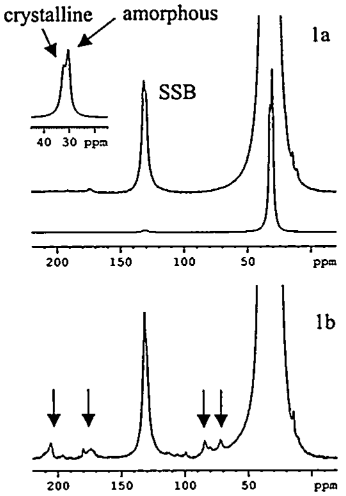

Figure 1. (a) The ^{13}C MAS NMR spectrum of unaged ^{13}C-polyethylene showing the crystalline and amorphous components of the main chain. SSB = spinning side band. (b) The ^{13}C MAS NMR spectrum of ^{13}C-polyethylene γ-irradiated in air for 7 days at 25 °C.

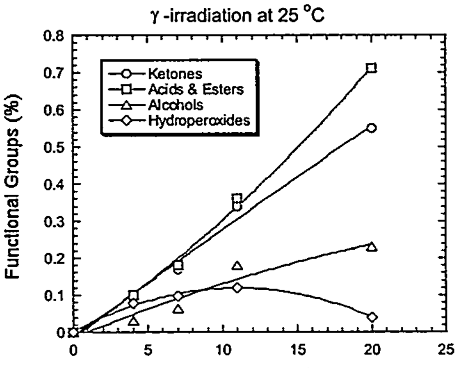

Figure 2. The distribution of functional groups vs. irradiation time at 25 °C.

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increases rapidly for short aging times, but then levels off and decreases significantly between 11 and 20 days. This behavior is characteristic of a reactive intermediate.

In addition to observing the formation of hydroperoxides, we are able to investigate the decomposition chemistry of these reactive species during subsequent thermal exposure. Figure 3 shows the hydroperoxide region of the sample radiatively aged for 7 days at 25 °C. The sample was then heated at 110 °C in air for the times indicated, returned to room temperature and its spectrum recorded. The intensity of the hydroperoxide resonance decreases rapidly as a function of annealing time. Additional samples that had also been radiatively aged for 7 days at 25 °C were annealed for various times at 95, 80 and 65 °C. The hydroperoxide concentrations were difficult to accurately quantify because of the broadness of the resonances and the uneven baselines. The hydroperoxide resonance also overlaps somewhat with a smaller unidentified resonance at 81 ppm. For these reasons, each spectrum was phased identically so that its baseline features were similar. Peak heights rather than peak areas of the hydroperoxide resonances were then measured. The annealing process was continued until the spectrum exhibited no further change. The normalized peak heights versus annealing times for the various annealing temperatures are shown in Figure 4a.

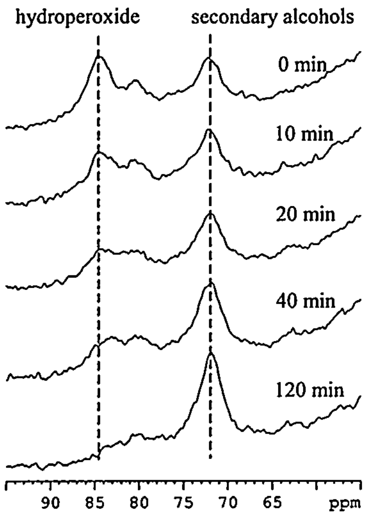

Figure 3. The ^{13}C MAS NMR spectra of ^{13}C-polyethylene annealed at 110°C in air for the times indicated. The sample had originally been exposed to γ-radiation for 7 days at 65 °C in air.

The best approach to determine the activation energy of the hydroperoxide composition is achieved by a time-temperature superposition.[10] The advantage of this approach is that it utilizes all of the data from each temperature experiment and does not require definitive knowledge of the underlying kinetic behavior. We first select the lowest temperature, 65 °C, as the reference temperature, T_{ref}. If increasing the temperature to T equally accelerates all of the reactions underlying the oxidation, then the time behavior of the decomposition will be accelerated by a constant multiplicative shift factor, a_T. For each higher temperature, we empirically determine the value of a_T that results in the best superposition with the data at T_{ref}. Figure 4b shows the superimposed results for the decomposition of the hydroperoxide species. If the shift factors follow Arrhenius behavior, then $\log(a_T)$ should be a linear function of inverse absolute temperature. Figure 5 shows that such a plot is consistent with Arrhenius behavior with an activation energy of 98 kJ/mol (25.7 kcal/mol) calculated from the slope. This result agrees quite well with the value of 105 kJ/mol measured by Chien using indirect methods.[11]

We have examined non-enriched, 25 °C γ-irradiated PE samples by EPR in order to determine the type and relative amounts of radicals that exist at the time of analysis, and to determine the environment of the hydroperoxide species based upon the radical species observed after UV photolysis. Several months after irradiation, spectra taken at room temperature show a large singlet ($g = 2.0045$), assignable to the polyenyl radical.[12] K-band room temperature spectra reveal a small peak assignable to the peroxy radical ($g \sim 2.009$).[8] The ratio of polyenyl to peroxy radicals is 1000 to 1.

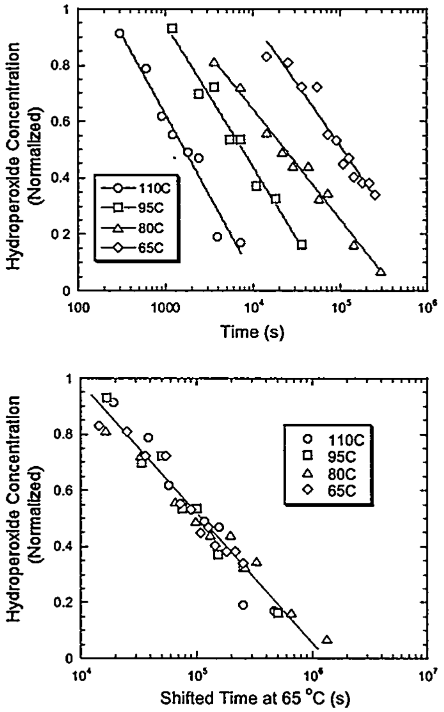

Figure 4. (a) Normalized peak heights of the hydroperoxide resonance as a function of annealing time at temperatures ranging from 65 to 110 °C. The sample had originally been exposed to γ-radiation for 7 days at 25 °C. (b) The time-temperature superposition of the normalized peak heights at a reference temperature of 22 °C.

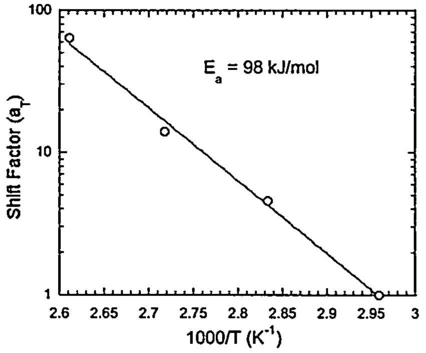

Figure 5. Arrhenius plot of the shift factors for loss of hydroperoxide species during thermal annealing. The activation energy is 98 kJ/mol.

During UV-light cleavage experiments, we employ high power (20 mW) to saturate the polyenyl radicals so that we can see the peroxy radicals that are at lower concentration.[8] In Figure 6, we show consecutive EPR spectra taken at 50 K. Upon exposure to UV light, the hydroperoxides are cleaved to alkoxy and hydroxy radicals that react further to create more peroxy radicals.[9] Subtraction of the spectrum taken before UV-irradiation from that taken immediately after UV-irradiation shows the rhombic nature of the nonrotating peroxy radical's g-values, with $g_1 = 2.026$ $g_2 = 2.011$, and $g_3 = 2.003$.[13] Note that the g_1 value for the peroxy radicals created by photolysis is slightly higher than the $g_1 = 2.025$ of the peroxy radicals that already exist in the polymer. A one hour room temperature anneal is sufficient to cause most of the UV-cleaved peroxides to decay. After a three-day room temperature anneal, the signal is nearly the same as before UV

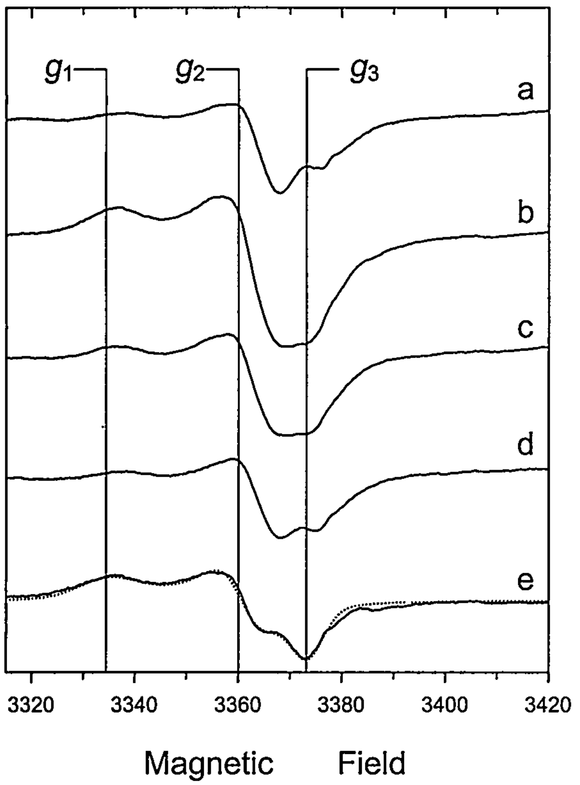

Figure 6. Creation of peroxide radicals in γ-irradiated polyethylene by UV cleavage of hydroperoxides. All EPR spectra were taken at a microwave power of 20 mW and temperature of 50 K. (a) Spectrum of the polyenyl radicals and the already-existing peroxy radicals in the sample. (b) Spectrum of the peroxy radicals created after *in-situ* UV illumination. (c) Spectrum of the sample after a 1 hour anneal at room temperature. (d) Spectrum of the sample after a 3 day anneal at room temperature. The signal has returned to its pre-irradiated state. (e) Spectrum of (a) subtracted from (b) and a computer simulation (dotted line) used to discern the g-values of the observed peroxy radical, $g_1 = 2.026$, $g_2 = 2.011$, $g_3 = 2.003$.

irradiation. The peroxy radicals observed immediately after UV irradiation are believed to come from the amorphous regions of polyethylene for two reasons. First, they are observed to decay much more quickly at room temperature than either the polyenyl or already existing peroxy radicals, which are thought to be in either crystalline or interfacial environments.[14] The decay rate of the UV-generated peroxy radicals is approximately that reported for peroxy radicals generated in amorphous regions of PE.[8] Second, there is a noticeable shift in the lowest *g*-value, suggesting a different environment for the UV-generated peroxy radicals than for the already-existing peroxy radicals.

Conclusions

We have shown that the hydroperoxide species in γ-irradiated ^{13}C-polyethylene can be directly observed by ^{13}C MAS NMR spectroscopy. The experiment was performed without the need for special sample preparation such as chemical derivatization or dissolution. Annealing experiments were employed to study the thermal decomposition of the hydroperoxide species and to measure an activation energy of 98 kJ/mol. EPR spectroscopy suggests that residual polyenyl and alkylperoxy radicals are predominately trapped in interfacial or crystalline regions, while the peroxy radicals observed after UV-photolysis of hydroperoxides are in amorphous regions.

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References

(1) Clough, R. L.; Billingham, N. C.; Gillen, K. T. *Polymer Durability, Degradation, Stabilization, and Lifetime Prediction*; American Chemical Society: Washington, DC, 1996; Vol. 249.

(2) Scheirs, J.; Carlsson, D. J.; Bigger, S. W. *Polym.-Plast. Technol. Eng.* 1995, *34*, 97.

(3) Luongo, J. P. *J. Polym. Sci.* **1960**, *42*, 139.

(4) Klemchuk, R. P.; Horng, P. L. *Polym. Deg. Stab.* 1984, *7*, 131.

(5) Cheng, H. N.; Schilling, F. C.; Bovey, F. A. *Macromolecules* 1976, *9*, 363.

(6) Jelinski, L. W.; Dumais, J. J.; Luongo, J. P.; Cholli, A. L. *Macromolecules* 1984, *17*, 1650.

(7) Alam, T. M.; Celina, M.; Assink, R. A.; Clough, R. L.; Gillen, K. T.; Wheeler, D. R. *Macromolecules* submitted.

(8) Ohnishi, S.I.; Sugimoto, S.I.; Nitta, I. *J. Polym. Sci. , Part A: Polym. Chem.* 1963, *1*, 605.

(9) Faucitano, A.; Buttafava, A.; Martinotti, F.; Gratani, F.; Bortolus, P. *J. Polym. Sci. , Polym. Chem. Ed.* 1985, *23*, 635.

(10) Gillen, K. T.; Celina, M.; Clough, R. L.; Wise J. *Trends in Polymer Science,* 1997, *5*, 250.

(11) Chien, J. C. W. *J. Polym. Sci. Pt A-1* 1968, *6*, 375.

(12) Jahan, M.S.; McKinny, K.S. *Nucl. Instrum. Methods Phys. Res. , Sect. B* 1999, *151*, 207.

(13) Schlick, S.; Kevan, L. *J. Am. Chem. Soc.* 1980, *102*, 4622.

(14) O'Neill, P.; Birkinshaw, C.; Leahy, J.J.; Barklie, R. *Polym. Degrad. Stab.* 1999, *63*, 31.