Carbon-13 NMR Study of the Solid-State Photochemistry of Poly(ethylene-*co*-carbon monoxide)

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ABSTRACT: The structure of an (E/CO) copolymer (1.4 wt % CO) has been studied by 50.3-MHz carbon-13 NMR spectroscopy. With model compounds, assignments of new structures and previously undetected products of photodegradation and photooxidation in the solid state were made. About 4% of the CO groups were accounted for as ethyl ketones with the remainder being randomly distributed along the polymer backbone chain. Evidence is presented for the formation of *cis,trans*-cyclobutanols, which have not been detected previously in the solid-state irradiation of ketone-containing polymers. A novel α-branched ketonic structure was found, also. The reactivity of ketonic groups will be discussed based on their morphological environment. The limits of detection of photooxidation products, carboxylic acids, and alcohols were determined based on the amount of oxygen absorbed.

Introduction

An understanding of the photochemistry of ketonic chromophores in polymers is important for several reasons. Present as trace impurities in polymers, carbonyl groups may be important as initiators for unwanted photodegradation and photooxidation.[1–4] When deliberately incorporated, ketonic groups can enhance the sensitivity of photopatternable materials used for micron-scale lithographic processes.[5] When present in the main chain of semicrystalline polyolefins, ketonic groups can function as reaction probes of morphology.

The photochemical reactivity of copolymers of ethylene and carbon monoxide (E/CO) has been studied extensively.[6,7] Earlier, we characterized a copolymer of 1.4% CO content and described its photodegradation and photooxidation in the solid state using a number of experimental techniques.[7,8] This paper reports a more detailed study of the (E/CO) molecular structure and the photochemical degradation and photooxidation using carbon-13 NMR spectroscopy. This copolymer is particularly suitable for NMR study because it did not cross-link under the experimental conditions. Although most CO groups were randomly located in the polymer backbone chain, a small fraction was present as ethyl ketone chain ends and short branches.

In addition to previously detected products of Norrish photochemical processes, evidence was found for the formation of cyclobutanols and a novel α-branched ketone. A reaction scheme is presented inferring a difference in the reactivity of ketonic groups in crystalline and amorphous regions. The limits for the detection of some of the products of oxidation were established.

Experimental Section

Samples of (E/CO) copolymer containing 1.4 and 18 wt % CO were obtained from the E. I. du Pont de Nemours and Co. The 1.4% CO sample was found to have a crystallinity content of 50% by differential scanning calorimetry.[8] Compression molded films were exposed in sealed cells under argon or oxygen as described previously.[7] The sample under argon was exposed for 120 h, and the sample under oxygen consumed 18.4 mL of oxygen/g of polymer during a 194-h exposure.

Carbon-13 NMR Spectroscopy. The 22.53-MHz carbon-13 NMR spectra of polymers and model compounds were obtained at 110 °C by using a JEOL FX90Q spectrometer. Scans were accumulated using complete proton decoupling with a pulse angle of 90° and a pulse interval of 4 s. The samples were ~15–20% polymer (by weight) in a 4:1 (v/v) solution of 1,2,4-trichlorobenzene and *p*-dioxane-d_8. Hexamethyldisiloxane (HMDS) was used as an internal reference (2.00 ppm vs TMS), and the dioxane-d_8 provided the internal deuterium lock. Higher field spectra of polymers were obtained at 110 °C by using a Varian XL200 spectrometer operating at 50.30 MHz. Typically, 10 000–15 000 scans were accumulated.

Synthesis of *cis,trans*-1-Nonyl-2-hexylcyclobutan-1-ols. A 0.01 M solution of 10-nonadecanone (Aldrich) in ethanol was deareated for 30 min with bubbling argon. The solution was irradiated in a 2.5-cm path length quartz cell with a 100-W medium-pressure Hg lamp (Applied Photophysics Quantum Yield Reactor) and a 2.5-cm water filter for 14 h. The solvent was evaporated under vacuum and the residue analyzed by gas chromatography on a Varian 1400 gas chromatograph with a thermal conductivity detector and a Hewlett Packard integrator. Preparative and quantitative analyses were made using a 2 m × $^1/_8$ in. stainless steel column packed with 1.5% OV 101 on Chromasorb GHP 100/120 and temperature programming at 180–325 °C of 5°/min. Optimum separations were made at helium flow rates of 35–50 mL/min.

Analysis of the residue indicated a mixture of >90% cyclobutanols with less than 5% starting material and the side products, 1-octene and 2-undecanone. A fraction of the purified cyclobutanols showed a satisfactory NMR spectrum for an equimolar mixture of *cis*- and *trans*-1-nonyl-2-hexylcyclobutan-1-ol.

Synthesis of 9-Octylnonadecan-10-one. The symmetrical ketone nonadecan-10-one was alkylated with *n*-octyl bromide by using NaH in dimethoxyethylene glycol.[9] The reaction was monitored by gas chromatography using the conditions described above and was stopped after 85% conversion of starting ketone with the formation of two major products in a 2:1 ratio. Analysis by NMR of a fraction of the lesser product was consistent with a structure assigned to the desired monoalkylated ketone, 9-octylnonadecan-10-one. The spectrum of the major product was consistent with a structure assigned to the dialkylated ketone, 9,11-dioctylnonadecan-10-one.

Solid-State Irradiation of 10-Nonadecanone. A thin film (<0.5 mm) of 10-nonadecanone was applied to a quartz plate by melting and cooling on a hot stage. The plate was placed in a sealed cell equipped with a Pyrex window and irradiated under nitrogen with a 450-W Hg lamp (Hanovia) for 520 h while the temperature was maintained at 42 °C by circulating water. After irradiation, the film became a viscous fluid. Gas chromatographic and NMR analysis showed that the products consisted of 1-octene, 2-undecanone, and *cis,trans*-1-nonyl-2-hexylcyclobutanols, as would be expected from an irradiation of the starting ketone in the melt. No branched ketones were detected within experimental limits.

Results

The similarity of the branched structure of 1.4% (E/CO) to that of high-pressure polyethylene was observed previously with 22.5-MHz ^{13}C NMR spectroscopy.[7] This study involves the examination at higher field of the structure of the original unirradiated (E/CO) copolymer, the structure of a sample irradiated for 120 h under argon, and the structure of a sample irradiated under oxygen for 190

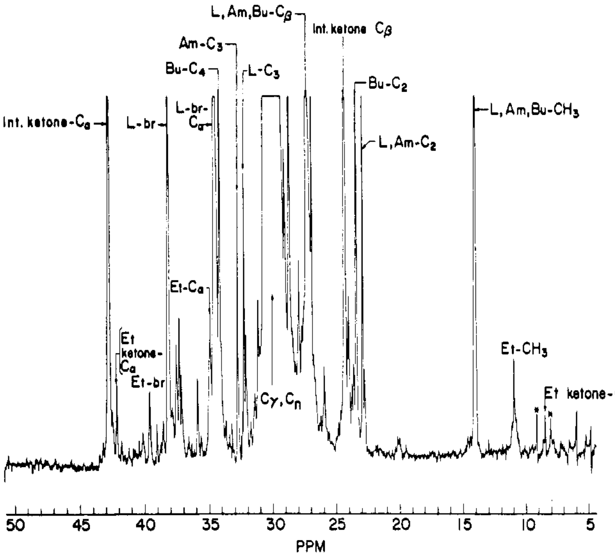


Figure 1. 50.3-MHz ^{13}C NMR spectrum of 1.4% (E/CO) copolymer. Assignments are made according to the structures of the scheme in the text. The starred peaks are unidentified and not observed in polyethylene spectra.

h. The copolymer, unlike polyethylene, remained soluble throughout the irradiations, thus permitting analysis by high-resolution NMR techniques.[10] The spectra were obtained under conditions resulting in a signal-to-noise ratio 10–15 times greater than that of the earlier study. The concentrations of various functional groups, determined from relative peak intensities, are uncorrected for differences in relaxation times and therefore only semiquantitative at best.

A 50.3-MHz spectrum of an unirradiated sample of (E/CO) is shown in Figure 1. Structural assignments are based on prior studies and are designated according to the scheme shown below.[11–13]

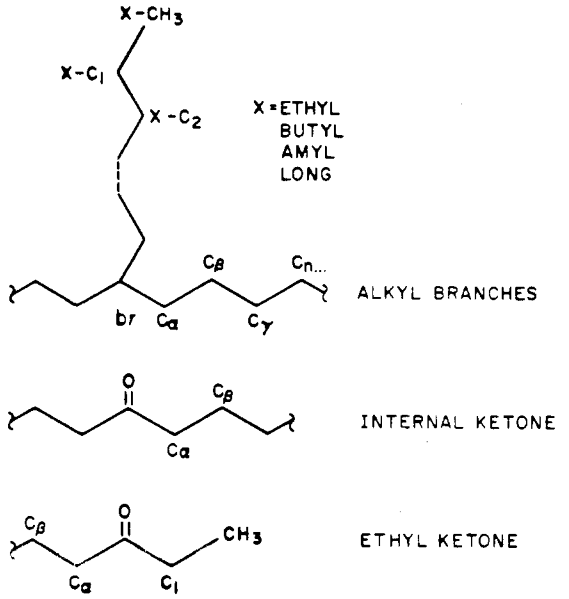
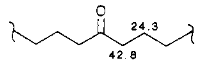
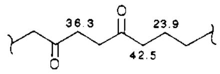
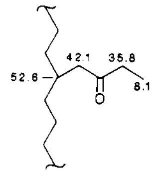
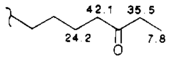
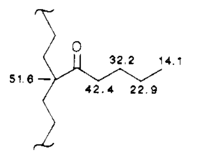
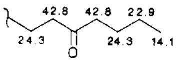
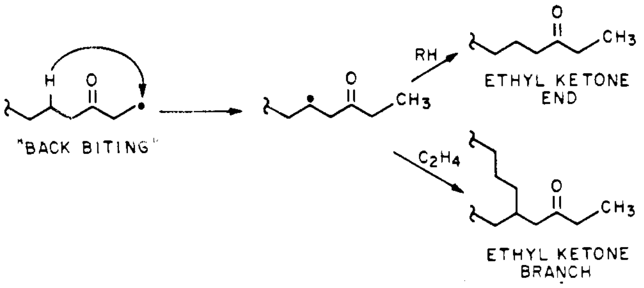


Table I
^{13}C NMR Assignments (ppm vs TMS) of CO-Containing Structures of 18% P(E/CO)

	internal ketone (72%)
	1,4-dione (24%)
	ethyl ketone branch (~0.9%)
	ethyl ketone end (~0.6%)
	butyl ketone branch (~0.4%)
	butyl ketone end (1.5%)

On the basis of the 22.5-MHz spectra, all of the CO groups were previously assigned to the polymer backbone chain only. At higher field, an additional peak for CO structure was observed at 42.2 ppm, Figure 1. This peak is assigned to the C_α of an ethyl ketone group based on the study of Wu, Ovenall, and Hoehn.[14] By comparison with the intensity of the internal ketonic C_α peak at 42.8 ppm, this peak accounted for about 4% of the CO groups in the 1.4% copolymer. The identity of the proposed ethyl ketone group was deduced from the spectrum of another E/CO copolymer of 18% CO content for which the carbonyl-containing structural assignments are summarized in Table I. The formation of ethyl ketonic groups during the propagation steps of synthesis can be accounted for by a backbiting reaction as shown below.[15] The hydrocarbon branches were formed in a similar manner.



No distinction between ethyl ketonic branched or chain-end structures can be made from the spectrum in Figure 1, since other characteristic peaks are either obscured or below detection limits.

Other carbonyl structures, such as 1,4-diones, were estimated to occur at much less than 0.1% concentration in 1.4% (E/CO) on the basis of a random distribution model and were not detected.[14] Butyl ketonic groups were indistinguishable from the long-chain internal ketonic groups in this sample.

The nonoxidative solid-state photochemistry of (E/CO) is expected to be dominated by Norrish type I and type II processes similar to those of lower molecular weight ketones in solution or in the gas phase.[16] The net loss of CO is shown by decreases in peaks at 208.2 (Figure 2), 42.6, 42.2, and 24.3 ppm (Figure 3). The ethyl ketonic groups appear to be far more reactive than those in the backbone,[6] since the peak at 42.2 ppm became undetectable. New peaks associated with CO-containing groups were found at 50.2, 43.8, and 42.4 ppm, Figure 2. Also noted were increases in peaks at 33.8, 114.2, and 139.1 ppm due to the formation of vinyl groups.

The peak at 43.8 ppm is assigned to C_α of acetyl groups. They are formed by the preponderant type II scission

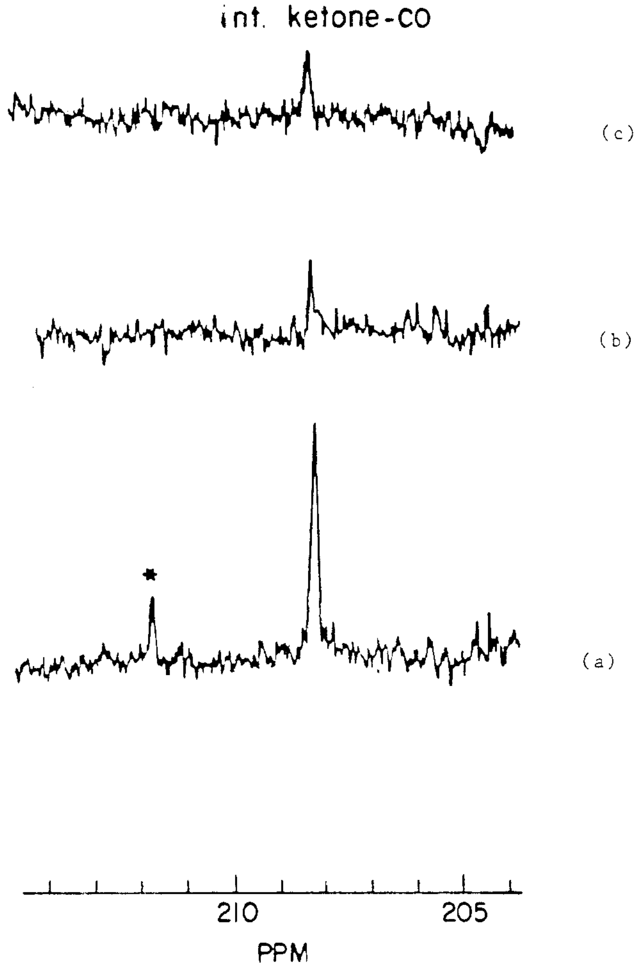
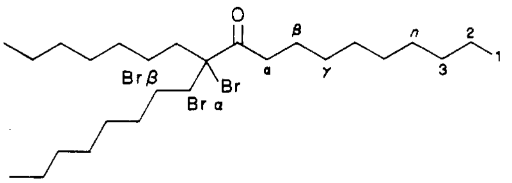


Figure 2. CO regions of NMR spectra of (a) 1.4% (E/CO) copolymer unirradiated, (b) after UV irradiation for 120 h under argon, and (c) after UV irradiation for 194 h under oxygen.

reaction. Previously, it was found that acetyl groups reached a maximum concentration in the earlier stages of irradiation and decreased or leveled off because they eventually decompose at a rate faster than they were formed.[7] Acetone is the major gaseous product of acetyl group photolysis by a type II process.

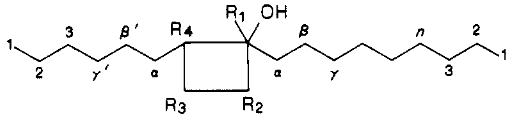
Chart I

^{13}C NMR Assignments (ppm vs TMS)



9-octylnonadecan-10-one

Br, 51.5	γ-n, 29.6-30.3
Br α, 31.4	1, 14.1
Br β, 27.9	2, 22.9
α, 42.9	3, 32.2
β, 24.9	



cis, *trans*-1-nonyl-2-hexylcyclobutanol

R_1, 76.4 (cis)	γ-n, 29.5-30.2
R_1, 76.2 (trans)	β', 28.1, 27.9
R_2 or α, 34.2, 33.3	α', 30.9, 30.6
R_3, 23.8, 23.4	β, 20.8, 19.4
R_4, 49.7, 45.4	1, 14.3
	2, 23.0
	3, 32.3

The peaks at 50.2 and 42.4 ppm are assigned to a novel product, an α-branched ketonic group, on the basis of the spectrum of branched ketone 9-octylnonadeca-10-one as summarized in Chart I. (Note the similar assignments to the butyl ketone branch of Table I). This kind of product has not been described in the literature as arising from ketone photolysis in either gas, liquid, or polymeric solid-phase reactions. The concentration found here is estimated to be about 4 groups/10 000 C atoms.

The presence of cyclobutanols was inferred from peaks at 77.1 and 76.8 ppm in Figure 4 as summarized in Chart I. The assignments of the model were based on empirical chemical shift parameters and an estimated spectrum obtained from an on-line computer substructural search.[17]

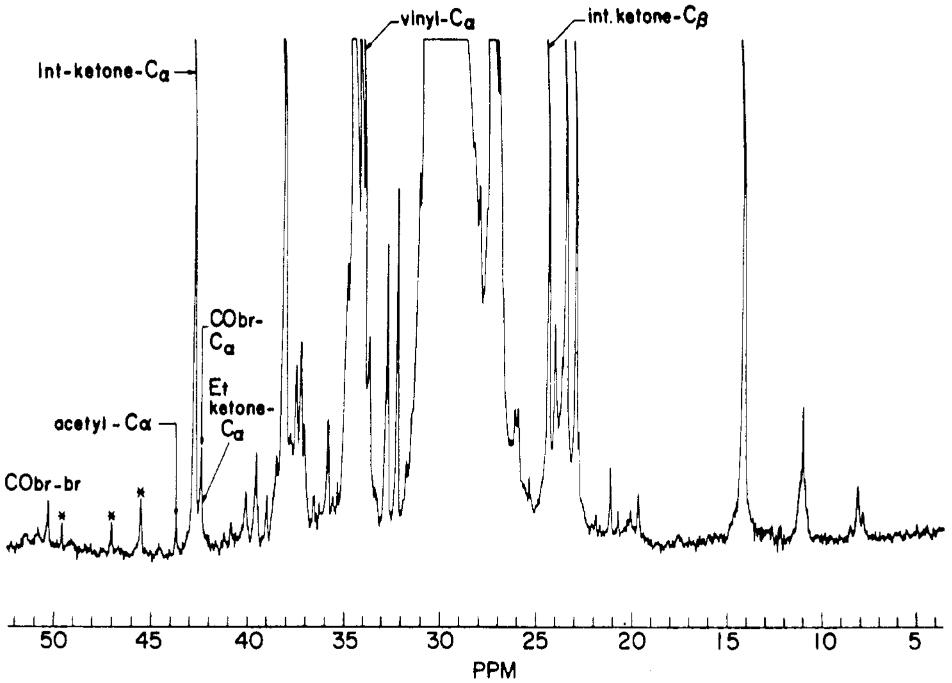


Figure 3. 50.3-MHz ^{13}C NMR spectrum of 1.4% (E/CO) copolymer after 120 h of UV irradiation under an argon atmosphere.

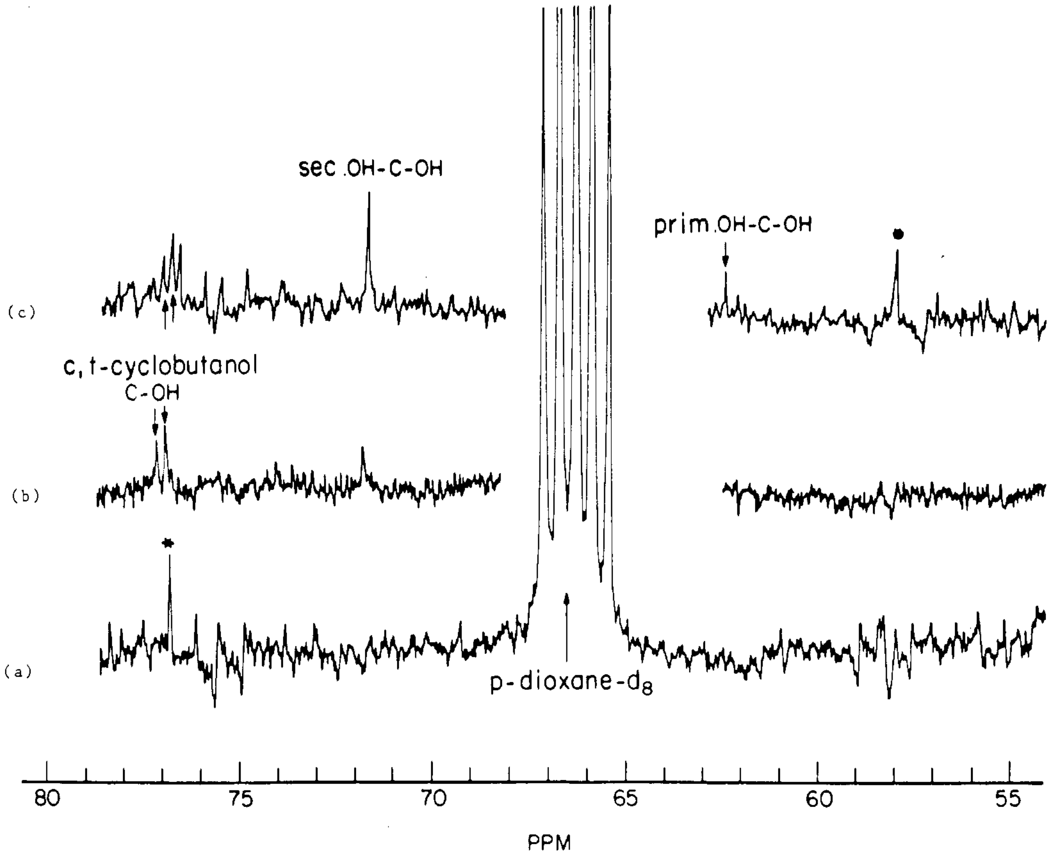


Figure 4. OH regions of NMR spectra of (a) 1.4% (E/CO) copolymer unirradiated, (b) after UV irradiation for 120 h under argon, and (c) after UV irradiation for 194 h under oxygen.

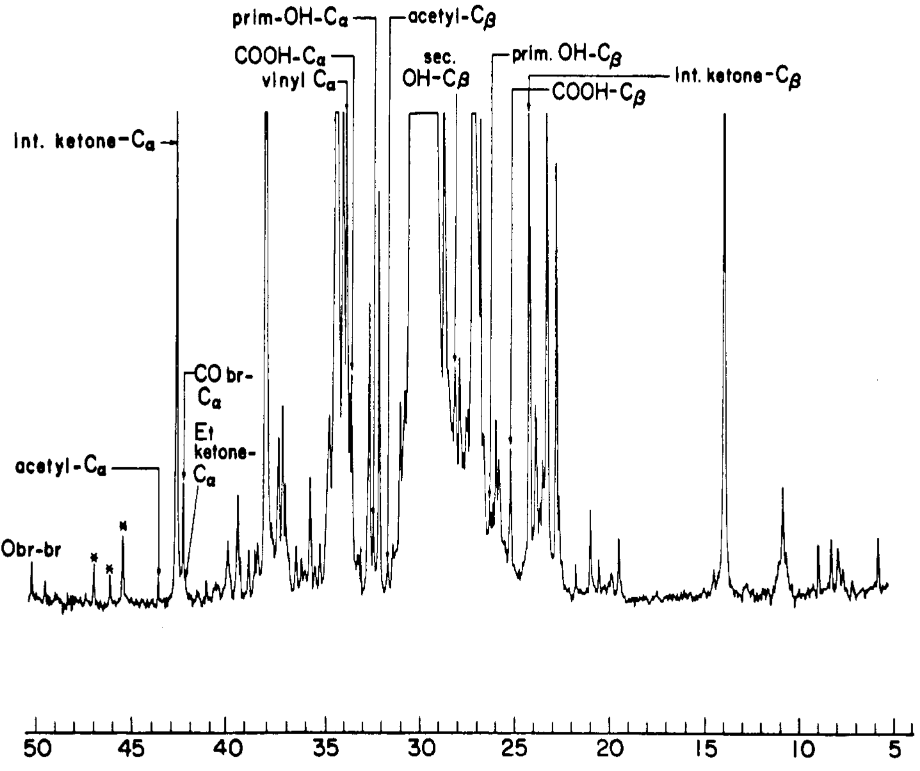


Figure 5. 50.3-MHz ^{13}C NMR spectrum of 1.4% (E/CO) copolymer after 194 h of UV irradiation under oxygen atmosphere. Oxygen uptake was 18.4 mL of oxygen/g of polymer.

The concentration for the cyclobutanols was estimated as being less than 2 groups/10 000 C atoms based on the intensities of the C–OH peaks. Other peaks of the cyclobutanols were apparently obscured. This is the first evidence found for the formation of cyclobutanols by the irradiation of a ketone-containing polymer in the solid state.

The upfield region of the 50.3-MHz spectrum of the sample irradiated under oxygen is shown in Figure 5. All of the photoproducts formed by degradation under argon

Scheme I

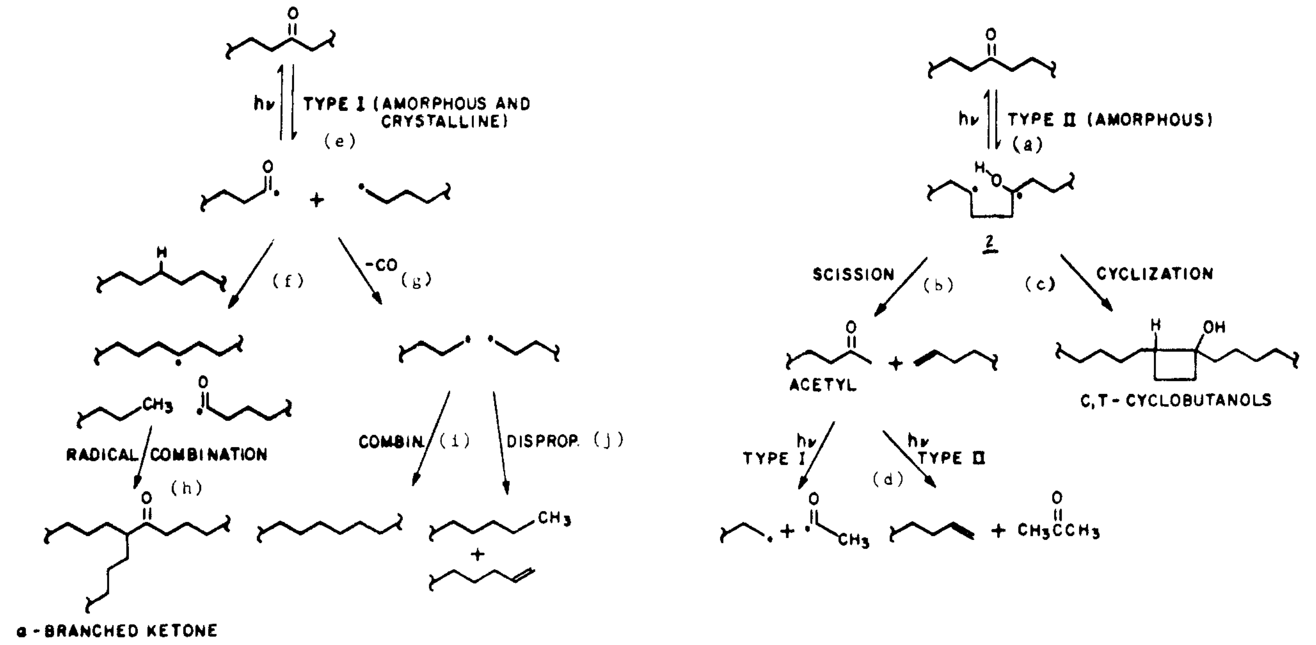
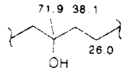
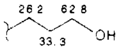
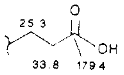
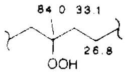
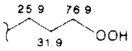
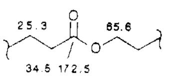


Table II
^{13}C NMR Assignments (ppm vs TMS) of Possible Products of Photooxidation of Polyethylene

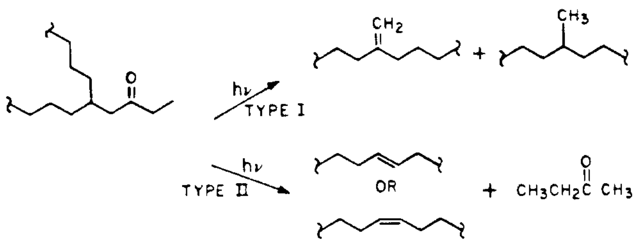
 71.9 38.1 26.0 OH	secondary alcohol
 26.2 62.8 33.3 OH	primary alcohol
 25.3 O OH 33.8 179.4	carboxylic acid
 84.0 33.1 26.8 OOH	secondary hydroperoxide
 25.9 76.9 31.9 OOH	primary hydroperoxide
 25.3 O 65.6 O 34.5 172.5	carboxylic acid ester

were found in this case, also. Additionally, peaks due to products of photooxidation were observed and assigned, on the basis of previous studies,[13,18,19] which are summarized in Table II. The most abundant product appeared to be carboxylic acid with peaks at 33.8 ppm (C_α) and 25.2 ppm (C_β). Secondary alcohol was inferred from the peaks at 38.1 ppm (C_α-obscured), 28.2 ppm (C_β), and 71.9 ppm (C–OH, Figure 4). A lesser amount of primary alcohol was deduced from peaks at 33.8 ppm (C_α), 26.7 ppm (C_β), and 61.8 (C–OH, Figure 3). No detectable peaks for hydroperoxides, esters, or γ-lactones were observed. The concentration of hydroperoxides was estimated previously to be less than 2 groups/10000 C atoms, due to the instability of hydroperoxides to UV light.[7]

Discussion

The photolysis of ketones is one of the most thoroughly studied and best understood photochemical reactions.[16] Recent studies of ketones in highly ordered and constrained environments have probed the effects of molecular order and restrained motion on their photochemical reactivity.[20] In organized fluid media, such as micelles,[21,22] and liquid crystals[23,24] where the hydrocarbon chains are fully extended, the formation of type II products is retarded relative to those formed in unorganized fluids. In solid environments, such as zeolites,[25] urea complexes,[26] deoxycholic and apocholic acid complexes,[27] cyclodextrins,[28] and crystals,[29] the product composition and stereochemistry are strongly affected by environment and restrictions on molecular motion. In ketone-containing polymers, product yields depend on state (solution or solid polymer) and temperature (whether above or below the glass transition).[30]

Scheme II



In the (E/CO) copolymer, the ketonic chromophores are randomly distributed throughout the morphological phases of the solid polyolefin matrix and are present in highly ordered, motionally constrained crystalline regions as well as in the less ordered, more mobile amorphous regions. Since upwards of 85% of the initial number of ketonic chromophores can be eliminated by prolonged irradiation, the photoprocesses observed in this study should represent reactions occurring in both crystalline and amorphous regions.[8] The (E/CO) copolymer is another system in which the effects of order and motional constraint on ketonic photoreactivity can be probed, or conversely the photoreactivity of ketones can probe the motional constraints and order of the polymer.

The nonoxidative photochemistry of (E/CO) is summarized in Scheme I. Processes arising via type I and type II reactions can be differentiated based on the morphological phases of the polymer. The effect of morphology on the oxidation and hydrolysis of polymers has been discussed previously.[31] The type II reaction (I-a) is expected to occur solely in the less restrained amorphous regions. About 80% of the initially reacting internal ketonic groups should follow this pathway.[4,5,7] The ethyl branch ketonic groups cannot fit into the crystalline lattice,[32] are therefore located in amorphous regions, and should react mostly via the type II pathway as shown in Scheme II. These groups should react faster than internal ketonic groups because of a greater degree of motional freedom. In this study, we found that the concentration of ethyl ketonic groups had decreased to below the detection limits when 25–30% of the internal ketonic groups remained unreacted. Similarly, all other ketonic groups at or near the ends of chains should show a greater photolability than internal groups.

The type II reaction has been found to occur through a 1,4-biradical intermediate I-2, which can undergo scission to form an acetyl group and a vinyl end group or undergo cyclization to a cyclobutanol.[16] This study reports the first evidence for this cyclization reaction in solid-state polymer. On the basis of amounts of products detected, less than 2% of the biradicals appears to follow this pathway. There appear to be nearly equal amounts of *cis*- and *trans*-cyclobutanol isomers, indicating that any steric constraints in the transition state for cyclization are outweighed by the motional constraints of further rotation. The photolability of the acetyl end groups over that of backbone carbonyl groups is demonstrated by the large ratio of vinyl to acetyl groups existing after prolonged irradiation.[7] Because of freer motion, acetyl groups are expected to react via a type II process to a larger extent (>95%) than the backbone ketonic groups, I-d.[33]

Type I reaction, a scission α to the carbonyl group, I-e, is important in one aspect. Although less than 20% of the ketonic chromophores can be expected to react via this pathway, the type I process is responsible for the generation of radicals, which are important as initiators and chain carriers in oxidative processes.[34] One outcome of type I scission is loss of CO. Since it has been found that over 85% of the initial CO amount can be eliminated from the polymer and the polymer is about 50% crystalline, this loss has to occur in crystalline as well as amorphous regions.[8] Earlier studies had indicated that the crystalline region of a polyolefin is inert to exposure to light.[35] The type II reaction is not expected to occur in a crystal lattice of a polyolefin containing ketonic groups because the polymer chains are extended in a close-packed zig-zag conformation.[36] This precludes attaining the cyclic conformation which facilitates α-hydrogen abstraction. Therefore, loss of CO from the crystalline region should occur only by a type I process.

After type I scission and CO loss, the resultant pair of alkyl radicals may combine to reform the backbone chain or disproportionate to form a methyl and a vinyl end group as shown in I-i and I-j. Based on the apparently constant number of hydrocarbon methyl end groups, the radical pair combination process is the most probable. In solution, the ratio of recombination to disproportionation for *n*-alkyl radicals is about 7 and shows little solvent dependence.[37]

In this study, there is strong evidence for the formation of an α-branched ketonic structure by exposure to UV light. The formation of this structure by a type I reaction is explained as follows: (1) the primary alkyl radical of the initially formed pair abstracts a hydrogen atom from a nearby hydrocarbon chain, generating a secondary alkyl radical and a methyl chain end (the alkyl radical is more reactive than the acyl radical), I-f; (2) the secondary radical and the initially formed acyl radical combine to form the α-branched ketonic structure, I-h.

Although this reaction has not been observed for ketones in solution or the gas phase, there are several analogues that support this proposal. Free radicals, generated by the photolysis of ketones in solution, can abstract hydrogen atoms from solvent molecules.[38] The hydrocarbon chain adjacent to a ketone-containing polymer chain can be thought of as a solvent molecule with abstractable H atoms. Lahav and co-workers[27] found that guest ketones, irradiated in the constrained cavities of deoxycholic and apocholic acid complexes, abstracted H atoms from host cavity molecules and formed addition products. Step 1 is analogous to the propagation step of the mechanism, proposed by Zhurkov[39] for the mechanical failure of stressed polymers, in which chain scission is promoted by hydrogen abstraction by a primary radical from an adjacent hydrocarbon chain. The secondary radical then undergoes rearrangement to a new primary radical and a vinyl end group. In our study, it is attractive to propose that formation of α-branched ketone is mediated by the crystalline lattice, which allows close approaches by adjacent polymer chains. The restricted motion of chains within the crystal keeps the secondary alkyl radical and acyl radical in close proximity to allow combination, step 2. As we have found here, the low efficiency of this reaction may have obscured its prior detection.

The formation of the α-branched ketone should increase the average molecular weight. Previously, we found that prolonged irradiation under an inert atmosphere led to formation of a higher molecular weight fraction while the net molecular weight decreased as detected by gel permeation chromatography.[7] Since this fraction constituted about 4% of the polymer mass, a very small number of cross-links is needed to account for this observation (~0.25 out of 10 000 C atoms).

The strength of high-resolution carbon-13 NMR for polymer analysis and characterization is best demonstrated in the analysis of the photooxidative products of (E/CO). Although lower limits of detection of some functional groups may be possible, using other instrumental methods such as IR or UV spectroscopy, no other method permits as wide an identification of functional groups, similar or dissimilar, as ^{13}C NMR. In this study, we detected carboxylic acids, in the presence of a much larger concentration of ketones, an analysis not possible using IR spectroscopy.[40] Other carbonyl-containing groups can be analyzed as easily. In addition, primary, secondary, and tertiary alcohols can be distinguished.

This study permits us to establish limits of detection based on the amount of oxygen absorbed. The concentrations of carboxylic acid and alcohols were estimated to be about 2–5 groups/10 000 C atoms with a spectral signal-to-noise ratio of about 10. Therefore, the oxygen-containing products from less than 2 mL/g of oxygen consumption should not be detectable by the experimental conditions of this study. With longer data acquisition times and commercially available higher field instruments, it is possible to detect concentrations of these products at least an order of magnitude lower.[10] The 0–10 mL/g of oxygen absorption range represents the early stage of the oxidation of polyethylene prior to embrittlement and should be accessible to detailed kinetic studies using ^{13}C NMR. The yield and fate of oxygen-containing functional groups should reflect the occurrence and reactions of alkyl and alkoxy radicals during polymer degradation.

Acknowledgment. We thank Dr. Martha D. Bruch of the E. I. du Pont de Nemours and Co. for providing a sample of 18% (E/CO) and Dr. Paul Dellevigne of the Scientific Information Services, Inc., for the substructural ^{13}C NMR spectral search.

Registry No. (E)(CO) (copolymer), 25052-62-4; 10-nonadecanone, 504-57-4; *trans*-1-nonyl-2-hexylcyclobutan-1-ol, 102396-

89-4; *cis*-1-nonyl-2-hexylcyclobutanol, 102396-77-0; octyl bromide, 111-83-1; 9-octylnonadecan-10-one, 112421-75-7; 9,11-dioctylnonadecan-10-one, 112421-76-8.

References and Notes

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Local Dynamics of Poly(*cis*-1,4-butadiene) Studied by Coupled Spin Relaxation

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ABSTRACT: The dynamics of an entangled linear polymer, poly(*cis*-1,4-butadiene), are studied by the coupled spin relaxation of a methylene group ($^{13}CH_2$). Relaxation experiments are performed on the solid, using magic-angle spinning, and in solution with CD_2Cl_2 at concentrations of 10–80 mol % monomer. By extrapolating the data taken between 10 and 40 mol % monomer to infinite dilution, four unique spectral densities are measured for the methylene. These can be expressed in terms of correlation times describing the reorientation of d-orbital-like functions oriented along a Cartesian axis system. The ratio of τ_{zz} to τ_{yy} to τ_{xy} is 2.4:1.0:0.48. These anisotropies of motion are very similar to those recently found for nonane and heneicosane. The anisotropy also agrees well with that calculated for a "crank-like" motion of polyethylene in a recent simulation.

I. Introduction

Understanding chain dynamics is important in a wide variety of problems, ranging from an understanding of the microscopic basis of the macroscopic properties of polymers to an understanding of transport of small molecules through biological membranes. Recent advances in computational methods have made theoretical modeling of such processes possible.[1-4] Experimental verification of

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