difference increases with increasing order of the reduced moments.

Since the lines of the Θ-chains are strongly curved in the range of small $1/n$ and an extrapolation may, therefore, give unreliable results, the data sets were fitted again, but this time to polynomials in $n^{-1/2}$ (Figure 4). The curves are more linear compared to those of Figure 3, but the result is similar for both fittings. The curve for $\rho = \langle r^2\rangle^{1/2}\langle 1/r_{\mathrm{H}}\rangle$ is also included in Figure 4b. The infinite n limit of this curve is 1.464 ± 0.002 and thereupon less than 1.5045 found for random-flight chains but greater than the Monte Carlo value of Guttman et al.[8] (1.40). The reason for the difference between our value and that of Guttman et al. is that the latter has been calculated with $\Phi_\theta = 0.275$, which is not correct for infinitely long chains.

The asymptotic values of the reduced moments together with their standard deviations are listed in Table II. We see that a part of the random flight values is beyond the 95% confidence interval of the Θ-chain values and that the latter are always smaller than the former. These deviations seem, therefore, to be systematic rather than due to chance and suggest the conclusion that the distribution functions of random-flight chains do not describe the behavior of Θ-chains. However, in view of the fact that this result is based on extrapolations, we cannot state it with certainty.

References and Notes

(1) Kuhn, W. *Kolloid-Z.* **1934**, *68*, 2.
(2) Eyring, H. *Phys. Rev.* **1932**, *39*, 746.
(3) Oka, S. *Proc. Phys. Math. Soc. Jpn.* **1942**, *24*, 657.
(4) See, for example: Flory, P. J. "Statistical Mechanics of Chain Molecules"; Interscience: New York, 1969.
(5) Janssens, M.; Bellemans, A. *Macromolecules* **1976**, *9*, 303.
(6) McCrackin, F. L.; Mazur, J.; Guttman, C. M. *Macromolecules* **1973**, *6*, 859.
(7) Rapaport, D. C. *Macromolecules* **1974**, *7*, 64.
(8) Guttman, C. M.; McCrackin, F. L.; Han, C. C. *Macromolecules* **1982**, *15*, 1205.
(9) Baumgärtner, A. *J. Chem. Phys.* **1980**, *72*, 871.
(10) Webman, I.; Lebowitz, J. L.; Kalos, M. H. *Macromolecules* **1981**, *14*, 1495.
(11) Bruns, W. *J. Chem. Phys.* **1980**, *73*, 1970.
(12) Kirste, R. G. *Discuss. Faraday Soc.* **1970**, *49*, 51.
(13) Olaj, O. F.; Lantschbauer, W.; Pelinka, K. H. *Macromolecules* **1980**, *13*, 299.
(14) McMillan, W. G.; Mayer, J. E. *J. Chem. Phys.* **1945**, *13*, 276.
(15) Yamakawa, H. "Modern Theory of Polymer Solutions"; Harper and Row: New York, 1971; Chapter IV.
(16) Mazur, J.; McCrackin, F. L. *J. Chem. Phys.* **1968**, *49*, 648.
(17) Finsy, R.; Janssens, M.; Bellemans, A. *J. Phys. A* **1975**, *A8*, L106.
(18) Rapaport, D. C. *J. Phys. A* **1977**, *A10*, 637.
(19) Kajiwara, K.; Burchard, W. *Macromolecules* **1982**, *15*, 660.

Solid-State Photochemistry of Poly(ethylene-*co*-carbon monoxide). Model Studies of Polyethylene Photochemistry

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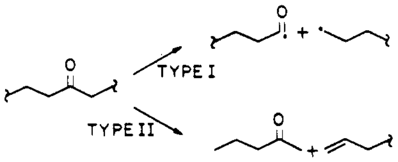
ABSTRACT: The solid-state photolysis of an ethylene–carbon monoxide (E/CO) copolymer was studied at wavelengths above 285 nm under both argon and oxygen atmospheres. Degradation was monitored and characterized by ultraviolet and infrared spectroscopy, gel permeation chromatography, gas evolution and uptake measurements, and quantum yield determinations. The microstructure of the copolymer, as determined by carbon-13 NMR spectroscopy, was found to be very similar to that of branched polyethylene, with nearly all of the oxygen accounted for as backbone ketonic carbonyl groups. Microstructural changes were also probed by this method. The changes in functional groups and the quantum yields were consistent with a dominant Norrish type II chain scission process. Acetyl group concentration, determined by NMR, reached a maximum during earlier exposure times. Reductions were observed at longer exposure times in the rate of gas evolution, the rate of chain scission, the rate of loss of carbonyl, and the rate of accumulation of vinyl groups. These rate decreases were attributed to a depletion of ketonic carbonyls that was more rapid in the amorphous regions than in the crystalline regions of the copolymer. In accord with earlier proposals, backbone ketonic carbonyl groups were found to be poor initiators in polyolefin photooxidation.

Introduction

The initiation of degradation and loss of physical properties of solid polyolefins during exposure to sunlight and air have been attributed to low concentrations of adventitious chromophores, since "pure" saturated hydrocarbons are not expected to adsorb light at wavelengths longer than 290 nm.[1,2] Many studies have attempted to identify the chromophores and to determine their importance in initiating and propagating degradation of the polymers.[3-5] Chromophores, including peroxides, ketonic carbonyls, and unsaturation, have been identified and their photochemistry has been examined.[6-8]

The embrittlement of polyethylene during photooxidation results from a combination of chain cross-linking and scission processes. Some of the scissions have been attributed to the following Norrish reactions of ketone groups located in the molecular chain.[9]



Guillet and co-workers have extensively studied the photochemistry of ketone-containing polymers under a wide range of experimental conditions.[10,11] They examined the effects of structure, viscosity, temperature, and wavelength on the photochemical and photophysical processes of these plastics, which they propose for use as environmentally favorable, photodegradable packaging

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materials.[12,13] Also, the photodegradation of polyethylene has been accelerated by introducing carbonyl groups through oxidation and hydrolysis.[14]

Since ketone groups are key intermediates in hydrocarbon oxidation, it seems likely that a copolymer of ethylene and carbon monoxide (E/CO) would be an appropriate model for simulating polyethylene photodegradation and photooxidation.[11,15] This paper reports a quantitative study of the solid-state photochemistry of an E/CO copolymer under conditions simulating solar-induced degradation and the subsequent characterization of its microstructure by carbon-13 NMR spectroscopy. This copolymer not only resembles branched polyethylene in molecular structure, but also it has the important advantage of remaining soluble throughout the irradiation. The reactivities and quantum yields measured here appear to be time dependent, reflecting the effects of morphology on the reactions of ketonic carbonyls. This study confirms the proposal that backbone ketonic carbonyl groups are rather ineffective initiators for oxidative photodegradation of polyolefins.[11,15]

Experimental Section

An E/CO copolymer prepared by high-pressure free radical polymerization was obtained from E. I. du Pont de Nemours and Co. Neutron activation analysis of this copolymer showed that it contained 0.788 ± 0.004% oxygen by weight (1.38% CO).[16] Films, 0.15–0.30 mm thick, were formed from pellets by compression-molding at 120–160 °C and 23 000 p.s.i. for 1 min followed by a chilled water quench in the press. All samples were soluble at 135 °C in 1,2,4-trichlorobenzene and at 110 °C in 80:20 trichlorobenzene–dioxane solutions. For comparison, films of an unstabilized low-density polyethylene (DYNK, Union Carbide) were also prepared.

Transmission infrared spectroscopy (Perkin-Elmer 667 IR spectrophotometer) and ultraviolet spectroscopy (Perkin-Elmer 320 UV–vis spectrophotometer) were used to characterize degradation products and to monitor reaction rates.

Irradiation Procedure. The light source was a Hanovia 450-W medium-pressure mercury lamp and a $^1/_2$-in. path length water filter. Samples were exposed in sealed brass cells maintained at 30–32 °C by a circulating-water bath. The cells were connected to mercury burets used to measure gas evolution or uptake. The cell windows were $^1/_8$-in.-thick Ernst Pyrex glass, transmitting light above 285 nm initially, with the absorption edge shifting only 1–2 nm to the red after prolonged use in these studies.

The films were placed on Nichrome screens and the cells were flushed, filled with argon or oxygen, connected to the burets, and placed 20 cm from the lamp for irradiation. In order to measure the uptake of O_2 reproducibly, a 5-Å molecular sieve was placed below the films to absorb evolved gases. Periodically, the volumetric changes during exposure were recorded in comparison to a reference cell and samples were taken for chromatographic and spectral analyses.

Hydroperoxide analyses were accomplished by placing irradiated films in a desiccator filled with sulfur dioxide (Matheson) for 1 h. The infrared spectra, which were recorded before and after exposure to SO_2 were analyzed according to the method of Mitchell and Perkins.[17]

Quantum Yield Determinations. Quantum yield measurements were made on films irradiated in sealed cells under an argon atmosphere at 22–25 °C. The light source was a 50-W 3000-Å phosphor lamp which had a uniform output varying no more than 5% over the area of the cell. Pyrex windows, $^1/_{16}$ in. thick, screened light below 260 nm and 95% of the transmitted light was in a broad band, 280–320 nm. The average light intensity was measured with a calibrated Eppley wire-wound copper–constantan thermopile and readout meter and was corrected for absorption and reflection losses of the cell windows. The absorption of light by the films was determined from the UV absorption spectra measured vs. a polyethylene film of similar thickness, to compensate for scattering and reflection of light.

Analyses of the gases evolved during irradiation were made with a Varian 1420 thermal conductivity gas chromatograph and standard gas mixtures. A $^1/_8$ in. × 12 ft stainless steel column of 40/60 silica gel was used to measure or detect CH_4, C_2H_4, and C_2H_6, a $^1/_8$ in. × 6 ft 45/60 5-Å molecular sieve column was used to determine CO, and a $^1/_8$ in. × 6 ft Porapak N 80/100 column was used for acetone analysis. The detection limits of these gases were in the range (2–5) × 10^{-8} mol/mL. No gases of higher molecular weight were detected in these analyses.

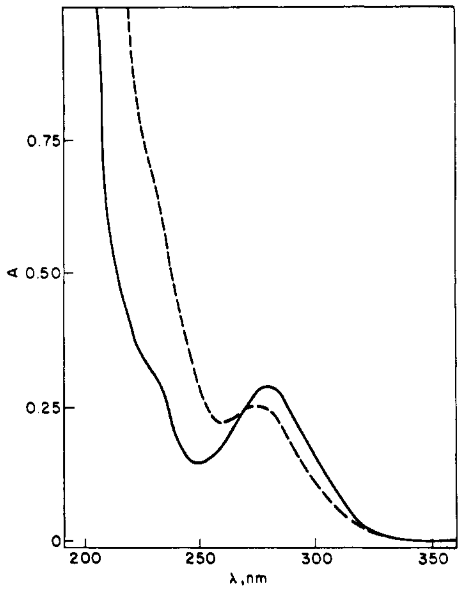


Figure 1. Initial UV–vis spectrum of 0.18-mm film of E/CO copolymer (—) and after 42-h exposure (---) to 3000-Å phosphor lamp. A 0.16-mm film of polyethylene was placed in the reference beam to compensate for reflection and scattering losses.

Gel Permeation Chromatography. Weighed samples of films were dissolved at 135 °C overnight in 25 mL of 1,2,4-trichlorobenzene containing 0.025 g of 3,5-di-*tert*-butylcatechol. Chromatograms were recorded with a Waters 150C ALC/GPC equipped with a matched Du Pont Zorbax TMS column set and a refractive index detector. Average molecular weights were computed from elution curves compared with those of standard linear polyethylene fractions.

Carbon-13 NMR Spectroscopy. The carbon-13 NMR spectra were obtained at 110 °C with a JEOL FX90Q spectrometer operating at 22.53 MHz. Typically, 5120 scans were accumulated, using complete proton noise decoupling to eliminate carbon-13–proton coupling. The pulse angle was 90° and the pulse interval was 10 s. The samples contained ~15% polymer (by weight) in a 4:1 (v/v) mixture of 1,2,4-trichlorobenzene and dioxane-d_8. Hexamethyldisiloxane (HMDS) was used as the internal reference (2.00 ppm vs. Me_4Si) and the dioxane-d_8 provided the internal deuterium lock. All samples were soluble, but the samples irradiated for 66 and 120 h under argon took noticeably longer to dissolve.

Results

The most marked chemical changes observed in the irradiation of the E/CO copolymer were loss of carbonyl groups and formation of vinyl groups. The UV spectra of films exposed under argon showed a progressive decrease in absorption of the band at λ_{max} = 278 nm, which has been assigned to a ketonic carbonyl n–π* absorption[18] (Figure 1). This band accounted for nearly all of the light absorption of the film during irradiation. Short-wavelength absorption of the films ($\lambda < 260$ nm) also increased with exposure time. In the infrared spectra, decreases with exposure were observed in peaks at 1720 and 1430 cm^{-1} ($>C{=}O$) and increases in peaks at 1640 ($>C{=}C<$), 990 ($CH{=}CH_2$), and 908 cm^{-1} ($CH{=}CH_2$).[19] The peaks at 964 cm^{-1}, assigned to internal trans unsaturation, and 888 cm^{-1}, assigned to vinylidene absorption ($>C{=}CH_2$), were invariant with exposure time or atmosphere.[19] Changes in the concentrations of carbonyl and vinyl groups with time

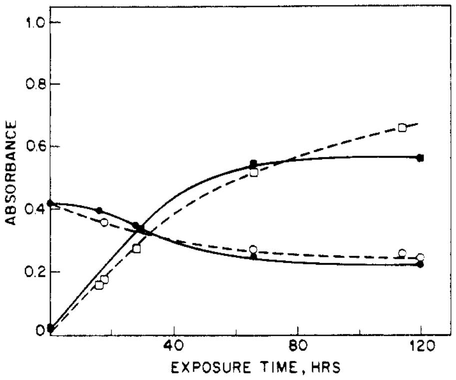
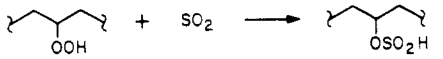


Figure 2. Infrared absorbance of copolymer films as a function of exposure time: (●) 1430 cm^{-1} under argon; (○) 1430 cm^{-1} under oxygen; (■) 908 cm^{-1} under argon; (□) 908 cm^{-1} under oxygen. Values are corrected for variances in film thickness and represent an average of four determinations.

for samples exposed under argon and oxygen are shown in Figure 2.

The net loss of CO from samples exposed under O_2 appears to be less than that under Ar. An accurate measure of CO loss using IR is obscured by the formation of carbonyl-containing oxidation products, e.g., carboxylic acids or esters, whose infrared peaks overlap those of ketonic carbonyls. Broadening of the carbonyl region was observed in the spectra of samples exposed under O_2. Also, a broad band at 3400 cm^{-1} developed with exposure due to OH groups formed. However, no sharp peak was found at 3550 cm^{-1}, the band that is assigned to free hydroperoxides and is observed in thermally oxidized polyethylene.[7,8] The SO_2 treatment of a film exposed for 120 h under O_2 did yield a slight decrease in absorption at 3550 cm^{-1} and the formation of a peak at 1190 cm^{-1}, presumably due to formation of the secondary hydrogen sulfate as shown in eq 1. An additional sulfate band, which should be observed at 920 cm^{-1}, is obscured by a strong vinyl absorption. On the basis of the analysis of Mitchell and Perkins,[17] a lower limit for hydroperoxides was found to be 2.3×10^{-2}/100 C atoms or 0.5/molecule. This is not surprising due to the low O_2 uptake of only ~10 mL/g of polymer and of the instability of hydroperoxides to light.[15a,20]



(1)

Another important trend in the spectral changes is that the rates of both CO loss and vinyl formation decrease at longer exposure. Although only about one-third of the chromophoric ketonic carbonyls are lost in the first 60 h, the relative changes over the next 60 h are only about one-fifth of the initial values. This decrease in rate is not due just to the decrease in light absorption and is also observed in other analytical methods. It is related to morphology, another important aspect of degradation to be considered later.

The accuracy of the quantum yield determinations was limited by a decrease in absorption over the wavelength range of the light source due to loss of carbonyl chromophores on exposure. However, since the decrease was usually less than 30%, an average of the absorbances (at $\lambda = 300$ nm), measured before and after exposure, was used in calculations. The quantum yields of evolved gases, of changes in some of the IR and UV peaks, and of chain scission are listed in Table I. Listed also in this table are values previously determined by others under experimental conditions close to those used in this study. With the exception of ϕ_{CH_4}, all of the quantum yields showed a time dependence and decreased at longer exposure.

Table I
Summary of Quantum Yield Determinations

expt	I_{abs}, einsteins $\times 10^3$	evolved gases ϕ_{CO}	$\phi_{C_2H_4}$	ϕ_{CH_4}	$\phi_{acetone}$
1	0.864	0.013	0.0016	0.00028	
2	1.34	0.012			0.0039
3	3.16	0.010	0.0012	0.00050	
av		0.012	0.0014	0.00039	0.0039
lit.[a]		(0.012)[b]	c	c	c

expt	ϕ_{lossCO}(UV)[d]	ϕ_{vinyl}(908 cm^{-1})[e]	ϕ_{cs}[f]
1	0.054	0.096	0.047
2	0.047	0.090	
3	0.024	0.068	0.019
av	0.042	0.084	0.033
lit.[a]	(0.075)[g]	(0.072)[h]	(0.040)[i]

[a] Values cited obtained under experimental conditions closest to those of this study. [b] Irradiated in heptane solution, 90 °C (ref 34). [c] Quantum yields not determined. Molar ratio of CO, acetone, C_2H_6, and CH_4 found 12.3:2.6:1:1 (ref 10). [d] $\epsilon_{300nm} = 35$ L mol^{-1} cm^{-1} (ref 10). [e] $\epsilon_{908cm^{-1}} = 129$ L mol^{-1} cm^{-1} (ref 10). [f] $\phi_{cs} = (\bar{M}_{n0}/\bar{M}_n - 1)_m/\bar{M}_{n0}I$, where m is the mass of the polymer irradiated and I is the absorbed radiation (ref 35). [g] ϕ_{lossCO} from decrease in IR absorbance at 1720 cm^{-1}, irradiation at 300 nm, 25 °C, solid state (ref 10). [h] Irradiation at 300 nm, 25 °C, solid state (ref 10). [i] Irradiation at 313 nm, 90 °C, heptane solution (ref 34).

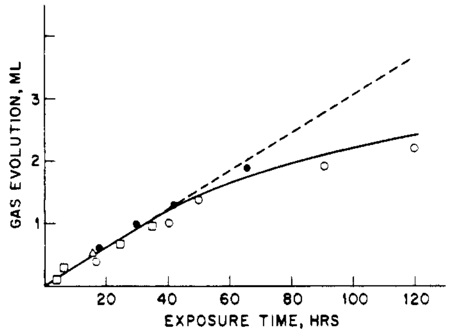


Figure 3. Corrected gas evolution for films exposed under argon up to (△) 16, (□) 30, (●) 66, and (○) 120 h.

The largest fraction of the evolved products was carbon monoxide (66%), formed mostly via a Norrish type I scission of the copolymer. Next in abundance was acetone, formed from consecutive type II reactions. Photolysis of the acetone accounted for formation of ethane, methane, and some of the CO. On the basis of the measured quantum yields, only about 10% of the CO was derived from acetone photolysis. The yields of CH_4 were found to be higher than would be expected from the gas-phase photolysis of acetone alone at room temperature, where equimolar quantities of C_2H_6 and CO should be the only detectable products.[21] Reaction of methyl radicals from acetone photolysis with the copolymer film can account for CH_4 formation, since it has been shown that CH_4 yields increase when acetone is photolyzed in the presence of H-atom donors.[22] In contrast to other quantum yields, the yield of CH_4 increased at longer exposure time, supporting a secondary photolysis process as its source.

Gas evolution of samples exposed under Ar is shown in Figure 3. Note that the rate of evolution decreased at longer times in accordance with changes in IR band intensities. Oxygen uptake by the E/CO copolymer increased constantly to about 12 mL/g of polymer at 120 h, while the polyethylene sample exposed under the same conditions consumed about half as much as shown in Figure 4. Although the concentration of ketonic carbonyls was over 2 orders of magnitude greater in the copolymer than in this polyethylene,[23] the rate of oxygen uptake did

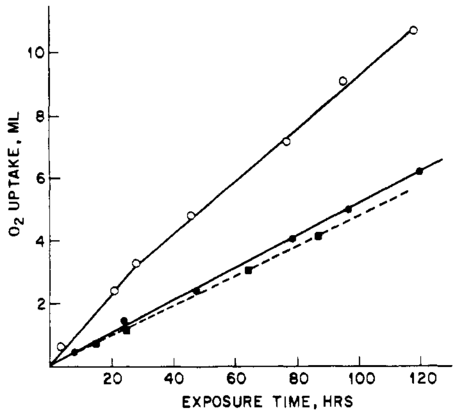


Figure 4. Corrected oxygen uptake per gram of E/CO copolymer (●) with no absorbent in cell and (○) with 5-Å molecular sieve ((■) for LDPE film).

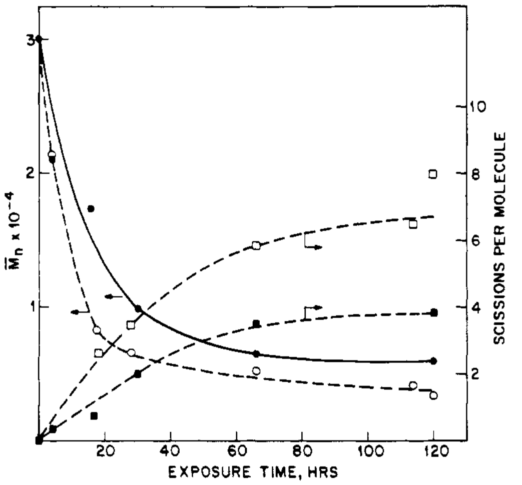


Figure 5. Number-average molecular weights ($\bar{M}_n$) and scissions per molecule as a function of time for samples exposed under argon (●, ■) and under oxygen (○, □).

not even double.[24] Thus ketonic carbonyls in the copolymer appear to be rather poor initiators of polyolefin photooxidation.

Scission processes accounted for the changes in physical properties due to exposure. The films became brittle as the molecular weights decreased under Ar and O_2 atmospheres. The change with time in number-average molecular weights ($\bar{M}_n$) and the number of scissions per molecule are compared in Figure 5. In the unexposed copolymer, there are about 16 CO sites per molecule, based on the CO content and average molecular weight.[23] Exposure under Ar approached a limit of about 45% CO loss (Figure 2) or a limit of about 4 scissions per molecule (25% of the CO sites). The number of scissions per molecule is not expected to equal the number of CO groups lost, since losses near the ends of the molecular chain or in branches would not affect molecular weights measurably. Also, single type II scission does not involve CO loss. Exposure under O_2 approached a limit of ~7 scissions per molecule (40% sites) for a corresponding 40% CO loss. Thus the overall scission rate is significantly enhanced by oxidative reactions.[25a]

There is some evidence for cross-linking occurring in the E/CO copolymer. The chromatographic peak is shifted progressively to a lower molecular weight range on exposure under Ar or O_2 as shown in Figure 6. But under Ar, a shoulder is observed in the higher weight region for the 66- and 120-h samples that is not present at shorter exposure times, and these samples did take longer to dissolve than the others. In the photooxidation of several polyethylenes, cross-linking occurred at an early stage and dominated the physical properties.[25] this cross-linking process was dependent on wavelength, temperature, and the initial physical properties of the polymer studied.

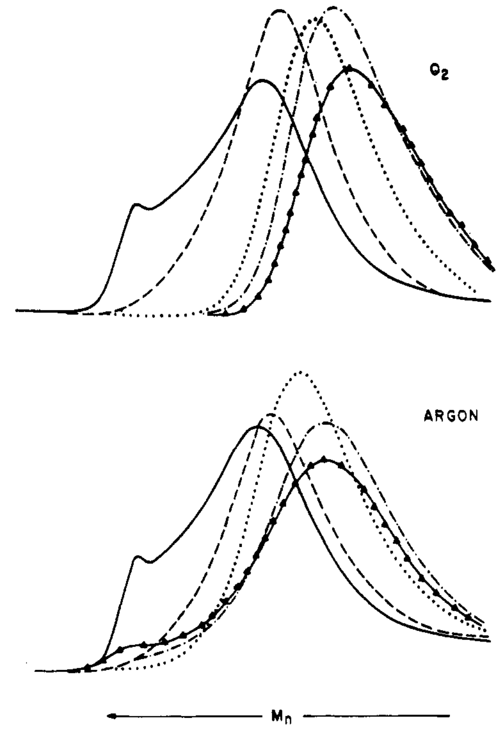


Figure 6. Chromatograms for samples exposed under oxygen (upper curves) at (—) 0, (---) 4, (···) 28, (-·-) 66, and (▲) 120 h and under argon (lower curves) at (—) 0, (---) 4, (···) 16, (-·-) 66, and (▲) 120 h.

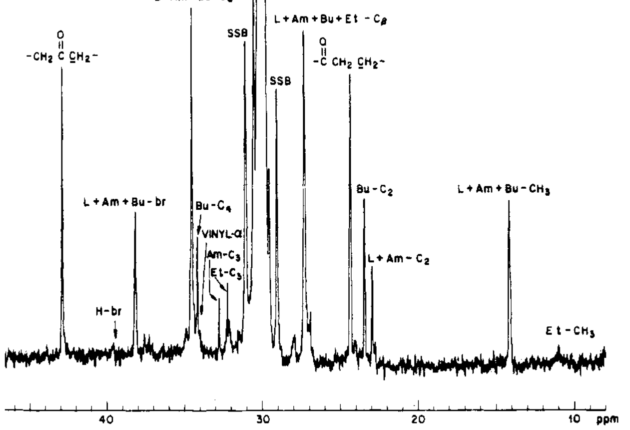


Figure 7. ^{13}C NMR spectrum of unexposed copolymer. SSB indicates spinning side bands.

A ^{13}C NMR spectrum of an unexposed sample of E/CO copolymer is shown in Figure 7. Assignments were made in accordance with previous work.[26-29] This spectrum is very similar to those for low-density polyethylene with the exception of peaks at 24.34 and 42.83 ppm due to backbone ketonic carbonyls.[26,30] The initial CO content, calculated from relative peak heights, was found to be 1.15% in comparison to 1.38% obtained from neutron activation analysis.[31]

In agreement with the other analyses, the peaks due to ketonic carbonyls decreased with exposure time while the peak at 33.9 ppm (vinyl α) increased, as shown in Figures 8 and 9. The changes in these peaks with time along with those assigned to acetyl groups, branches, and chain ends are shown in Figures 10 and 11.

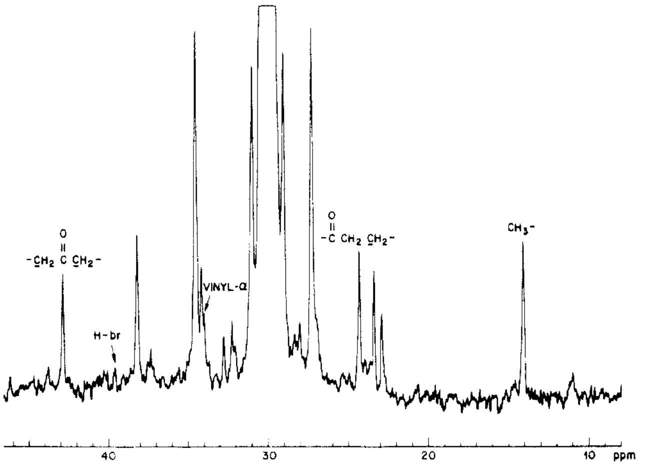


Figure 8. ^{13}C NMR spectrum of sample exposed for 120 h under argon.

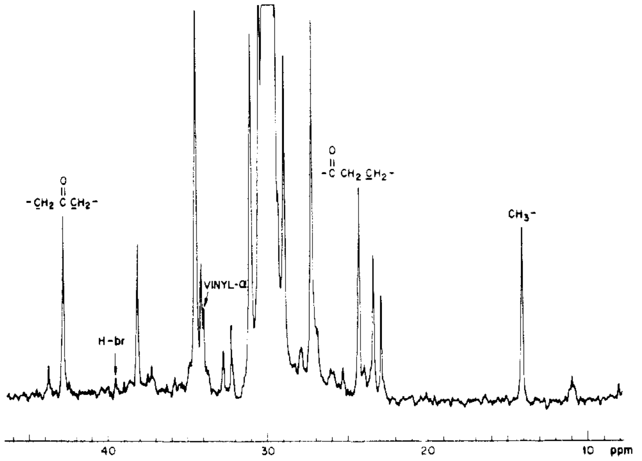


Figure 9. ^{13}C NMR spectrum of sample exposed for 66 h under oxygen.

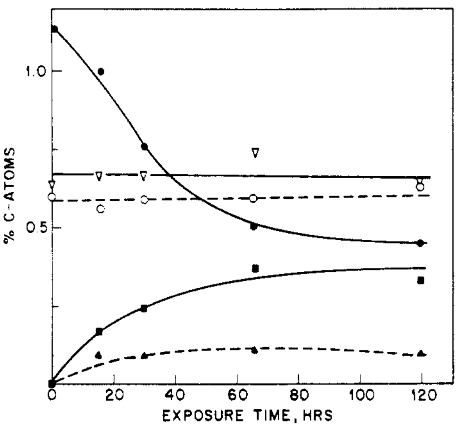


Figure 10. Relative intensities of functional groups vs. exposure time under argon obtained from NMR spectra: (●) ketonic carbonyl C_α; (■) vinyl; (▲) acetyl; (▽) methyl ends; (○) T branches (×10).

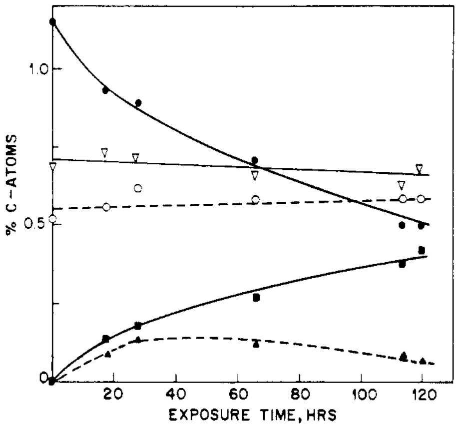


Figure 11. Relative intensities of functional groups vs. exposure time under oxygen obtained from NMR spectra: (●) ketonic carbonyl C_α; (■) vinyl; (▲) acetyl; (▽) methyl ends; (○) T branches.

The formation of acetyl groups appears to correspond to vinyl group formation initially (<30 h, Figures 10 and 11) but levels off or even decreases at longer times where their rate of loss is faster than their rate of formation. The number of branches and methyl end groups were invariant under Ar or O_2 over the exposure times of this study. There were no changes in concentrations of these groups within detectable limits for even the 66- and 120-h Ar samples, where cross-linking was evident in the GPC chromatograms.

Examination of the spectral regions where oxidation products such as carboxylic acids, alcohols, hydroperoxides, esters, or ketones might be expected revealed none in even the most highly oxidized samples. This is consistent with the results of Bovey, Cheng, and Schilling.[26] Thermally oxidized polyethylene samples at and below 10 mL/g oxygen uptake were found to contain concentrations of oxidation products at levels ≤0.2–0.5/100 C atoms.[26]

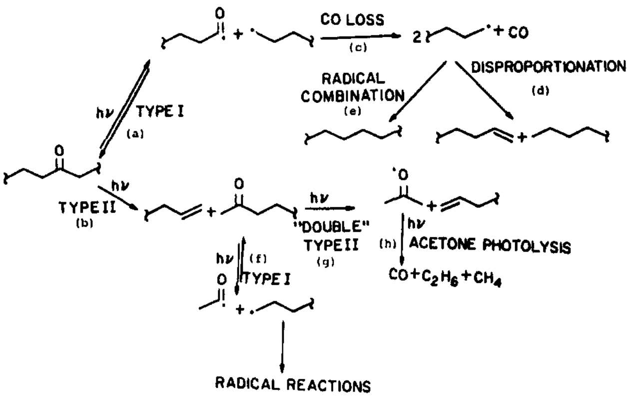
Discussion

Wu and co-workers[27] examined the monomer sequence distribution for a series of E/CO copolymers of varying CO content (7–35%) by NMR spectroscopy. They found that as the CO content decreased, it approached a random distribution. The distribution of 1,4-dione groups was actually found to be slightly less than that expected for a random copolymerization.[32] In addition, the kind and number of end groups and short-chain branches were found to be similar to those of low-density branched polyethylene. In this study, ^{13}C NMR spectroscopy confirms this structural similarity and provides mechanistic details which are unavailable from other methods of spectral analyses. We have found a good correlation among the various analytical methods and possible evidence for an effect related to the morphology of the copolymer.[33]

The photolysis of ketone-containing polymers, including E/CO copolymers, has been studied extensively by Guillet and co-workers.[10,11,34-36] The irradiation of the polymers with light between 250 and 320 nm resulted in a molecular weight decrease, formation of unsaturated sites, and the evolution of low molecular weight gases, the largest fraction being CO.[10] Specifically, for E/CO copolymers where the CO groups are mostly in the backbone chain, the unsaturated sites formed were terminal vinyl groups. Degradation was found to occur about 3 times faster for CO groups located in side chains than those located in the backbone chain.[10,11] The observed degradation was explained best in terms of the Norrish type I and II reactions of ketones. The scission rate via the Norrish type I process was strongly temperature dependent, while type II scission rates appeared to be relatively insensitive to temperatures above the glass transition temperature of the polymer and to the physical state.[34] At room temperature in the solid state, the type II prrocess accounted for over 90% of the scission processes. But, as temperature increased, the type I rate increased to where it was comparable with the type II rate above 120 °C.[34]

In this study, the quantum yields for the various functional group changes were determined under identical experimental conditions: argon atmosphere, room tem-

Scheme I



perature (22–24 °C), $\bar{\lambda} = 300$ nm. When compared to values measured by Guillet and co-workers for E/CO copolymers, the agreement is generally fair to good (Table I). Our results can be rationalized by Norrish processes as shown in Scheme I.

If the carbonyl groups are located mostly in the polymer backbone and are randomly distributed, there should be a correspondence among the various quantum yields of functional group changes and gaseous products measured. The largest quantum yields found were those for vinyl group formation (ϕ_{vinyl}), for loss of carbonyl absorbance ($\phi_{\text{-CO}}$), and for chain scission (ϕ_{cs}). If the unreacted polymer degraded solely via the Norrish type II reaction, there should be an equal number of chain scissions, of vinyl groups, and of acetyl groups formed (Scheme I, step b). Although subsequent photolysis of the acetyl end groups complicates this simple correlation, the quantum yield for photolysis of the acetyl groups ($\phi_{\text{type II double}}$) can be estimated by the following relationship (steps g and h):

$$\phi_{\text{type II double}} = \phi_{\text{acetone}} + \phi_{C_2H_4} + \tfrac{1}{2}\phi_{CH_4} \cong 0.0055$$

An estimate of the one-step type II reaction can be made from preliminary NMR studies, where the number of acetyl end groups was found to be about half of the measured vinyl groups.

$$\phi_{\text{type II single}} \cong \phi_{\text{acetyl groups}} \cong 0.5\phi_{\text{vinyl}}$$

Thus,

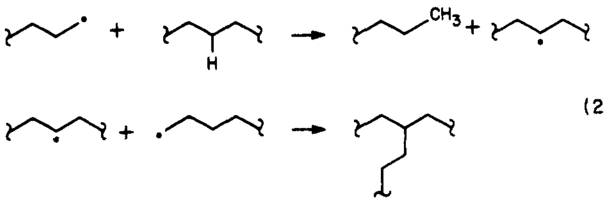
$$\phi_{\text{type II total}} \cong \phi_{\text{type II single}} + \phi_{\text{type II double}} \cong 0.049$$

Reaction via a single type II process leads initially to a vinyl end group and an acetyl end group (step b). The acetyl groups are more reactive photochemically since they can attain the conformation necessary for the abstraction and scission reactions far more easily than backbone carbonyls (step g).[10,11] Thus the NMR ratio of vinyl to acetyl groups increases with time as the rate of photolysis of acetyl groups increases relative to the rate of their formation. On the basis of the CO yield, the extent of type I fragmentation can be estimated from the following relationship (assuming step f is negligible):

$$\phi_{\text{CO}} = \phi_{\text{type I}} + \phi_{\text{CO}}(\text{from acetone})$$

$$\phi_{\text{type I}} \cong 0.010$$

At room temperature the extent of type I reaction is estimated to occur at a maximum rate only one-fifth that of the type II reactions. This is in agreement with the restuls of Hartley and Guillet,[34,38] where the type I reaction was found to account for only 10% of the total reaction at 25 °C. The assumption that step f is negligible is based on the study of 2-alkanones where the ratios of type II to type I reactions were found to be about 40:1.[39] The macroradicals are expected to recombine in the "solvent cage" rather than to disproportionate, since the number of methyl end groups was found not to change with time. Reaction of the macroradicals outside of the cage also should be at a minimum, because the number of branches was found to be invariant (eq 2). However, such a process



(2)

may be needed to account for the low degree of cross-linking observed at longer times under Ar. In this respect it would be similar to the increase in branching found when polyethylene was thermally degraded under N_2.[29]

The quantum yield of vinyl group formation should correspond to the yields of type I and II reactions, accordingly (steps b and g and steps a, c, and d)

$$\phi_{\text{vinyl}} = \phi_{\text{type II total}} + \phi_{\text{type I}}(\text{fragmentation and disproportionation}) \cong 0.05$$

This value is less than the average measured value from IR spectra of 0.084, but it is within the range of the values found, 0.046–0.096. Similarly, the chain scission yield should correspond to yields of the type I and II processes (steps b and a, c, d).

$$\phi_{\text{cs}} = \phi_{\text{type II single}} + \phi_{\text{type I}}(\text{fragmentation and disproportionation}) \cong 0.05$$

This value is greater than the average of the measured values of 0.033 but close to the shortest time measured value.

The greatest discrepancy is found in the relationship of the yield of CO absorbance loss vs. the measured value of 0.040.

$$\phi_{\text{CO loss}} \cong \phi_{\text{CO evolution}} + \phi_{\text{acetone}} \cong 0.016$$

Part of this discrepancy may be due to differences in the extinction coefficients (IR and UV) of the reactant carbonyl groups and product carbonyl groups of the type II reaction, step b.

The generally fair to good correspondence found in the yields of the various groups and gaseous products tends to support our previous assumptions that (1) the carbonyl groups in the E/CO copolymer used in this study are distributed randomly in the polymer chain with few located in branches and (2) the Norrish reactions dominate the photochemistry of these copolymers, with the type II reactions occurring over 4 times faster than type I reactions.

The characterization of cross-linking processes by NMR involves a fine balance between forming sufficient quantities of functional groups for analysis and maintaining soluble samples for analysis. At present, this dilemma does not restrict this study of E/CO copolymer as much as previous studies on polyethylene photooxidation.[25c] Solid-state techniques do not yet appear to have the sensitivity necessary for characterization of low levels of cross-linking or of other functional group changes in the earlier stages of degradation.

The decrease in rates of gas evolution, chain scission, buildup of vinyl groups, and decrease in carbonyl groups at longer exposure times is significant (Figures 2, 3, 5, 10 and 11). One possibility for this observation may be that structurally or chemically different chromophores react at different rates, e.g., pendant vs. backbone carbonyls or hydroperoxides vs. ketonic groups. However, there is no evidence for structurally different carbonyls in the unexposed copolymer. Pendant carbonyls may be ruled out because the formation of vinylene unsaturation was insignificant. It would be expected that a ketonic carbonyl has to be in a short branch in orrder for its reactivity to differ greatly from that of a backbone carbonyl.[11] Hydroperoxides or other different oxygen-containing species can be ruled out since the backbone content, as determined by NMR, accounts for nearly all of the oxygen measured by activation analysis (1.15 and 1.38%, respectively). Thus the morphology of the copolymer can be considered as a likely explanation for the observed decreases in rates. Solid polyolefins can contain amorphous regions where no apparent order exists and microcrystalline regions where the polymeric chains are orderly aligned.[40]

The photochemistry of ketones has been studied extensively.[41,42] In particular, Norrish type II reactions have been well characterized and found to depend very strongly on molecular conformation. In the first chemical step, a hydrogen atom, usually in the γ-position, must be close to the excited carbonyl oxygen to allow abstraction. Secondly, scission requires a different conformation from that of reverse hydrogen transfer or of cyclobutanol formation. It has been found that the yield of type II scission is markedly reduced when the medium is changed from one that is unorganized (solution) to a highly organized one (as in micelles[43] or crystallites[44]). Similarly in polymers, type II scission is retarded at temperatures below the glass transition temperature, where chain motion is restricted.[45]

Since CO groups present in the polymer chain readily fit into crystalline regions, they should be distributed randomly throughout the solid copolymer.[46] In a crystalline region where the chains are packed in a trans–trans (zigzig) conformation, intramolecular γ-hydrogen transfer should be minimal, and type II scission should be retarded in relation to that expected in the more mobile amorphous region.[47] Therefore, type II scission, the predominant photolysis process, occurs faster in the amorphous phase of the copolymer than in the crystalline phase, and constraint of nearly half of the carbonyls in crystalline regions accounts for the gradual leveling off of the degradation rate.

The influence of morphology on the oxidative or hydrolytic stability of some polymers has been observed.[48,49] Where oxidation or hydrolysis is diffusion dependent, it is confined mostly to amorphous regions, while the more inaccessible crystalline regions are resistant to degradation. Therefore, the uptake of oxygen by polyethylene was found to be inversely proportional to the crystalline content of the polymer.[50]

The comparison between oxidation rates of the copolymer and branched polyethylene in Figure 4 is interesting, since the reaction conditions, morphologies, and gas permeabilities of the polymers are similar. Yet the copolymer, with a carbonyl concentration several orders of magnitude greater than that of the polyethylene, oxidizes at a rate only about twofold faster and is virtually unaffected by loss of carbonyl during exposure. This implies that oxidation products other than ketonic groups may be the dominant initiators in the photooxidation of polyolefins. Peroxy and hydroperoxy groups have been proposed as dominant initiators, because of the efficiency of photochemical degradation of these groups.[8,51] Alternatively, sensitization of these groups by ketonic chromophores has been proposed,[51] although there is some question about the efficiency of this process.[52]

Studies are continuing on the morphology of solid copolymer samples studied, on possible morphological changes due to irradiation, and on trying to distinguish the reactivity and chemistry of morphologically different ketonic chromorphores.

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References and Notes

(1) Carlsson, D. J.; Wiles, D. M. *Macromolecules* **1971**, *4*, 179.

(2) Winslow, F. H. *Pure Appl. Chem.* **1977**, *49*, 495 and references cited therein.

(3) Heacock, J. F.; Mallory, F. B.; Gay, F. P. *J. Polym. Sci., Part A-1* **1968** *6*, 2921.

(4) Adams, J. H. *J. Polym. Sci., Part A-1* **1970**, *8* 1279.

(5) Hawkins, W. L.; Winslow, F. H. In "Crystalline Olefin Polymers"; Raff, R. A. V., Doak, K. W., Eds., Wiley: New York, 1964; Part II, p 361.

(6) Pross, A. W.; Black, R. M. *J. Soc. Chem. Ind., London* **1950**, *69*, 113.

(7) Burgess, A. R. *Natl. Bur. Stand. (U.S.), Circ.* **1953**, *525*, 149.

(8) (a) Carlsson, D. J.; Wiles, D. M. *Macromolecules* **1969**, *2*, 597. (b) *J. Macromol. Sci., Rev. Macromol. Chem.* **1976**, *C14*, 65.

(9) (a) Turro, N. J.; Dalton, J. C.; Dawes, K.; Farrington, G.; Hautala, R.; Morton, D.; Niemczyk, M.; Schore, N. *Acc. Chem. Res.* **1972**, *5*, 92. (b) Wagner, P. J. *Acc. Chem. Res.* **1971**, *4*, 168.

(10) Li, S. K. L.; Guillet, J. E. *J. Polym. Sci., Polym. Chem. Ed.* **1980**, *18*, 2221 and earlier references cited therein.

(11) Sitek, F.; Guillet, J. E.; Heskins, M. *J. Polym. Sci., Polym. Symp.* **1976**, *No. 57*, 543.

(12) Guillet, J. E. Br. Patent 1 372 830, Nov 6, 1974; *Chem. Abstr.* **1975**, *83*, 116416*h*.

(13) Guillet, J. E. *Degradability Polym. Plast. (Prepr.) Conf. 4* **1975**, *Chem. Abstr.* **1976**, *85*, 78745*w*.

(14) Pozzi, V.; Silvers, A. E.; Giuffre, L.; Cernia, E. *J. Appl. Polym. Sci.* **1975**, *19*, 923.

(15) (a) Winslow, F. H.; Matreyek, W.; Trozzolo, A. M. *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* **1969**, *10*, 1271. (b) *SPE J.* **1972**, *28*, 19.

(16) Nargolwalla, S. S.; Przybylowicz, E. P. In "Activation Analysis with Neutron Generators"; Wiley: New York, 1973.

(17) Mitchell, J.; Perkins, L. R. In "Weatherability of Plastics Materials"; Kamal, M. R., Ked.; Interscience: New York, 1968; p 167.

(18) Lee, E. K. C.; Lewis, R. S. *Adv. Photochem.* **1980**, *12*, 1.

(19) Aggarwal, S. L. In "Polymer Handbook"; Brandrup, J., Immergut, E. H., Eds.; Wiley: New York, 1966; pp V148–9.

(20) Chien, J. C. W. In "Degradation and Stabilisation of Polymers"; Gueskins, G., Ed.; Wiley: New York, 1975; p 95.

(21) (a) Noyes, W. A., Jr.; Dorfman, L. M. *J. Chem. Phys.* **1948**, *16*, 788. (b) Noyes, W. A., Jr.; Porter, G. B.; Jolley, J. E. *Chem. Rev.* **1965**, *56*, 49 and references cited therein.

(22) (a) Taylor, H. S.; Rosenblum, C. *J. Chem. Phys.* **1938**, *6*, 119. (b) Imai, N.; Toyama, O. *Bull. Chem. Soc. Jpn.* **1960**, *33*, 652.

(23) On the basis of the IR absorbance at 1720 cm^{-1}, the concentration of carbonyl in the polyethylene sample was less than 0.5% that of the copolymer. Neutron activation analysis of the polyethylene found an oxygen content of less than 50 ppm. McCall, D. W.; Douglass, D. C.; Blyler, L. L., Jr.; Johnson, G. E.; Jelinski, L. W.; Bair, H. E. *Macromolecules* **1984**, *17*, 1644.

(24) A reviewer has indicated that only the initial rate of oxidation should be substantially affected by changes in concentration of ketonic carbonyls and that at best the overall rate of oxidation should show a square root dependence of the rate of initiation. On the basis of this limiting case and differences in ketonic carbonyls, the oxidation rate of this copolymer should be over 30 times faster than the oxidation rate for polyethylene, if ketonic carbonyls are the sole initiators. The actual rate of oxygen uptake in the copolymer was found to be only slightly faster in the earlier stage (<30 h, Figure 4) of reaction.

(25) (a) Winslow, F. H. In "Durability of Macromolecules Materials"; Eby, R. K., Ed.; American Chemical Society: Washington, DC, 1979, ACS Symp. Ser. No. 95, Chapter 2. (b)

Macromolecules **1984**, *17*, 2837–2846 **2837**

Cotten, G. R.; Sacks, W. *J. Polym. Sci., Part A* **1963**, *1*, 1345. (c) Feit, E. D., unpublished studies.

(26) (a) Cheng, H. N.; Schilling, F. C.; Bovey, F. A. *Macromolecules* **1976**, *9*, 363. (b) Bovey, F. A.; Schilling, F. C.; Cheng, H. N. In "Stabilization and Degradation of Polymers"; Allara, D. L., Hawkins, W.L., Eds.; American Chemical Society; Washington, DC, 1978; Adv. Chem. Ser. No. 169, p 133.

(27) Wu, T. K.; Ovenall, D. W.; Hoehn, H. H. In "Applications of Polymer Spectroscopy"; Brame, E. G., Ed.; Academic Press: New York, 1978; pp 19–40.

(28) Bennett, R. L.; Keller, A.; Stejny, J.; Murray, M. *J. Polym. Sci., Polym. Chem. Ed.* **1976**, *14*, 3027.

(29) Kuroki, T.; Sawaguchi, T.; Nikuni, S.; Ikemura, T. *J. Polym. Sci., Polym. Chem. Ed.* **1983**, *21*, 703.

(30) Bovey, F. A.; Schilling, F. C.; McCrackin, F. L.; Wagner, H. L. *Macromolecules* **1976**, *9*, 76.

(31) In this case, the number percent (NMR) and weight percent (activation analysis) are the same since CO and ethylene have nearly the same molecular weights.

(32) For a random model, % 1,4-dione = 100(% CO/% E)^2, where % CO and % E are the molar percents of CO and ethylene in the feed stock, respectively. Thus the % 1,4-diones structures expected in a 1.5% CO content is 0.023.[27]

(33) Correlation coefficients and confidence limits for IR and NMR data: carbonyl–Ar, 0.98 (99.9%); vinyl–Ar, 0.99 (99.9%); carbonyl–O_2, 1.00 (99.9%); vinyl–O_2, 0.91 (95%). Calculated following statistics programs of "Calculator Decision-Making Sourcebook"; Texas Instruments, 1977.

(34) Hartley, G. H.; Guillet, J. E. *Macromolecules* **1968**, *1*, 165.

(35) Dan, E.; Guillet, J. E. *Macromolecules* **1973**, *6*, 230.

(36) Guillet, J. E. *Naturwissenschaften* **1972**, *59*, 503.

(37) Schilling, F. C., unpublished studies.

(38) Hartley, G. H.; Guillet, J. E. *Macromolcules* **1968**, *1*, 413.

(39) Golemba, F. J.; Guillet, J. E. *Macromolecules* **1972**, *5*, 63.

(40) (a) Schultz, J. in "Polymer Materials Science"; Prentice-Hall: Englewood Cliffs, NJ, 1974; Chapter 2. (b) Wunderlich, B. in "Macromolecular Physics"; Academic Press: New York, 1973; Vol. 1, Chapter 3.

(41) Wagner, P. J. *Acc. Chem. Res.* **1971**, *4*, 168.

(42) Barltrop, J. A.; Coyle, J. D. In "Excited States in Organic Chemistry;" Wiley: New York, 1975, Chapter 7.

(43) Winkle, J. R.; Worsham, P. R.; Schanze, K. S.; Whitten, D. G. *J. Am. Chem. Soc.* **1983**, *105*, 3951.

(44) Slivinskas, J. A.; Guillet, J. E. *J. Polym. Sci., Polym. Chem. Ed.* **1973**, *11*, 3043.

(45) Dan, E.; Guillet, J. E. *Macromolecules* **1973**, *5*, 230.

(46) Wunderlich, B.; Poland, D. *J. Polym. Sci., Part A* **1963**, *1*, 357.

(47) As an alternative, consider chain packing in a trans–gauche conformation. Although γ-hydrogen transfer may be favored due to close proximity of the reaction centers, scission would be retarded due to restricted rotation. See ref 42 for examples of rotationally restricted ketones.

(48) Kamiya, Y.; Niki, E. In "Aspects of Degradation and Stabilization of Polymers"; Jellinek, H. H. G.,Ed.; Elsevier: New York, 1978; pp 80–147.

(49) Winslow, F. H.; Hellman, M. Y.; Matreyek, W.; Stills, S. M. *Polym. Eng. Sci.* **1966**, 273.

(50) Winslow, F. H.; Aloisio, C. J.; Hawkins, W. L.; Matreyek, W.; Matsuoka, S. *Chem. Ind.* **1963**, 533.

(51) Li, S. K. L.; Guillet, J. E. *Macromolecules* **1984**, *17*, 41.

(52) Wismontski-Knittel, T.; Kilp, T. *J. Polym. Sci., Polym. Chem. Ed.*, **1983**, *21*, 3209.

Backbone Dynamics of Poly(isopropyl acrylate) in Chloroform. A Deuterium NMR Study

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ABSTRACT: The backbone dynamics of poly(isopropyl acrylate) (PIPA) in chloroform have been studied over a wide composition and temperature range using deuterium NMR. The polymer was specifically labeled with deuterium in the methine position so that only one resonance would be seen. The results of T_1 and T_2 measurements were used to test the log χ^2, VJGM, Bendler–Yaris (BY), and Skolnick–Yaris (SY) models of polymer reorientation. It was found that, even though all the models could mimic the data, they did not always fit the data in a physically realistic way. The log χ^2 model yielded results which were not physically realistic even in dilute solution. The results from the VJGM, BY, and SY models were roughly indistinguishable despite their different formulations. All three models contain two parameters, each of which are dominated by either fast or slow motions. Further, it was seen that in dilute solution, the fast motion has an energy of activation of about 5 kcal/mol which is independent of concentration. In more concentrated solutions the energies of activation for the slow-motion parameters are concentration dependent and range from 12 to 30 kcal/mol. In concentrated solutions, it was found that T_1 and T_2 cannot be represented by a single model but the T_2 measurements can be used to define a division between semidilute and concentrated solution when $[\eta]C_c \cong 30$ for PIPA–$CHCl_3$. It was also found that the T_2 values for the concentrated solutions could be fit by using a free volume approach. The free volume parameters were calculated and judged to be reasonable when compared to the other systems.

Introduction

The dynamics of the backbone and side chain of polymer molecules in solution have been studied by a wide variety of techniques.[1] The results from techniques such as dielectric relaxation, fluorescence depolarization, ESR spin labeling, and NMR relaxation studies can be used to test proposed models of polymer motion. The results from all of these techniques suggest that the reorientation of polymer segments is not adequately described as simple isotropic reorientation. NMR is particularly versatile for the study of polymer motion because it can be used to probe different moieties in a repeating unit, provided that each has a "resolved" resonance. Studies of relaxation times from ^{1}H, ^{13}C, and ^{2}H (to a lesser extent) NMR in dilute polymer solutions have been reviewed by Heatley[2] within the framework of models existing at that time.

The study of polymer dynamics using NMR in concentrated solutions is more complicated than in dilute solutions. As polymer concentrations are increased, the line widths broaden to the point of severe overlap, which makes it difficult to assign spectral features to individual resonances. Thus, detailed dynamics studies become difficult to perform with ^{1}H, ^{13}C, or ^{2}H NMR at natural abundance. Therefore, most quantitative polymer dynamics studies are carried out at concentrations less than 30 wt %. In the limit of bulk polymer, some of these problems can be overcome through the use of specialized techniques such as magic angle spinning. However, these are not easily

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