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Thermal Oxidation and Its Analysis at Low Levels in Polyethylene

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ABSTRACT: Water causes electrical breakdown and erosion processes to occur in polyethylene dielectric material at voltages lower than in the dry polymer. It has recently been shown that solubility and diffusion of water in branched polyethylene are related to the degree of oxidation of the polymer. This report concerns (1) the chemical identification and quantification of the sites of oxidation in polyethylene that has been thermally oxidized at low levels (0.6–1.9% oxygen) and (2) assessment of the motional nature of water in oxidized polyethylene. Carbon-13 NMR is shown to be an effective spectroscopic technique that can identify oxidation products at the 0.05% level. Ketones, secondary alcohols, secondary hydroperoxides, and carboxylic acids are found as the major oxygen-containing groups. The striking differences in the distribution of these species that are found between linear low-density polyethylene (LLDPE) and low-density polyethylene (LDPE) are attributed to differences in thermal treatment and branch patterns. Proton NMR, infrared spectroscopy, and ultraviolet spectroscopy provide complementary data. The motional state of water is determined by solid-state quadrupole echo deuterium NMR spectroscopy of oxidized polyethylene that has been saturated with D_2O. The water associated with polyethylene has an approximate correlation time of 10^{-9} s at 20 °C.

Introduction

Polymer degradation, early recognized as the Achilles' heel in polymer applications, continues to be an active area of research. Whether caused by autoxidation, photooxidation, thermal treatment, mechanical stress, hydrolysis, or environmental pollutants, the degradative effects (e.g., cross-linking, embrittlement, and chain scission) invariably lead to an inferior material.[1] Production of new polymer materials and development of more effective polymer stabilizers require an understanding of the chemistry of the degradative process, which in turn requires that one be able to accurately identify and quantify the polymer degradation sites in ever-lower concentrations.

Of particular technological interest in the area of polymer degradation and stabilization is the interaction of polyethylene dielectric material with water. Water causes electrical breakdown and erosion processes to occur in polyethylene at voltages lower than in the dry material.[2] It has recently been shown that water solubility and diffusion in branched polyethylene are related to the degree of oxidation of the polymer.[3,4] A model has been developed to explain this dependence in polyethylene samples that have been oxidized to low levels by thermal means.[4] In the model, the oxygen-containing groups in polyethylene are considered to act as traps that partially immobilize the water. As a water molecule diffuses through an oxidized polyethylene it moves rapidly through the hydrocarbon matrix but spends part of its time restricted in the traps.

In this report we present ^{13}C NMR, ^{1}H NMR, IR, and UV results that identify and quantify the nature of these traps. In addition, we estimate the correlation time for a water molecule in a trap site from solid-state ^{2}H NMR evidence. These experiments are very demanding in terms of sensitivity, dynamic range, and resolution, as the total concentration of oxidized species in these samples ranges from 0.5 to 1.9% and the water content is substantially less.[4] This investigation exploits major advances that have been made in the sensitivity of spectroscopic techniques in the past several years, particularly in the area of NMR. We show that discrete oxidized groups can be chemically identified and quantified in polyethylene at levels below 0.05%. Additionally, we illustrate the utility of solid-state deuterium NMR spectroscopy for the determination of water mobility at low water contents (ca. 600 ppm D_2O).

The ability to distinguish at low levels among primary, secondary, and tertiary alcohols, for example, is used to identify and quantify the trap sites in this work. These techniques not only are useful in the present context but hold promise in the general area of polymer stabilization and degradation. Detailed chemical identification and quantification of oxidized species can provide useful information regarding the mechanisms and kinetics of polymer degradation. Furthermore, the ability to perform routine analyses at low degrees of oxidation makes possible a rigorous assessment of the effect of various stabilizers on the degradation processes.

Table I
Physical Data for Polyethylene Samples

sample	process	T_m, °C	melt flow index, g/10 min	O content, ppm
A	ethylene/CO copolymer	114		7880
B, control	linear low density	114	0.46	97
B, oxidized				18900
C, control	low density	109	0.22	550
C, oxidized				8200
C, oxidized				11000
D, control	low density	108	0.59	<55
D, oxidized				6260
E	ethylene/acrylic acid copolymer	105		27800[a]

[a] Determined by ^{13}C NMR.

Materials and Methods

Samples. The samples used in this work are of commercial origin and do not contain halogens or metals above the ca. 10 ppm level. Sample A is an ethylene/carbon monoxide copolymer. Sample B is a linear low-density polyethylene (LLDPE), and its oxidized version was prepared by oven-aging the material for 45 days at 60 °C. Samples C and D are low-density polyethylene (LDPE), and the oxidized polymers C and D were prepared by milling the polyethylene samples at 160 °C for 3 h. Sample E is an ethylene/acrylic acid copolymer. Neutron activation analysis was used to determine the amount of oxygen in the "control" (unoxidized) and oxidized samples. The physical data for these samples are summarized in Table I.

Carbon-13 NMR Measurements. Matched samples of oxidized and "control" polyethylene were prepared for solution-state NMR spectroscopy under a nitrogen atmosphere. Small pieces of the polymer were added in increments to degassed (three freeze–pump–thaw cycles) 1,2,4-trichlorobenzene (Aldrich, Gold Label) held at 110 °C. Santonox-R antioxidant (4,4′-thiobis(2-*tert*-butyl-5-methylphenol)) was added at ca. 0.05% concentration. Samples were stirred as necessary under the nitrogen atmosphere.

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Table II
Branch Contents for Polyethylene Samples

	sample		
branches per 1000 CH_2 groups	B	C	D
ethyl	9.9	3.0	2
butyl	0.7	10.4	7.7
amyl		3.1	3
long		3.7	5
total branches per 1000 CH_2 groups	10.6	20.2	17.7

Complete solution required 12–24 h at 110 °C. Final concentrations of 24–30% (w/v) were obtained.

NMR spectra were recorded at 50.3 MHz for ^{13}C on a Varian XL-200 NMR spectrometer using a high-sensitivity, fixed-frequency 10-mm probe. Double-precision (32-bit word) and floating-point arithmetic were used for all analyses.

The spectra for oxidation determinations were obtained with an Overhauser enhancement, and sample temperature was maintained at either 110 or 120 °C. In all cases, tandem spectra were obtained for both the "control" and the oxidized material. Equivalent results were obtained with a 10.3-s delay between pulses (70° pulse width) or a 3.3-s delay (79° pulse width). Approximately 20 000 transients were accumulated for each run.

The distribution of oxidation products was analyzed for each sample according to the method of Cheng et al.[5] Two "cut-and-weigh" measurements were made for each of two separate NMR data accumulations. The CH_2 peaks were used exclusively for quantification, although other peaks were used for diagnostic purposes.

The NMR spectra used for branch analysis were obtained at 120 °C, using a 15-s delay between pulses and a 90° pulse width. The nuclear Overhauser enhancement was suppressed, and approximately 3000 transients were collected for each run. The main branch points were analyzed according to the assignments of Dorman et al.[6] and Bovey et al.[7] Intensities from the peaks arising from low concentrations of other branches were neglected. Duplicate "cut-and-weigh" analyses were used for each branch determination. The branch contents of the samples are listed in Table II.

Proton NMR Measurements of Solid Polyethylene. A solid sample of dry polyethylene C (oxidized, 8200 ppm oxygen content) and an oxidized sample containing 240 ppm water were examined by proton NMR at 200 MHz using the decoupler coil of the high-sensitivity 10-mm carbon probe for the Varian XL-200 NMR spectrometer. "Block averaging" was used to avoid dynamic range problems. A 90° pulse width was employed with a 5-a delay between pulses. Signal averaging was continued until the digitizer was filled.

Proton NMR Measurements of Polyethylene in Solution. Matched samples of oxidized and "control" polyethylenes B, C, and D and sample A were prepared for solution-state NMR spectroscopy. The samples were placed in the NMR sample tubes while under a nitrogen atmosphere. A fresh "snap-vial" of nitrobenzene-d_5 (Aldrich, Gold Label) was opened under the nitrogen atmosphere and 0.5 mL of this solvent was added to each tube. Enough polymer was added to produce a 2% (w/v) solution. These samples were then heated to 115 °C and stirred as necessary under the nitrogen atmosphere. Total solution was not achieved in all cases.

NMR spectra were recorded at 200 MHz for ^1H on a Varian XL-200 NMR spectrometer using a 5-mm probe with a sample temperature of 120 °C. Double precision (32-bit word) was used for all acquisitions. A 5.3-μs pulse (90° pulse) was used with a 10-s delay between pulses. Sixty-four transients were accumulated for each spectrum.

Deuterium NMR Spectroscopy of Solid Polyethylene. Dried, oxidized polyethylene sample B was soaked in deuterium oxide (D_2O). A duplicate sample was saturated with water (H_2O) for control purposes. The diffusion process required approximately 1 week at 20 °C. Prior to NMR measurement, the precut polyethylene samples were blotted and allowed to equilibrate in a 99% relative humidity D_2O chamber[8] for at least 2 days. The samples were transferred to equilibrated NMR sample cells, which were then sealed.

Table III
Distribution of Oxidation Products for Polyethylene Samples

	sample				
	A	B	C	D	E
total % oxygen	0.8	1.9	1.1	0.6	2.8
distribution of oxidation products					
ketone	100	57	21	18	
secondary alcohol		14	55	40	
tertiary alcohol and "other" products		7	6[b]	7	5
carboxylic acids		22	4	4	95
secondary hydroperoxides[a]			15	32	

[a] Decomposes to secondary alcohol during sample preparation and NMR measurement. [b] Primarily esters, initially present in the unoxidized material.

The Varian XL-200 NMR spectrometer, operating at 30.7 MHz for ^2H, was used to observe any sharp D_2O lines that may be present. In excess of 80 000 scans were accumulated with a 1-s repetition time.

Quadrupole echo deuterium NMR spectra were observed at 55.26 MHz on a home-built spectrometer[9] operating at 360 MHz for protons. The quadrupole echo pulse sequence[10,11] was used with a 10-MHz digitization rate, a 30-μs delay within the sequence, and a 2-s repetition rate. Approximately 40 000 scans were accumulated.

Moisture analyses were performed upon completion of some of the deuterium NMR experiments to ensure that D_2O was present in the samples during NMR measurement.

Infrared Measurements. Infrared measurements were performed on both the control and oxidized samples using a Perkin-Elmer model 283B spectrometer. The samples were prepared by hot molding films of the samples 13 mils thick.

Ultraviolet Spectroscopy Measurements. The UV spectra of the 13-mil samples were recorded on a Perkin-Elmer Model 330 UV spectrometer.

Results and Discussion

Chemical Identification of Oxidation Products by Carbon-13 NMR. Carbon-13 NMR spectroscopy was used as the major tool for chemical identification of the oxidized sites. Previous studies of model compounds and of highly oxidized polyethylene samples have shown that the chemical shifts for the CH_2 carbons α and β to carbons bearing oxygen can be used to identify the oxidation sites.[5] The present study differs from earlier ones in that here the oxidized sites are present in 1–2 orders of magnitude less concentration. Nevertheless, quantitative data could be obtained by careful comparison of carbon NMR spectra of the specific polyethylene samples before and after oxidation. Figures 1 and 2 illustrate the type of spectra obtained for the oxidized polyethylene samples and additionally show the general assignments used in this work. The results of the carbon NMR analyses of oxidation products are summarized in Table III.

The striking differences between LLDPE and LDPE oxidation patterns (Table III) are attributed to differences in the thermal treatment and in the distribution and identity of branch sites (see Table II). The two samples of LDPE show similar patterns in the distribution of oxidation products, once the conversion of hydroperoxides to secondary alcohols is considered. Some conversion of hydroperoxide to secondary alcohol occurs during the process of dissolution and recording the NMR spectra. Nevertheless, the IR data (see below) indicate that the relative hydroperoxide concentrations shown in Table III are correct. The differences in oxidized products for samples C and D may be due to the presence of different additives in the two materials. (The UV data suggest that sample C contains additives not present in sample D.)

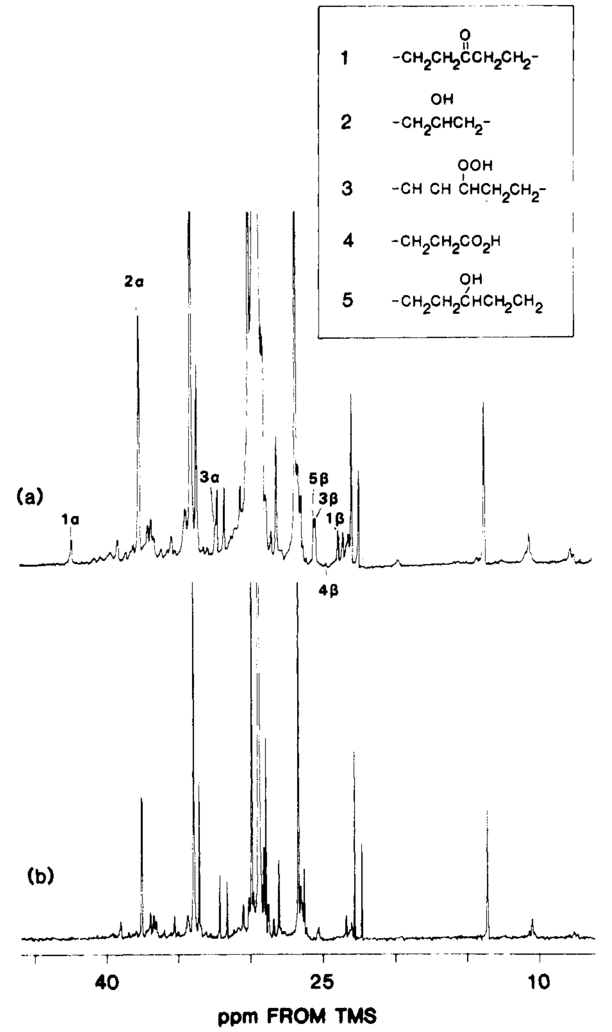

Figure 1. Carbon-13 NMR spectra of the CH_2 region of control (bottom) and oxidized (top) LDPE (sample D). Assignments are shown in the inset.

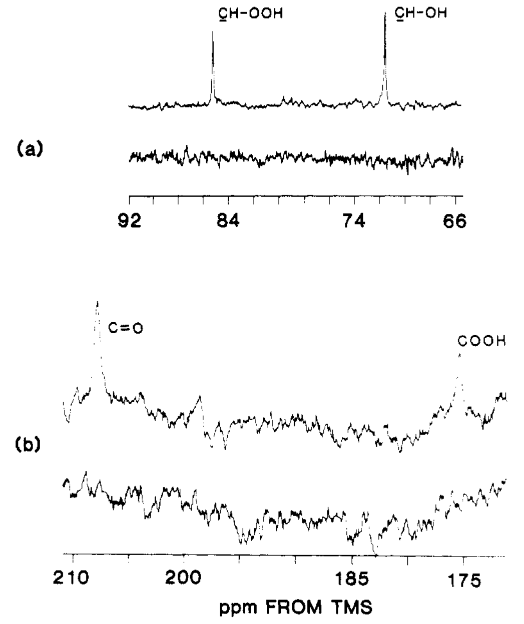

Figure 2. Carbon-13 NMR spectra of (a) the methine region of sample D and (b) the C=O region of sample B. The top spectrum of each set is of the oxidized material; the bottom is the control.

Identification of the Oxidation Sites by Proton NMR. Although carbon NMR has proved to be the method of choice for measuring stereochemical configurations and subtle structural differences in polymers, it suffers from relatively low sensitivity due to the low natural abundance of the carbon-13 isotope. Proton NMR has the advantage of high sensitivity but has the drawback of a narrow chemical shift range. Here we explore the utility of proton NMR as a method for the rapid assessment of oxidation products in polyethylene.

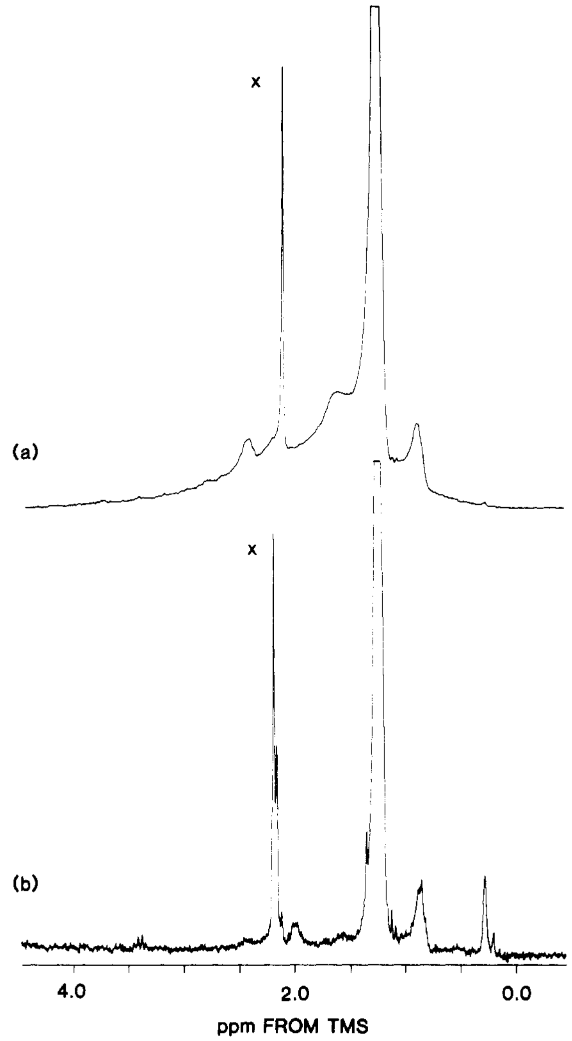

Figure 3. Proton NMR spectra of LLDPE (sample B): (a) oxidized; (b) control. X = solvent impurity.

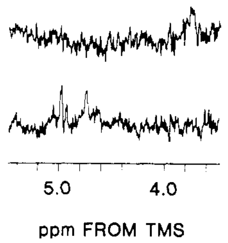

Figure 4. Proton NMR spectra of the olefinic region of LLDPE (sample B): top, oxidized material; bottom, control.

Figure 3 illustrates proton NMR spectra of oxidized and control LLDPE (sample B). Characteristic differences are noted between the proton NMR spectra of the control and oxidized samples. New peaks are observed at ca. 1.6 and 2.4 ppm. The line width differences observed between the control and oxidized samples are attributed to cross-linking that has occurred during thermal oxidation.

Figure 4 shows the 3.6–5.4 ppm region of the ^1H NMR spectra of oxidized and unoxidized polyethylene sample B. The resonances in the spectrum of the control sample (lower spectrum in Figure 4) are due to double bonds and are weak in intensity. Upon oxidation, it is observed that these resonances disappear (Figure 4, top). It is noted that most polyethylene chains contain a small proportion of vinyl ($-CH{=}CH_2$), vinylidene ($=CH_2$), and vinylene ($-CH{=}CH-$) groups. Disappearance of these resonances in the spectrum of the oxidized sample indicates that the double bonds are vulnerable to the free radicals present during thermal oxidation. The IR spectra (see below) support this observation.

The proton NMR spectra of the oxidized material are in qualitative agreement with the ^{13}C NMR results. The proton spectra, although useful for qualitative assessment of polyethylene oxidation, are not suitable for quantitative determinations.

Chemical Identification of Oxidation Sites by Infrared Spectroscopy. The NMR results are subject to relatively low sensitivity when compared to IR and UV techniques. However, NMR data have the advantage that they can be obtained under quantitative conditions when proper attention is paid to Overhauser effects and relaxation times. Such considerations make the NMR analysis an ideal technique when both quantitative measurements and identification information are required. Complementing the NMR measurements are infrared determinations which are particularly sensitive to C–O bonds and thus afford high sensitivity for assessment of the oxidation products in solid polyethylene.[12,13]

The IR results provide excellent corroboration of the NMR data. Examples of IR spectra of the oxidized polyethylene samples are shown in Figure 5.

The spectra of the oxidized samples all show the presence of hydroxyl structres near 3400 cm^{-1} which are approximately the same intensity. The profiles of the sample C and sample D –OH absorptions are similar (i.e., the 3360-cm^{-1} absorption is stronger than the 3420-cm^{-1} component). However, the –OH absorption of the oxidized LLDPE sample (sample B) shows the 3420-cm^{-1} component stronger than the 3360 cm^{-1} component, indicating a different distribution of –OH-containing groups in the oxidized LLDPE sample. This finding is consistent with the carbon NMR results (Table III), in which the LLDPE sample contains large amounts of acid groups, not found in samples C and D.

In addition, the structural modifications due to oxidation can be noted in all samples by the appearance of strong absorption bands near 1700 cm^{-1}. The LLDPE sample has the strongest carbonyl absorption band (maxima at 1718 cm^{-1}) due to ketonic C=O moieties. Other C=O-containing structures are evident at 1785 (peresters), 1738 (esters), and 1700 cm^{-1} (acids). The strength of the carbonyl absorption band decreases in going from sample B (LLDPE) to sample C to sample D.

The depression of the background between 800 and 1300 cm^{-1} is due to the formation of other oxygen-containing structures such as C–O–C and C–OH. This background depression arises because the absorption band envelope is composed of many unresolved peaks. In addition, the bands in the 800–900-cm^{-1} region, due to vinyl groups,[14] decrease in intensity upon oxidation.

The –OOH absorption at 3555 cm^{-1} is particularly diagnostic. This peak is extremely weak or absent in the sample of LLDPE (B) but is present in LDPE samples C and D. The intensity of the –OOH absorption in sample D (A = 0.085) is approximately twice as strong as the –OOH absorption in sample C (A = 0.043) (Figure 5). This is in agreement with the relative amounts of secondary hydroperoxide determined by ^{13}C NMR analysis (Table III).

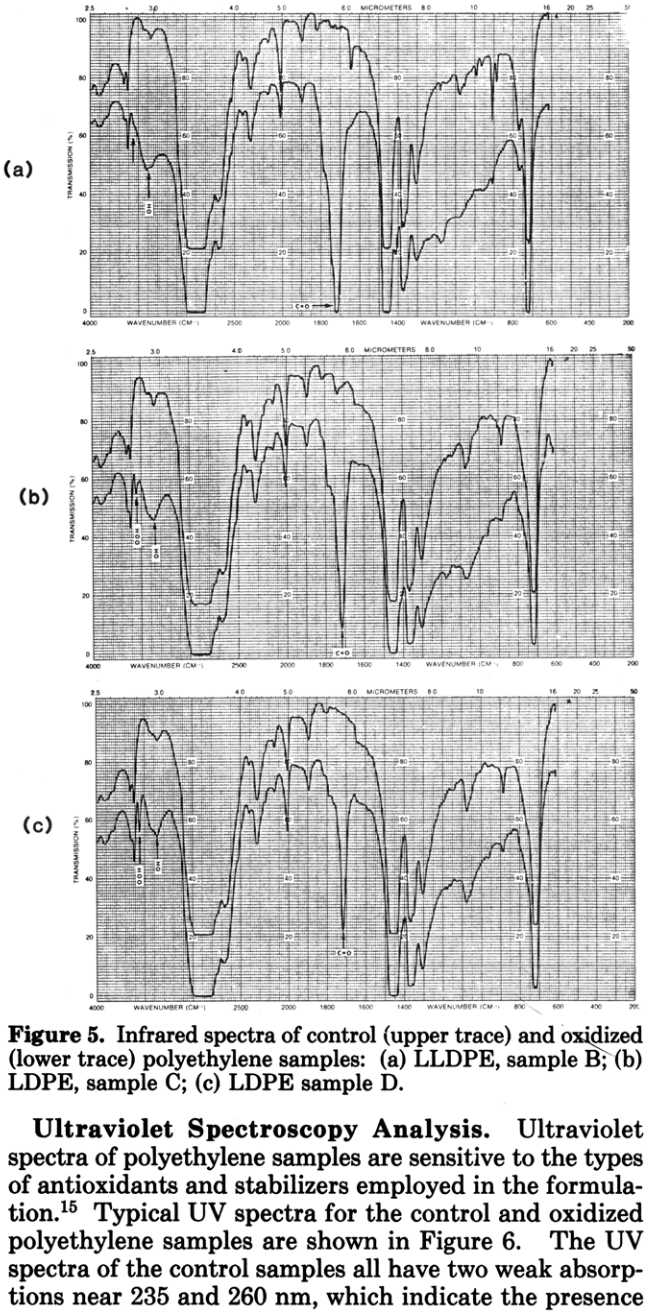

Figure 5. Infrared spectra of control (upper trace) and oxidized (lower trace) polyethylene samples: (a) LLDPE, sample B; (b) LDPE, sample C; (c) LDPE sample D.

Ultraviolet Spectroscopy Analysis. Ultraviolet spectra of polyethylene samples are sensitive to the types of antioxidants and stabilizers employed in the formulation.[15] Typical UV spectra for the control and oxidized polyethylene samples are shown in Figure 6. The UV spectra of the control samples all have two weak absorptions near 235 and 260 nm, which indicate the presence of an aromatic substance, probably a low (ca. 0.01 % (w/w)) concentration of a "shelf-life" antioxidant. These two absorptions are the strongest in sample C, followed by sample D, and are weakest in sample B. The UV spectra of the oxidized samples all show the characteristic oxidation absorption at 270 nm.

NMR Analysis of Water Associated with Polyethylene. Diffusion and solubility of water in polyethylene have been shown to be a function of the degree of oxidation of the material.[3,4] Approximately 1 ppm of water is entrained for every 30 ppm of oxygen in the polymer.[4] NMR data were sought to determine the state of the water associated with the oxidized polyethylene samples. All of the NMR experiments indicate that the water molecules are partially immobilized.

Attempts to observed sharp water lines were performed by observing the proton resonance of solid, water-saturated, oxidized polyethylene sample C. A broad line (ca. 1 kHz at half-height) was observed for this solid material. No sharp features were evident. The strong broad signal is attributed to the protons in the amorphous part of this sample.

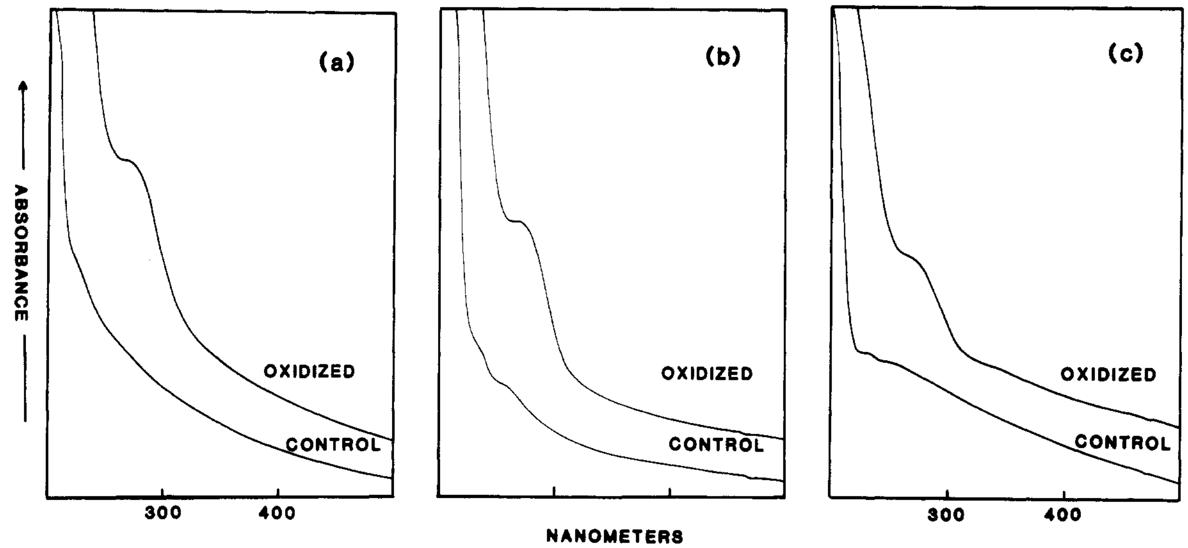

Figure 6. Ultraviolet spectra of oxidized and control polyethylene samples: (a) B; (b) C; (c) D.

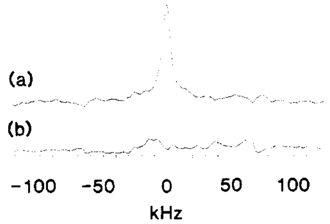

Figure 7. Solid-state quadrupole echo deuterium NMR spectra of D_2O-saturated oxidized LLDPE sample B (top) and H_2O-saturated oxidized LLDPE sample B (bottom).

The above experiment was repeated using instead high-resolution deuterium NMR and D_2O-diffused polyethylene, to eliminate the possibility of dynamic range considerations obscuring a sharp signal from the water in sample C. Under the conditions of the high-resolution experiment, only a broad, featureless line was observed, and no sharp peaks were evident. Taken together, the high-resolution proton and deuterium NMR experiments provide strong evidence that the water associated with the oxidized polyethylene is not isotropically mobile on a 10^{11}-s^{-1} time scale.

NMR resonances for deuterated water in the oxidized sample B were observed by using solid-state deuterium NMR techniques. The deuterium spectrum observed when the quadrupole echo pulse sequence is used is composed of two components: a narrow one with a width at half-height of 3kHz, and a much weaker and broader Pake doublet with $d\nu_q$ of approximately 90 kHz (Figure 7). The relatively narrow line is attributed to partially immobilized water, and the broader component is attributed to R-COOH and R-OH groups in the polymer that have exchanged with D_2D.

Observation of a relatively narrow component with the quadrupole echo pulse sequence indicates that there are time constraints on the motion of the water.[16] (If the water were isotropically mobile, essentially no signal would have been observed with this sequence.) However, the 5-kHz line represents substantial motional narrowing when compared to the ca. 140-kHz Pake splitting expected for frozen water. These considerations suggest that the narrow component has a correlation time in the range of 10^{-9} s.

Summary

Carbon-13 NMR spectroscopy is shown to be an effective spectroscopic method for identifying and quantifying oxidation sites in polyethylene samples that have been thermally oxidized at low levels (0.6–1.9% oxygen). Individual oxidation products can be identified and quantified at approximately the 0.05% level. Ketones, secondary alcohols, secondary hydroperoxides, and carboxylic acids are identified as the primary oxidized species. The carbon NMR results show a striking variation in the distribution of oxidation products between LLDPE and LDPE. These differences in oxidation patterns are attributed to different branch contents and to different thermal treatment of these polymers.

Complementary data are obtained from IR measurements. The sensitivity of IR to C-O-type bonds makes this technique particularly useful for the qualitative identification of oxidation products in solid polyethylene. The IR and NMR results presented here are in excellent agreement. UV determinations provide information on the amount of stabilizer present in the polymer.

Finally, solid-state deuterium NMR spectroscopy is shown to be a powerful method for the analysis of water (D_2O) mobility in polymer samples containing low levels of water. The water associated with oxidized polyethylene has an approximate correlation time of 10^{-9} s.

Taken together, the results of these experiments provide chemical identifications for the water trap sites in oxidized polyethylene and further provide information of the motional state of water in the polymer. It is predicted that major advances in the understanding of oxidation mechanisms and in the knowledge of how stabilizers inhibit oxidation will occur through combined spectroscopic methods and through detailed NMR analyses of oxidized polymers at still higher magnetic field strengths.

Acknowledgment. We are grateful to H. E. Bair for performing the thermal measurements on the polyethylene samples.

Registry No. (Ethylene)·(carbon monoxide) (copolymer), 25052-62-4; polyethylene (homopolymer), 9002-88-4; (ethylene)·(acrylic acid) (copolymer), 9010-77-9; water, 7732-18-5.

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Radiation-Induced Degradation of Poly(α-methylstyrene) in Solution[1]

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ABSTRACT: Radiation-induced degradation of poly(α-methylstyrene) was studied in benzene solution. Random scission of the polymer chain was confirmed by GPC measurements. The G value for chain scission was found to be independent of dose rate and was estimated to be 0.78. The degradation was accelerated by the addition of chlorine-containing compounds with high G values for radical production. The ESR spectroscopy spin trapping technique revealed that phenyl and trichloromethyl radicals were derived during γ-irradiation from chlorobenzene and carbon tetrachloride, respectively. The trapped polymer radical was identified as the species formed through hydrogen abstraction from methylene groups of the polymer chain. These results indicate that the attack of a reactive radical on the polymer chain, followed by hydrogen abstraction, plays an important role in radiation-induced degradation of poly(α-methylstyrene) in dilute solution.

Introduction

A number of investigations have been performed on the radiation chemistry of polymers, being devoted to chemical changes of polymers such as degradation and cross-linking.[4] As proposed by Miller,[5] polymers can be generally classified into two groups, degradation-type polymers and cross-linking-type polymers, with exposure to γ-rays or electron beams. Poly(methyl methacrylate) (PMMA) is well-known as a typical degradation-type polymer, and experiments on this polymer have been extensively carried out. However, little attention has been paid to the radiation-induced degradation of poly(α-methylstyrene) (PMSt), which is also a degradation-type polymer.

The radiolysis of PMSt in bulk was first reported by Kotliar.[6] He interpreted the observed degradation in terms of a simple scission of a carbon–carbon bond in the main chain of the polymer. Recent experiments performed by Yamamoto et al.[7] revealed that various kinds of dimer are formed in the radiolysis of PMSt at high temperatures by an ionic chain reaction.

The radiation-induced degradation of polymers in bulk has been well understood by the mechanism of the above-mentioned chain scission.[4d] On the other hand, the radiolysis of polymers in solution has been found to be very complicated, depending on several factors such as the nature of solvent, the concentration of polymer, and the atmosphere.[4c] The present paper is concerned with the radiation-induced degradation of PMSt in benzene. The effect of added chlorine-containing compounds on the chain scission has been studied and interpreted on the basis of ESR measurements by means of the spin trapping technique.

Experimental Section

PMSt was prepared by cationic polymerization and then purified by conventional methods. 2-Methyl-2-nitrosopropane (t-BuNO) was carefully purified as reported in the previous paper.[8] Similar precautions were taken to exclude light because t-BuNO is easily photolyzed by long-wave visible light to form di-*tert*-butyl nitroxide.[9] Additives were the best grades commercially available and were once distilled prior to use, the middle cuts being employed. Ethanol contained in chloroform was removed by Vogel's method.[10] Spectroscopic grade benzene was distilled over sodium metal just before use.

γ-Irradiations were performed with a 12 000-Ci ^{60}Co source at the Research Reactor Institute, Kyoto University. The apparatus used for evaluation of the extent of chain scission was composed of a cylindrical quartz tube with an attached capillary viscometer. All samples were degassed by several freeze–thaw cycles under high vacuum and then sealed off.

In the present study, the polymer concentrations are expressed as moles per liter based on the monomer unit, and all experiments on degradation were carried out at the constant polymer concentration of 4.2×10^{-2} M (0.5 g/dL).

Molecular weight distributions of the polymer were measured with a Toyo Soda Model 801A gel permeation chromatograph calibrated to a standard PMSt sample for GPC measurements. From analogous considerations on the molecular weight distribution of the polymer as in the case of photosensitized degradation of PMSt,[11] the molecular weight of the polymer and the extent of chain scission were determined by viscometry. All G values for chain scission were calculated on the basis of the radiation energy that was absorbed by the polymer itself.

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