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Analysis of Hydroperoxides in Solid Polyethylene by MAS ^{13}C NMR and EPR

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ABSTRACT: ^{13}C-enriched polyethylene was subjected to γ-irradiation in the presence of air at 25 and 80 °C for total doses ranging from 71 to 355 kGy. Significant quantities of hydroperoxides were detected in the 25 °C irradiated sample by ^{13}C magic angle spinning NMR spectroscopy. This method of detection was performed on the solid polymer and required no chemical derivatization or addition of solvent. The chemical stability and subsequent products of the hydroperoxide species were studied by annealing the irradiated samples in air at temperatures ranging from 22 to 110 °C. A time−temperature superposition analysis provided an activation energy of 108 kJ/mol for the hydroperoxide decomposition process. The primary products of hydroperoxide decomposition were ketones and secondary alcohols with lesser amounts of acids and esters. EPR measurements suggest that the reactive hydroperoxide species reside in the amorphous phase of polyethylene, consistent with degradation occurring in the amorphous phase.

Introduction

Hydroperoxides play a key role in the oxidative degradation of many polyolefins and are believed to be the first product formed during oxidative degradation driven by either thermal, UV, or radiative stresses.[1−3] As degradation continues, the hydroperoxides react to form a variety of secondary products including alcohols, ketones, acids, and esters. Characterization of hydroperoxide formation and the subsequent reaction products has proven to be a valuable tool for understanding the aging mechanism of polymers with and without antioxidants. Peroxides are also intentionally introduced into polyethylene and other polyolefins by γ-irradiation or e-beam treatment of the polymer in the presence of air, as the first step in a graft polymerization process. Subsequent thermal treatment of the peroxide-containing polymer in the presence of a monomer such as acrylonitrile or acrylic acid results in grafting at the sites of radicals formed by the decomposition of the polymeric peroxides.[4] In this paper we present a study of the generation of hydroperoxides by γ-irradiation and their subsequent thermal degradation in solid ^{13}C-enriched polyethylene by magic angle spinning (MAS) ^{13}C NMR spectroscopy.

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.[5] The approaches can be classified as either direct or indirect, where indirect requires that the hydroperoxide be chemically derivatized before detection.

The most common indirect approaches are colorimetric methods that depend on either iodometric analysis[6] or ferrometric complexation.[7] These colorimetric methods require that the polymer be dissolved or swollen to enable the reactants to diffuse freely throughout the polymer. The elevated temperatures required for the dissolution of many polymers, including polyethylene, lead to further reaction of the hydroperoxides during the experiment. Also, the reaction times for complete derivatization have been the subject of some debate and depend on such factors as the film thickness. Indirect methods also include infrared detection of alkyl hydrosulfates after treatment with sulfur dioxide[8] or of nitrate groups after treatment with nitric oxide.[9] All of the indirect approaches suffer from the disadvantage of disturbing the sample chemically. Study of the subsequent reactions of hydroperoxide species requires that a new sample be used for each kinetic measurement. Carlsson and Lacoste[10] have recently provided a critical evaluation of several indirect methods used for measuring hydroperoxide concentrations in oxidized polyolefins.

Direct methods that do not rely on derivatization include infrared and NMR spectroscopies. Although the weak infrared absorption for isolated hydroperoxides has been observed,[11−13] the detection of hydrogen-bonded hydroperoxide groups is complicated by the overlap of their absorption with that of other hydroxyl groups.[14−16] NMR spectroscopy has been used extensively to study scission and cross-linking in polymers subjected to irradiation.[17−19] The study of oxidative products is less common, although solution state ^{13}C NMR spectroscopy has been used successfully to detect hydroperoxides in dissolved samples of thermally aged polyethylene.[20,21] Hydroperoxides have also been recently observed by ^{17}O NMR spectroscopy of pentacontane that was thermally aged under ^{17}O-enriched molecular oxygen.[22]

We have extended the ^{13}C studies in two ways: first, the use of ^{13}C-enriched polyethylene provides an increase in detection sensitivity of nearly 2 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 bulk polymer after radiation and during subsequent annealing experiments. Analysis of the temperature dependence of hydroperoxide decomposition enabled the ac-

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tivation energy of the degradation process to be determined. We have also used electron paramagnetic resonance (EPR) 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 which may be either reactants in hydroperoxide formation or products of hydroperoxide degradation.[23] Also, photolysis with UV light has previously been employed to create EPR-observable radicals from hydroperoxides in polymers.[24,25] Thus, EPR is an indirect technique, as the polymer samples must be modified by UV so that hydroperoxide decomposition products can be detected.

Experimental Section

Materials. Polyethylene, ^{13}C enriched at 99%, was purchased from Isotec Inc. Films were pressed at 170 °C and quenched in cool water. The DSC analysis showed the main crystalline melting point at 129.3 °C with a melting onset of 124.7 °C and a 4.0 °C width at half-height. The percent crystallinity by DSC was 52.9%.

Radiation Aging. Samples were γ-irradiated under flowing air conditions at 25 and 80 °C in a ^{60}Co source at a dose rate of approximately 0.74 kGy/h for times ranging from 4 to 20 days. The total doses ranged from 71 to 355 kGy. Substantial embrittlement of this material was encountered at approximately 200 kGy.

Instrumentation. The MAS ^{13}C 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 a delay time of 4 s and typically 256 scans. The resonance of the amorphous component of the backbone and all decomposition resonances exhibited complete recovery, within the limits of experimental error, after 2 s. Spectra with limited numbers of scans were recorded with delay times of 60 and 240 s in order to quantitatively record the resonance of the crystalline component and to ensure that all decomposition products had fully recovered after a 4 s delay time. 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 1 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.[26] The relative proportion of the crystalline and amorphous phases changes modestly during γ-irradiation and will be the subject of a later publication. The resonance at 133 ppm corresponds to a spinning sideband of the chain backbone. Although the intensity of the amorphous component is greater than that of the crystalline component in the central resonance, the situation is reversed for the spinning sideband resonance. The amorphous resonance is not expected to contribute as much to the spinning sideband manifold because its spectrum is narrowed to a greater degree by chain motions. 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.[27] The small resonance at 175 ppm corresponds to a high field spinning sideband that has been reflected into the spectrum.

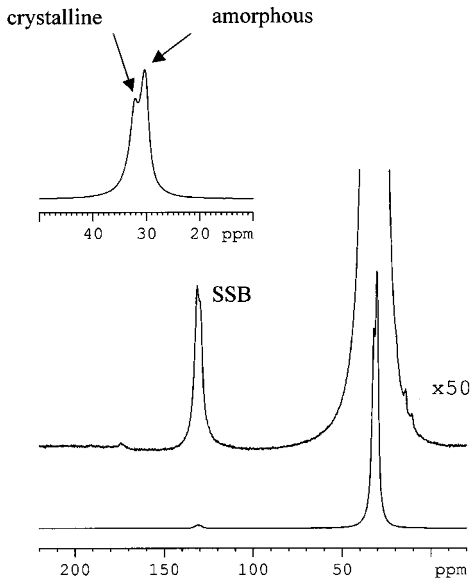

Figure 1. ^{13}C MAS NMR spectrum of unaged ^{13}C-polyethylene showing the crystalline and amorphous components of the main chain. SSB = spinning sideband.

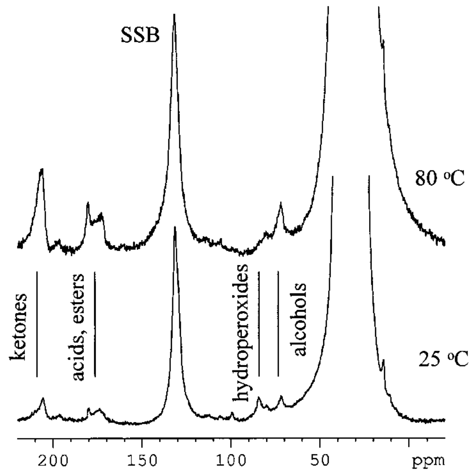

Figure 2. ^{13}C MAS NMR spectra of ^{13}C-polyethylene γ-irradiated for 7 days at 25 and 80 °C. Resonances corresponding to ketones, acids, esters, hydroperoxides, and alcohols are identified.

The spectra of ^{13}C-enriched polyethylene samples that were exposed to 7 days of γ-radiation in the presence of air at 25 and 80 °C are shown in Figure 2. Each spectrum has been expanded vertically by a factor of 50. The 80 °C sample exhibits increased noise levels because the sample size was smaller. The line width of the $-CH_2-$ backbone unit has increased somewhat for the 25 °C sample and has increased significantly for the 80 °C sample. This increase is attributed to contributions from carbons that are β-position relative to the oxidative products. Each spectrum exhibits the original resonances discussed in the preceding paragraph and in addition has resonances at 72, 85, 172−184, and 207 ppm corresponding to the primary oxidative degradation products. These resonances have been previously assigned to secondary alcohols, hydroperoxides, acid and esters, and ketones, respectively.[20,21] Minor resonances at 81, 99, and 194 ppm have been identified as a dialkyl peroxide,[28] a vinyl carbon, and an aldehyde. The intensities of these resonances are much less than those of the primary degradation products. Because they cannot be accurately measured, these minor resonances will not be discussed further in this paper.

The general features of the primary degradation products for the two temperatures are similar with two exceptions. First, the concentration of degradation products at 80 °C is much higher than that at 25 °C. Second, while the spectrum of the sample irradiated at 25 °C has a distinct resonance at 85 ppm corresponding to hydroperoxides, this resonance is not observed for the sample irradiated at 80 °C. Since the hydroperoxide is a reactive intermediate, this second observation is not surprising. We will show later that the half-life for the decay of hydroperoxide species at 80 °C in this material is approximately 6 h. Thus, while considerable amounts of hydroperoxide species should have been produced, most of them would have quickly undergone further reactions during the radiation process.

The spectra were recorded by direct polarization experiments using a delay time of 4 s. The resonances attributed to the degradation products and the main chains in the amorphous phase are considered quantitative since, within the limits of experimental error, they appear completely recovered after only 2 s. The resonance attributed to the main chains in the crystalline phase, however, was not fully recovered after a 4 s delay. Therefore, to correctly account for the total number of carbons in the sample, the intensity of the crystalline resonance was assigned the value observed for spectra recorded with a 240 s delay time and fewer scans. The relative concentrations of the various functional groups were determined by peak integration. These concentrations were adjusted downward by a factor of 1.22 to account for incomplete relaxation of the crystalline phase as determined from spectra recorded with a 240 s delay time. The results for radiation exposure at 25 and 80 °C are shown in Figure 3, a and b. The concentration of hydroperoxide species formed at 25 °C increases rapidly for short irradiation times but then levels off and decreases significantly between 11 and 20 days. This behavior is characteristic of a reactive intermediate. The concentration of secondary alcohols is the smallest of the three primary degradation products for samples aged at both 25 and 80 °C. The concentration of ketones is comparable to that of acids and esters at 25 °C. At 80 °C the concentration of acids and esters is low initially but then increases until their concentration surpasses that of ketones for long aging times.

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 4 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 and returned to room temperature, and its spectrum was 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. In addition, the hydroperoxide resonance overlaps somewhat with a smaller dialkyl peroxide 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 change after additional annealing time. The normalized peak heights versus annealing times

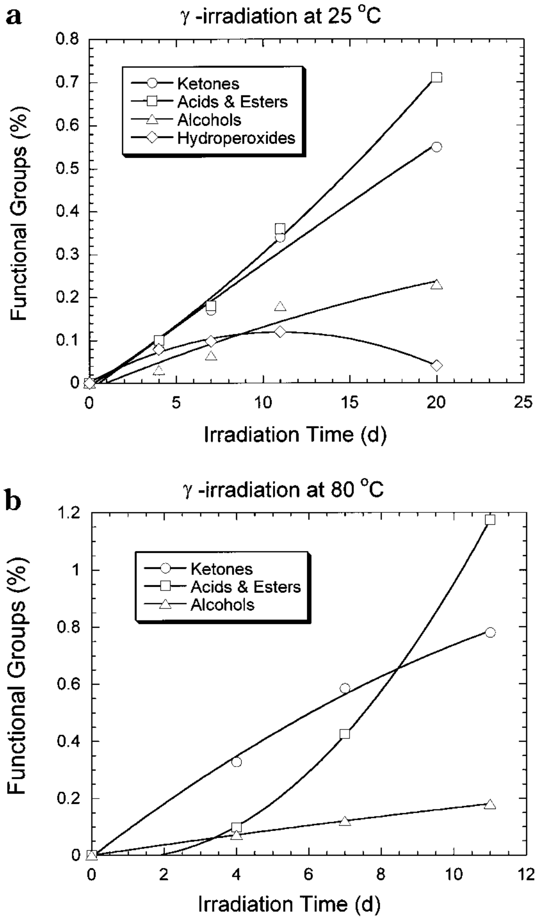

Figure 3. Distribution of functional groups vs irradiation time at (a) 25 and (b) 80 °C. The percents shown represent the percent carbons associated with each degradation species compared to the total carbon population.

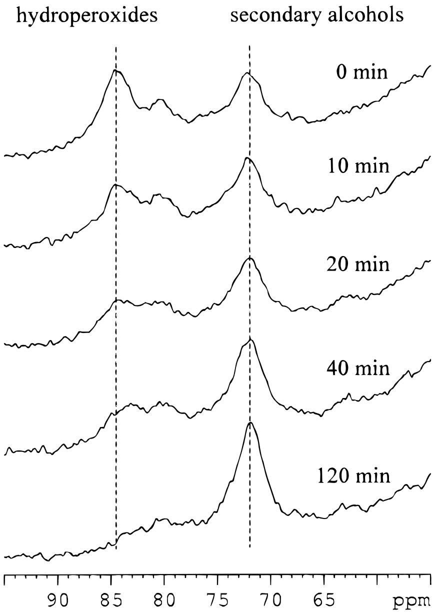

Figure 4. ^{13}C MAS NMR spectra of ^{13}C-polyethylene annealed at 110 °C for the times indicated. The sample had originally been exposed to γ-radiation for 7 days at 25 °C.

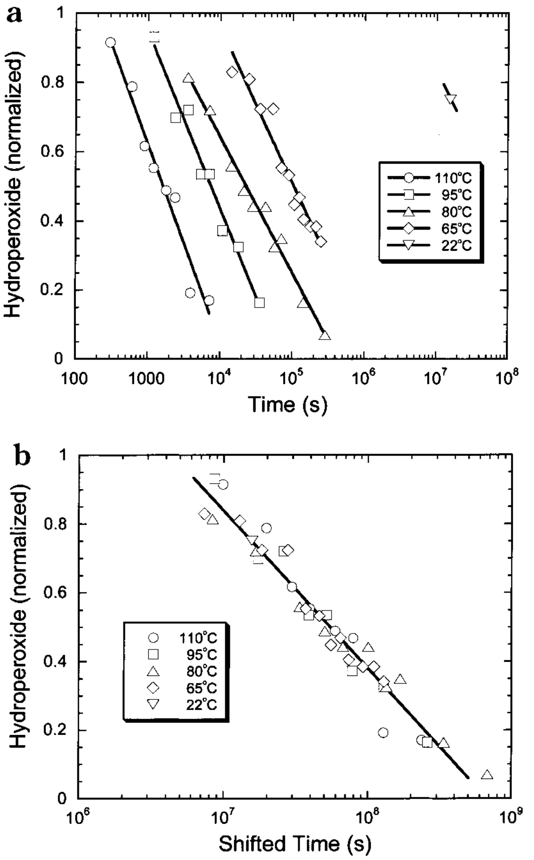

Figure 5. (a) Normalized peak heights of the hydroperoxide resonance as a function of annealing time at temperatures ranging from 22 to 110 °C. The sample had originally been exposed to γ radiation for 7 days at 25 °C. (b) Time–temperature superposition of the normalized peak heights at a reference temperature of 22 °C.

for the various annealing temperatures are shown in Figure 5a. Also shown in Figure 5a is a single measurement of the hydroperoxide concentration in a sample that had been stored at ambient laboratory conditions for 6 months.

The first half of the decomposition curve at each temperature was used to calculate a rate constant assuming first-order kinetics. A least-squares fit of the data provided rates of 3.7×10^{-4}, 0.72×10^{-4}, 0.20×10^{-4}, and 0.048×10^{-4} s^{-1} at 110, 95, 80, and 65 °C, respectively. These rates can be compared to those measured by Chien[29] for the decomposition of hydroperoxides in low-density polyethylenes. In those studies the hydroperoxides were prepared by low-temperature autoxidation initiated by AIBN and the degradation rates measured at 100, 120, and 135 °C. An interpolation of our results predicts that the rate constant at 100 °C is 1.32×10^{-4} s^{-1} compared to an average value of 0.32×10^{-4} s^{-1} reported by Chien. We believe that this difference is not unreasonable considering the difference in materials and in the method used to generate the hydroperoxide species. Degradation rates are known to depend on local conditions and the distribution of hydroperoxide species. Chien also reported that from 0 to 15% of the hydroperoxides decayed at a rate approximately an order of magnitude slower than the initial rate. Our sensitivity at long reaction times, during which the hydroperoxide resonance is merging with the baseline, is insufficient to detect evidence for this behavior.

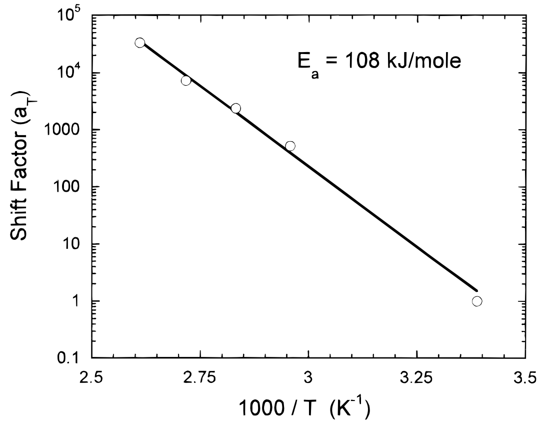

Figure 6. Arrhenius plot of the shift factors for loss of hydroperoxide species during thermal annealing. The activation energy is 108 kJ/mol.

The temperature dependence (activation energy) of hydroperoxide decomposition was calculated by the time–temperature superposition method.[30,31] 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 (i.e., first- or second-order kinetics). We first select the lowest temperature, 22 °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 5b shows the superimposed results for the decomposition of the hydroperoxide species. Figure 6 shows the shift factors, on a logarithmic scale, plotted versus inverse temperature. We observe Arrhenius behavior of $\log(a_T)$ versus inverse temperature and calculate an activation energy of 108 kJ/mol (25.7 kcal/mol) for this process. The shift factor for hydroperoxide decomposition at 22 °C was given one-third the weight of the shift factors for the elevated temperatures since the complete decomposition curve was not measured at this temperature. We had earlier reported an activation energy of 98 kJ/mol that did not utilize the decomposition data obtained at 22 °C.[32]

Figure 7 shows selected portions of the difference spectrum in which the spectrum of the 7 day radiatively aged sample without annealing was subtracted from the spectrum of the same sample after it had been annealed for 2 h at 110 °C. These conditions correspond to nearly complete elimination of the hydroperoxide resonance (see Figures 4 and 5a). The reduction in the hydroperoxide concentration is depicted by the inverted resonance at 85 ppm. The production of ketones, acids and esters, and alcohols is depicted by additional intensity at their respective positions.

The chemical mechanisms for the degradation of hydroperoxide species can be classified into four stages: initiation, propagation, branching, and termination.[33] The initiation stage yields both alkoxy and hydroxyl radicals. These radicals rapidly abstract hydrogen atoms from polyethylene to form alcohols and water:

$$RO^{\bullet} + RH \rightarrow R^{\bullet} + ROH$$

$$HO^{\bullet} + RH \rightarrow R^{\bullet} + H_2O$$

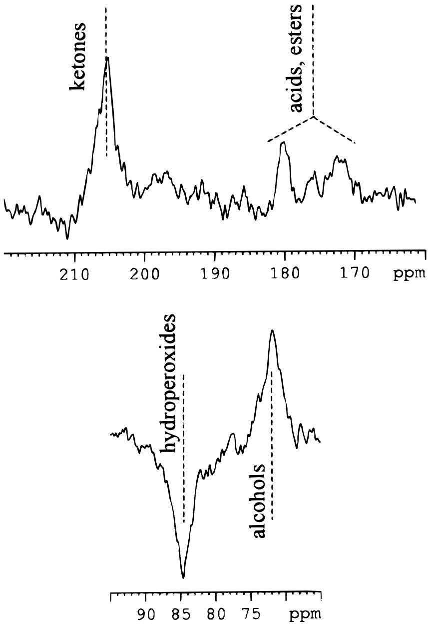

Figure 7. The ^{13}C spectrum of the sample that had been radiatively aged at 25 °C for 7 days was subtracted from the spectrum of the same sample after it had been annealed for 2 h at 110 °C. Portions of the difference spectrum show the loss of hydroperoxides and formation of ketones, acids, esters, and alcohols attributed to the annealing process.

When oxygen is available, as in these experiments, the alkyl radicals can form peroxy radicals that undergo a propagation step:

$$R^{\bullet} + O_2 \rightarrow RO_2^{\bullet}$$

$$RO_2^{\bullet} + RH \rightarrow RO_2H + R^{\bullet}$$

A scission step involving alkoxy radicals can yield an aldehyde or ketone, while a bimolecular termination step involving two peroxy radicals yields alcohols and ketones. Additional experiments comparing rates and product distributions with and without oxygen are being performed.

We have also used EPR to study both enriched and nonenriched polyethylene samples that were irradiated at 25 °C. These experiments were conducted to determine the type and relative amounts of radicals that exist after irradiation and to characterize the environment of the hydroperoxide species on the basis of the radical species observed after UV photolysis of the irradiated sample.

We initially (a month after irradiation) observed a large singlet ($g = 2.0045$) superimposed upon a multiple-line spectrum of low intensity. This multiple-line spectrum decayed and was not observable after several more weeks. We assign such a signal to the alkyl radical,[34] though at the time of our observation its signal was weak and partially obscured by the large singlet, so there may be some contribution from the allyl radical.[35] This is consistent with previous observations of long-lived alkyl and allyl radicals in irradiated polyethylene, thought to be in crystalline or interfacial regions.[36] Additionally, singlet signals have been observed previously in air-irradiated polyethylene and have been assigned to either peroxy[36] or polyenyl[37] radicals. We believe the singlet we observe results from polyenyl and not from peroxy radicals for several reasons. First, the signal we observe in either X- or K-band (9.4 and 24.0 GHz, respectively) is strongly power dependent, suggesting that the spin−lattice relaxation time is much more like that of a carbon-based radical rather than an oxygen-based radical.[23] Second, we observe a marked dependence of the peak width upon whether we are observing irradiated polyethylene with a normal abundance of ^{13}C ($\Delta H_{pp} = 5.9$ G) or that which is enriched to 99% ^{13}C ($\Delta H_{pp} = 12.7$ G). This change in peak width indicates that the unpaired electron causing the singlet is interacting primarily with carbon atoms. The unpaired electron of a peroxy radical is localized on the peroxy's terminal oxygen and would therefore have little interaction with the carbon to which the peroxy is attached. Upon cooling the irradiated polyethylene sample and employing low microwave power, no g value anisotropy was observed, contrasting with observations typical of peroxy radicals in polyethylene.[38] Consequently, we assign the singlet to the polyenyl radical.

At room temperature, X-band spectra of nonenriched irradiated polyethylene show only a singlet after exposure to air for at least a month, while K-band spectra also show a small signal at $g \sim 2.009$. Because this signal is at a higher g value than the polyenyl radical, and is not susceptible to power saturation, we assign it to the peroxy radical. The double integrals of the two signals (taken at low power to avoid saturating the polyenyl radical) are in the ratio of approximately 1000 polyenyl to 1 peroxy. Comparing the double integral of the polyenyl signal to that of weak pitch, we calculate approximately 10^{16} polyenyl and 10^{13} peroxy radicals per gram of polyethylene.

To investigate the environment of the hydroperoxides, we have used UV photolysis to cleave the hydroperoxides and have studied the decay characteristics of the resulting radicals by EPR.[24,25] To avoid seeing an EPR signal that is dominated by the polyenyl radical background, we operate at high power (20 mW) so that these radicals are saturated.[23,39] Figure 8 shows EPR spectra, recorded at 50 K, of the sample that had been γ-irradiated for 7 days at 25 °C. Spectrum a, taken before UV exposure, is a mixture of peroxy and power-saturated polyenyl radicals. Upon exposure to UV light, spectrum b, the hydroperoxides have been cleaved to alkoxy and hydroxy radicals, quickly resulting in the formation of peroxy radicals via H abstraction and participation of oxygen.[40] Further evidence that the radicals we observe are peroxy and not alkoxy is garnered from the fact that alkoxy g_1 values (2.03−2.11) are generally well above the g_1 values observed here (see below).[41] The UV irradiation was for 30 min at a power on the order of 0.01−0.1 W/cm^2 at the sample. For clarity, we have included spectrum e, which is obtained by subtracting the spectrum acquired before UV irradiation from that acquired immediately after UV irradiation. Spectrum e clearly shows the rhombic nature of the nonrotating peroxy radical's g values, with $g_1 = 2.026$, $g_2 = 2.011$, and $g_3 = 2.003$.[42] We note that the signal near $g = 2.026$ (peroxy) shifts to slightly higher g value after irradiation. Spectrum c shows that annealing for 1 h at room temperature is sufficient to cause most of the radicals originating from the UV-cleaved peroxides to decay. After annealing for 3 days at room temperature, spectrum d, the signal is nearly the same as before UV irradiation. Therefore, we believe that the peroxy radicals observed after UV irradiation reside in the amorphous regions of polyethylene. The half-life of these radicals is on the order of minutes, corresponding to

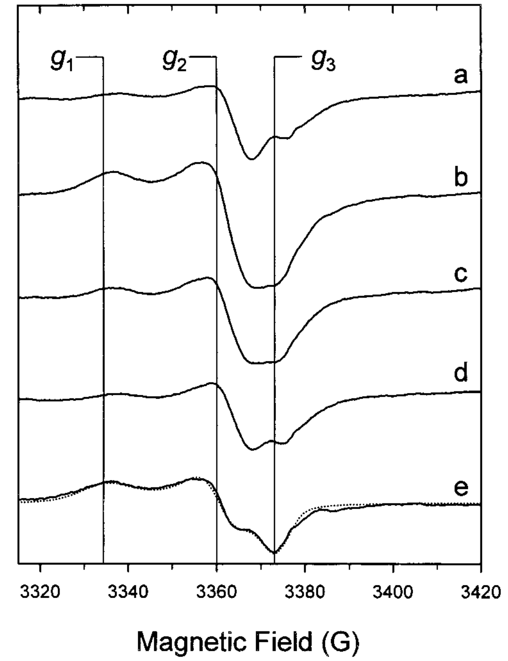

Figure 8. Creation of peroxy radicals in γ-irradiated polyethylene by UV cleavage of hydroperoxides. All EPR spectra were taken at a microwave power of 20 mW and temperature of 50 K. (a) Spectrum of the polyenyl radicals and the already-existing peroxy radical in the γ-irradiated sample. (b) Spectrum of the peroxy radicals created after in-situ UV illumination. (c) Spectrum of the sample after annealing for 1 h at RT. (d) Spectrum of the sample after annealing for 3 days at RT. The signal has returned to its preirradiated 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, $g_1 = 2.026$, $g_2 = 2.011$, $g_3 = 2.003$.

what was observed previously for peroxy radicals in the amorphous phase.[23] Conversely, the peroxy radicals existing before UV irradiation were observed to decay extremely slowly, with a half-life on the order of months. Consequently, these radicals are thought to be in either crystalline or interfacial environments.[36,43] In summary, the quick decay of the UV-generated peroxy radicals indicates that these radicals, and thus the hydroperoxides they arise from, are in the amorphous phase.

Conclusions

We have shown that the hydroperoxide species in γ-irradiated ^{13}C-polyethylene can be directly monitored by MAS ^{13}C NMR spectroscopy. The experiments were performed without the need for special sample preparation such as chemical derivatization or dissolution. Annealing experiments demonstrated that the hydroperoxide species are thermally unstable and illustrated why this species was not observed in the sample irradiated at 80 °C. We could readily observe the disappearance of the peroxide resonance and the simultaneous growth of product resonances corresponding to alcohols, ketones, and acids/esters. A combination of propagation, chain branching, and termination steps is required to account for the distribution of product species. An activation energy for peroxide decomposition of 108 kJ/mol was calculated from annealing data gathered at a series of temperatures. EPR spectroscopy suggests that residual polyenyl and a very low concentration of peroxy radicals are predominately trapped in interfacial or crystalline regions. Peroxy radicals observed after UV photolysis of hydroperoxides are in amorphous regions, consistent with degradation occurring in the amorphous phase.

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