Conclusion

We can conclude that the effect of chain interdependence and cross-link mobility in this simple non-Gaussian network system is to reduce the number of "elastically and photoelastically effective chains" but the number of links in these "effective chains" differs for each case. Previous extrapolations to more realistic network models[3-5] do not appear to be well founded and hence we have not attempted it herein. A new approach is needed which incorporates the main features of this simple calculation: cross-link mobility and chain interdependence.

References and Notes

(1) Supported in part by National Science Foundation Grant NSF-DMR-72-03026.

(2) R. J. Gaylord, Ph.D. Thesis, State University of New York, College of Environmental Science and Forestry, 1973.

(3) K. J. Smith, Jr., and R. J. Gaylord, *J. Polym. Sci., Polym. Phys. Ed.*, **13**, 2069 (1975).

(4) W. W. Graessley, *Macromolecules*, **8**, 186 (1975).

(5) J. A. Duiser and A. J. Staverman, "Physics of Non-Crystalline Solids", J. A. Prins, Ed., North-Holland Publishing Co., Amsterdam, 1965, pp 376-387.

(6) M. Wang and E. Guth, *J. Chem. Phys.*, **20**, 1144 (1952).

(7) Unpublished results.

(8) K. J. Smith, Jr., and D. Pruett, *J. Appl. Phys.*, **37**, 346 (1966).

Communications to the Editor

^{13}C Nuclear Magnetic Resonance Observation of the Oxidation of Polyethylene

The oxidation of polyolefins is a problem of considerable technological importance and scientific interest. The literature is voluminous (see ref 1–3 for reviews) and the general outlines of the thermal reaction are now generally felt to be quite well understood. Lingering doubts persist, however, as to the details of the mechanism, particularly from the quantitative standpoint, and the exact nature of the oxidation products is by no means completely clear.[4-7] This is in large part due to heavy reliance on ir spectroscopy in studies reported to date. Informative as it is, ir spectroscopy suffers from the difficulty of band overlap, particularly in the important carbonyl stretch region near 1725 cm^{-1}, and from the troublesome necessity of establishing reliable extinction coefficients.

Because of the wide range of ^{13}C chemical shifts, over 200 ppm for the resonances of interest, peak overlap does not present a problem. In addition, because of the sensitivity of ^{13}C chemical shifts to local structure, much more positive and detailed identification of oxygen-containing groups is possible. A third major advantage of FT ^{13}C NMR is that with due attention to spin–lattice relaxation, i.e., by selecting pulse intervals equal to at least $3T_1$, quantitative estimation of the oxidation products can be carried out directly from peak intensity measurements.[8]

We wish to report in a preliminary fashion our utilization of FT ^{13}C NMR for the observation and measurement of the oxidation products of low density (i.e., branched) polyethylene. The polymers employed were commercial materials from Union Carbide having the properties shown in Table I. The branch contents were determined by ^{13}C NMR as described by Dorman et al.[10] and by Bovey et al.[11] Spectra were observed at 25 MHz at a temperature of 110°.[12] The polymers were exposed to 1 atm of oxygen in the form of 5-in. diameter circular films of 5-mil thickness (ca. 1.4 g) placed in flat-bottomed conical oxidation cells held in a 140° oil bath and connected to mercury manometers. After the desired volume of oxygen was absorbed, the oxidized polymer was dissolved as 30% (w/v) solutions in a 4:1 (by volume) mixture of 1,2,4-trichlorobenzene and deuteriobenzene. The solutions were placed in 12-mm NMR tubes which were then flushed with argon and stoppered.

Figure 1 shows the ^{13}C spectrum of polymer B (Table I) before (a) and after (b and c) thermal oxidation. The principal peak at 30 ppm (vs. TMS) is that of the methylene carbons which are four or more carbons removed from any branch, chain ends, or oxidized groups. The resonances associated with branches are known[10,11] and are indicated on spectrum (a). In spectra (b) and (c) the new peaks resulting from oxidation are shaded. Most of these have been unequivocally assigned. This was done by comparison with appropriate long-chain model compounds[14] which were individually observed as 20% (w/v) solutions under identical conditions. In order to simulate the polymer solutions still more closely, mixed solutions of model compounds were also observed. Deviations from the chemical shifts of the pure compounds were less than 0.1 ppm in the alkyl region and ca. 1 ppm in the carbonyl region. (Smaller deviations are to be expected for the actual polymer solutions, in which functional group concentrations were smaller.)

Table I

	Polymer A	Polymer B
Melt index	0.3	21.9
$\overline{M}_w$	3.50×10^5	1.43×10^5
Density, g cm^{-3}	0.9175	0.9245
Branch content[a]		
Methyl	0	0
Ethyl	2.6	1.9
n-Butyl	11.4	9.7
n-Amyl	4.4	2.1
"Long"	4.1	3.4
Total branch points	22.5	17.1

[a] Branch points per 1000 CH$_2$.

As Figure 1 (b and c) shows, the groups believed to be unequivocally assigned were: long-chain ketones, long-chain carboxylic acids, long-chain secondary alcohols, long-chain secondary hydroperoxides, esters of long-chain carboxylic acids with long-chain secondary alcohols, and long-chain γ-lactones. *Not* observed at our present level of detection (ca. 0.3%) were the following groups: aldehydes, conjugated ketones, olefins, peresters, primary and tertiary hydroperoxides, and primary and tertiary alcohols and their esters. The presence of all of these has been proposed or reported by various authors.[1,4,5,7]

In other respects, our data agree in a general way with ir findings,[5] but provide considerably more detailed structural information as well as a sounder quantitative basis for mechanistic conclusions. In Figure 2, the distribution of established oxidation products is depicted as a function of time and extent of oxidation. The highest extent of oxida-

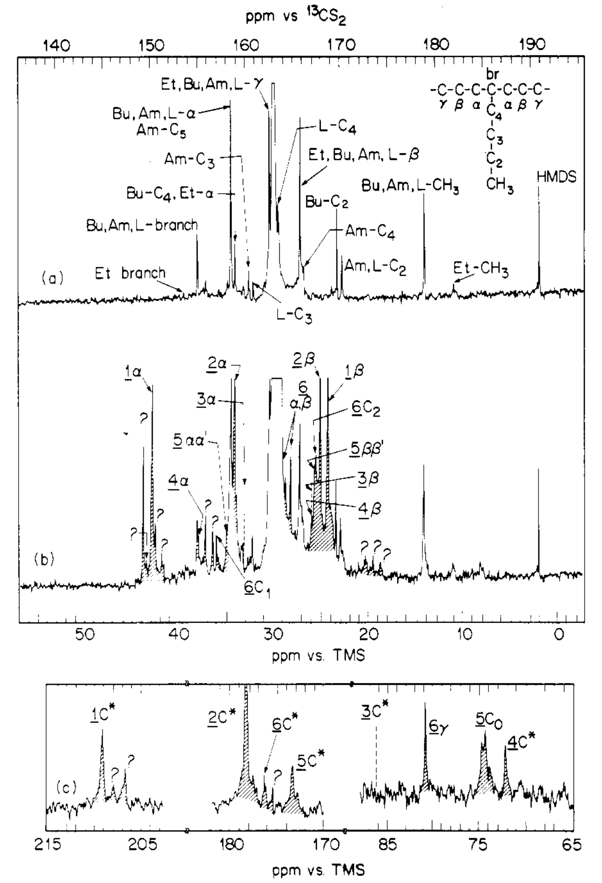
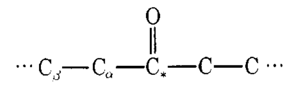
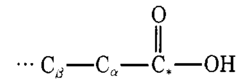


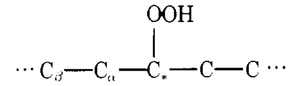
Figure 1. C^{13} spectra of polymer B: (a) before oxidation, where Bu, Am, L refer respectively to butyl and amyl branches and long-chain ends; (b) and (c) after being oxidized to 108 ml/g. The oxidized products are identified by numbers as follows:


$\cdots C_\beta - C_\alpha - \overset{\overset{O}{\|}}{C}_* - C - C \cdots$

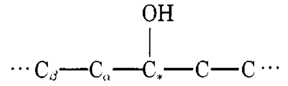
1 = ketones


$\cdots C_\beta - C_\alpha - \overset{\overset{O}{\|}}{C}_* - OH$

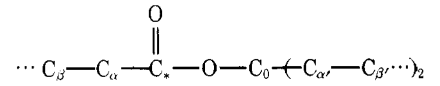
2 = acids


$\cdots C_\beta - C_\alpha - \overset{\overset{OOH}{|}}{C}_* - C - C \cdots$

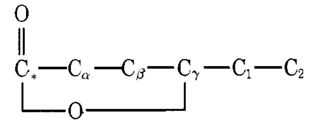
3 = secondary hydroperoxides


$\cdots C_\beta - C_\alpha - \overset{\overset{OH}{|}}{C}_* - C - C \cdots$

4 = secondary alcohols


$\cdots C_\beta - C_\alpha - \overset{\overset{O}{\|}}{C}_* - O - C_0 \left(- C_{\alpha'} - C_{\beta'} \cdots \right)_2$

5 = esters of acid and secondary alcohols


$\overset{\overset{O}{\|}}{C}_* - C_\alpha - C_\beta - C_\gamma - C_1 - C_2$

6 = γ-lactones

At the oxidation level shown, the hydroperoxides have mostly degraded; however, the appropriate resonances are indicated by dotted lines.

tion, 108 ml per gram of polymer, corresponds to a degree of advancement of about 4.5% toward total oxidation to H_2O and CO_2. (Some H_2O is lost up to this stage of reaction but considerably less CO_2.) The secondary hydroperoxides reach a maximum at ca. 40 ml g^{-1} and then decrease as other products accumulate. The results appear to agree well with those of model reaction calculations,[15] and to support the presently accepted oxidative scheme for linear chains (Scheme I).

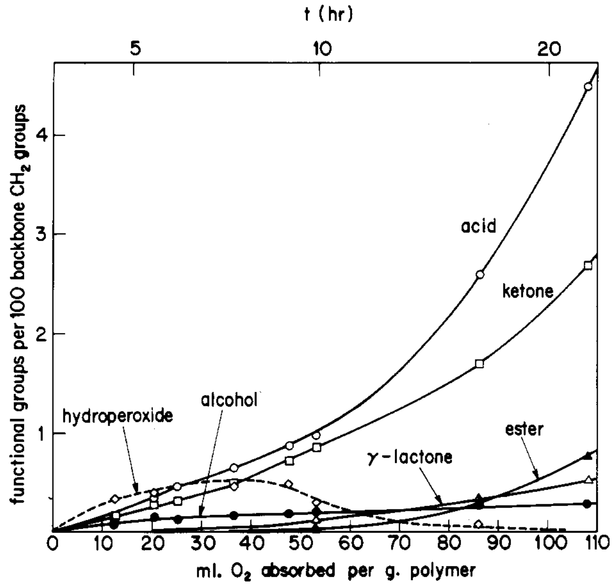
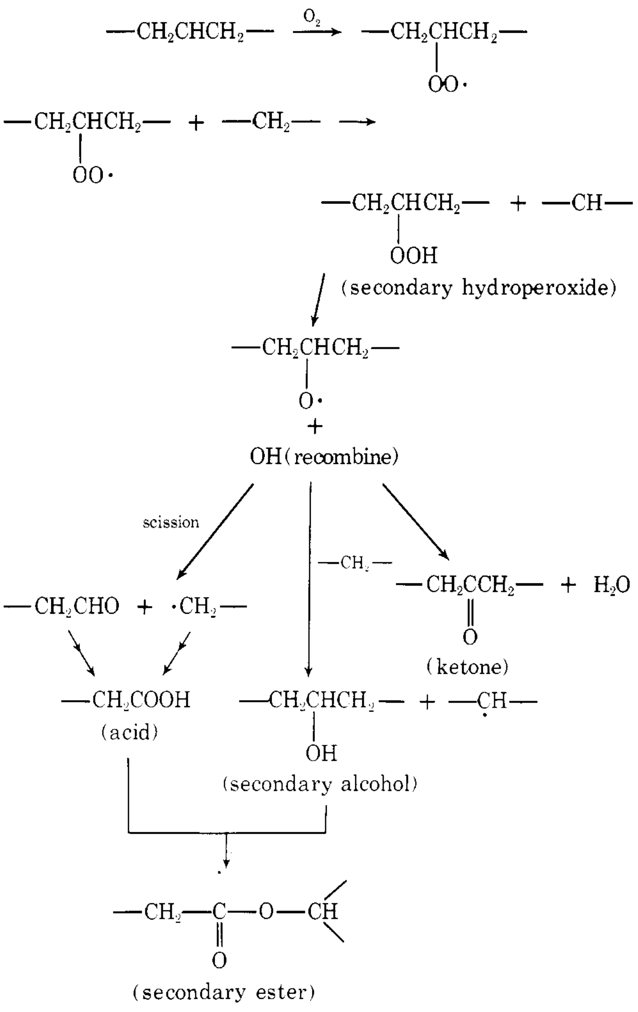
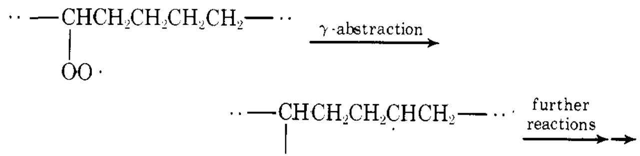


Figure 2. Distribution of oxidation products of polyethylene as a function of the extent of oxidation (lower scale: O_2 absorbed; upper scale: time of reaction). The vertical scale refers to the intensity of the backbone CH_2 resonance at 30 ppm; no correction is made for CH_2 groups neighboring the functional groups. The hydroperoxide decomposes gradually at 110°C; the concentrations shown above are the estimated values extrapolated back to zero time assuming first-order decay.

Scheme I

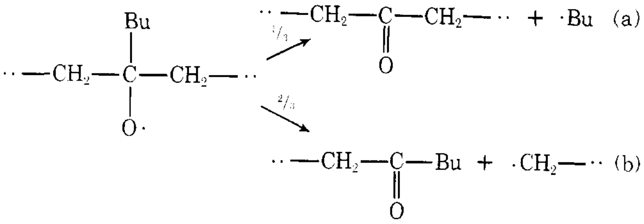


Over 80% of the oxygen consumed can be accounted for by the known products observed.[16] However, it appears at present that this scheme is not complete, as there are products for which it does not account. For example, γ-lactone, also reported by Adams in the oxidation of polyolefins, may be formed either via intramolecular attack by the peroxyacyl radical[5] or alternatively via an intrachain "back-biting" scheme parallel to that suggested by Rust[17] and by Chien et al.[18]



In addition, it is important to reiterate that not all the observed peaks are as yet assigned. Some of these may represent products resulting from intrachain reactions initiated as above. Particularly conspicuous is a peak at 43.7 ppm, and two keto carbonyl resonances at 206.8 and 208.0 ppm. These appear to correspond to products not yet recognized in any published oxidation scheme. The resonance at 175.0 ppm is tentatively assigned to the carbonyl of peracid, -C(=O)OOH, generally accepted as an intermediate in the oxidation of aldehyde to carboxylic acid.

Our data also provide an estimate of the ratio of reactivity to oxidative attack of branch points compared to linear hydrocarbon chains. It is observed that the butyl C-2 carbon resonance intensity at 23.4 ppm (Figure 1b) decreases from 9.7 to 6.6 per 1000 CH_2 upon absorption of 53 ml g^{-1} of oxygen. Oxidative cleavage at an *n*-butyl (or longer) branch point is believed to occur as follows[15,18,19] (the tertiary alkoxy radical having been generated by steps parallel to those shown above):



Reactions (a) and (b) occur with statistical probability giving long-chain ketone and butyl ketone, which are indeed observable in our experiments. Model compound measurements show that in the *n*-butyl ketone group the butyl C_2 carbon resonance moves from 23.4 to 22.7 ppm, becoming coincident with the C_2 resonance of "amyl + long" branches, the intensity of which correspondingly increases upon oxidation. By comparing these results quantitatively with the overall production of oxidized structures, it can be shown (by calculations which we shall not detail here) that the reactivity ratio of branch points to linear chains is 9.8 ± 1.0, a result in good agreement with the value of 8 derived from model hydrocarbon oxidation studies.[15]

Preliminary studies of the photoxidation of low-density polyethylene, to be reported in detail later, indicate a substantial production of terminal vinyl groups together with a decreased appearance of oxygen-containing groups in the polymer chains as compared to thermal oxidation.

Acknowledgment. The authors wish to express their thanks to Dr. D. L. Allara for helpful discussions, to Mr. Martin Kaplan for supplying several peroxides as well as information concerning their synthesis and properties, to Mr. John Daane for supplying the polyethylene samples together with their densities and melt indices, and to Mrs. M. Hellman for GPC measurements of $\bar{M}_w$.

References and Notes

(1) W. L. Hawkins, "Polymer Stabilization", Wiley-Interscience, New York, N.Y., 1972.

(2) J. A. Howard, *Rubber Chem. Technol.*, **47**, 976 (1974).

(3) D. J. Carlsson and D. M. Wiles, *Rubber Chem. Technol.*, **47**, 991 (1974), and references therein.

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

(5) J. H. Adams, *J. Polym. Sci., Part A-1*, **8**, 1077, 1279 (1970).

(6) M. M. Émanuél, *Izv. Akad. Nauk SSSR., Ser. Khim.*, **5**, 1056 (1974).

(7) D. L. Tabb, J. J. Sevcik, and J. L. Koenig, *J. Polym. Sci., Polym. Phys. Ed.*, **13**, 815 (1975), and references therein.

(8) The possible occurrence of differential Overhauser effects is a frequently mentioned bugbear in quantitative ^{13}C work, especially with polymers. We do not believe that this is a serious matter in the present study; Inoue et al.[9] report a full threefold Overhauser enhancement for polyethylene at 140°, and there appears to be no valid reason to expect less than this value for the upfield resonances used by us for all quantitative measurements.

(9) Y. Inoue, A. Nishioka, and R. Chûjô, *Makromol. Chem.*, **168**, 163 (1973).

(10) D. E. Dorman, E. P. Otocka, and F. A. Bovey, *Macromolecules*, **5**, 574 (1972).

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

(12) The spectra were obtained using a Varian XL-100 spectrometer modified for FT operation and interfaced with a Nicolet 1080 computer.[13] Proton ^{13}C couplings were eliminated using a noise-modulated decoupling field. The free induction decays were stored in 8K computer locations using a dwell time of 83 μsec (i.e., a spectral window of 6024 Hz). The pulse was located at the high-field end of the spectrum at 25.16032 MHz, the pulse width being 63 μsec for an approximately 90° pulse. Pulse intervals were 6 to 10 sec. Hexamethyldisiloxane (HMDS) was used as internal reference (2.00 ppm from TMS) and C_6D_6 as internal deuterium lock. At the observing temperature (110°), T_1 for the main chain carbons is ca. 1.4 sec.[9]

(13) H. Sternlicht and D. M. Zuckerman, *Rev. Sci. Instrum.*, **43**, 525 (1972).

(14) The principal model compounds employed were: (a) alcohols: 1-dodecanol, 7-tridecanol, 5-butyl-5-nonanol; (b) ethers: dihexadecyl ether, di-*sec*-butyl ether; (c) peroxides: peroxybutyric acid, 1-hydroperoxyhexane, 3-hydroperoxyhexane, and *tert*-butyl hydroperoxide; (d) olefins: *cis*- and *trans*-9-nonadecene, 1-docosene, 2-hexyl-1-octene, and 5-butyl-4-nonene; (e) ketones: 10-nonadecanone, 1-penten-3-one, 5-tetradecanone, and 3-hexadecanone; (f) acids: stearic, *trans*-2-decenoic; (g) aldehydes: dodecanal, 2-butenal; (i) lactones: γ-nonalactone, δ-nonalactone, ϵ-nonalactone; (h) esters: *n*-butyl stearate, 7-tridecyl stearate.

(15) D. L. Allara and D. Edelson, *Rubber Chem. Technol.*, **45**, 437 (1972).

(16) This estimate is based on the assumption that in the mechanism shown the formation of each ketone, alcohol, and hydroperoxide group consumes one O_2 molecule; each acid and lactone group two O_2 molecules; and each ester group three O_2 molecules. Thus for the sample consuming 53 ml of O_2 per gram of polymer, the material balance, corrected to the original polymer, is: polymer = 71.4 mmol of CH_2/g; O_2 = 2.37 mmol; carboxyl = 0.550 mmol × 2 = 1.100 mmol; ketone = 0.493 mmol × 1 = 0.493 mmol; hydroperoxide = 0.164 mmol × 1 = 0.164 mmol; secondary alcohol = 0.114 mmol × 1 = 0.114 mmol; γ-lactone = 0.079 mmol × 2 = 0.158 mmol; ester ≈ 0; total oxygenated groups = 2.039 mmol/2.37 mmol O_2 consumed = 86%. The oxygen unaccounted for presumably consists of volatiles other than H_2O, principally CO_2, and unidentified products.

(17) F. F. Rust, *J. Am. Chem. Soc.*, **79**, 4000 (1957).

(18) J. C. W. Chien, E. J. Vandenberg, and H. Jabloner, *J. Polym. Sci., Part A-1*, **6**, 381 (1968).

(19) T. Mill, H. Richardson, and F. R. Mayo, *J. Polym. Sci., Polym. Chem. Ed.*, 11, 2899 (1973).

H. N. Cheng, F. C. Schilling, and F. A. Bovey
Bell Laboratories, Murray Hill, New Jersey 07974

Received August 26, 1975

A New Class of Synthetic Polyelectrolytes. Acidic Polyesters of Phosphoric Acid, (Poly(hydroxyalkylene phosphates))

We have previously[1] discussed the possibility of preparation of the acidic polyesters of phosphoric acid (poly(hydroxyalkylene phosphates)), starting from polymers of 2-aryloxy-2-oxo-1,3,2-dioxaphosphorinanes. These mono-