(4) Seymour, R. W.; Allegrezza, A. E., Jr.; Cooper, S. L. *Macromolecules* **1973**, *6*, 896.
(5) Allegrezza, A. E., Jr.; Seymour, R. W.; Ng, N. H.; Cooper, S. L. *Polymer* **1974**, *15*, 433.
(6) Kimura, I.; Ishihara, H.; Ono, H.; Yoshihara, N.; Nomura, S.; Kawai, H. *Macromolecules* **1974**, *7*, 355.
(7) Khranovskii, V. A. *Dokl. Akad. Nauk SSSR* **1979**, *244* (2), 408.
(8) Abourzahr, S.; Wilkes, G. L.; Sung, C. S. P., manuscript in preparation.
(9) Schneider, N. S.; Sung, C. S. P.; Matton, R. W.; Illinger, J. L. *Macromolecules* **1975**, *8*, 62.

Distinction between Hexyl and Longer Branches in Polyethylene by 67.9-MHz Carbon-13 Nuclear Magnetic Resonance

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Almost all papers concerning the analysis of branched polyethylene by ^{13}C NMR[1-5] repeat in some way the statement of Randall[1] that branches of lengths of 1–5 carbon atoms can be mutually distinguished but that at a branch length of six carbon atoms the array of chemical shifts associated with branch length may no longer change with increasing chain length. Only in one instance[2] has it been claimed that amyl branches could not be recognized separately from ethyl, propyl, butyl, and higher branches, but the feasibility of this distinction has again been demonstrated by Randall.[3]

In his early work,[1] Randall performed a 25.2-MHz analysis of ethylene copolymers with olefins ranging from propene to octene. For the heptene copolymer, he found that the resonances of the carbons C-4 and C-β[7] ($\Delta\delta = 0.57$ ppm) could be easily resolved, while those of C-5 and C-α could hardly be resolved with the experimental techniques applied at that time. In the octene copolymer, C-5 and C-6 are equivalent to C-4 and C-5 in the heptene copolymer with respect to their distance from the branching point. No difference between the chemical shifts of C-5 and C-β on the one hand and C-6 and C-α on the other hand was detected by Randall for the octene copolymer.

In a more recent work, Axelson, Levy, and Mandelkern[5] again conclude that "long branches cannot be distinguished from hexyl at the present time". Furthermore, they state that "while high magnetic fields lead to a greater dispersion of chemical shifts, we have found that a comparison of spectra obtained at 67.9 MHz with that at 22.6 MHz does not reveal significant changes in the information content".

This is not entirely true, at least regarding the distinction between hexyl and longer branches. In our view, the ability to resolve the resonances of C-5 and C-β in polymers bearing the hexyl group is crucial to this distinction. Other branch carbon resonances are not suited to this purpose. C-6 is too far away from the branch end to reflect the effects of its increasing length; C-4 and C-(4 + n) in branches of length (6 + n) will be obscured by the resonance of unperturbed main-chain methylene carbons; other branch carbons will behave like C-4 or will be indistinguishable from terminal main-chain carbons.

We performed a comparative analysis at 25.2 and 67.9 MHz of two octene copolymers. One was a commercial linear low-density polyethylene sample, Dow 61500.49; the other was prepared in our laboratories. The 67.9-MHz carbon-13 spectrum of the latter is shown in Figure 1.

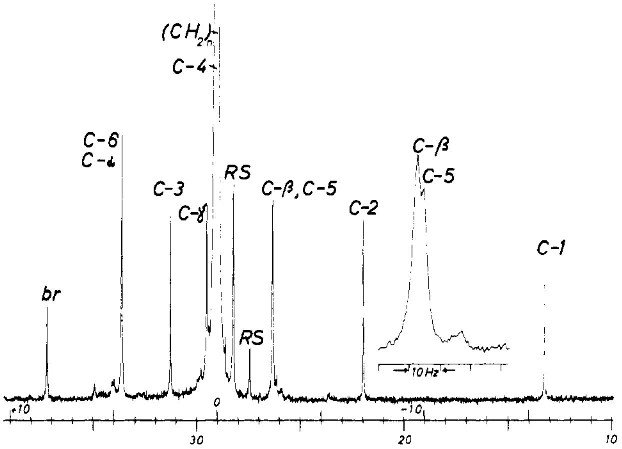

Figure 1. 67.9-MHz ^{13}C NMR spectrum of an ethylene–octene copolymer. RS = rotational sideband.

Table I
Carbon-13 Chemical Shifts (ppm) in the Ethylene-Octene Copolymer

carbon	shift[a]	shift[b]
branch	37.214	8.198
C-α, C-6	33.610	4.593
C-3	31.273	2.225
C-γ	29.502	0.485
C-4	obscured by $(CH_2)_n$	
$(CH_2)_n$	29.016	0.000
C-β	26.329	−2.688
C-5	26.302	−2.715
C-2	21.960	−7.056
C-1	13.250	−15.767

[a] Referenced to the resonance of internal octamethylcyclotetrasiloxane. [b] Referenced to the main methylene resonance.

In both cases, we were able to resolve the C-5 and C-β resonances at 67.9 MHz, their separation amounting to 0.027 ppm (1.8 Hz); the less intense high-field resonance is assigned to C-5. The chemical shifts of all carbon nuclei detected at 67.9 MHz are summarized in Table I.

On the contrary, the 25.2-MHz spectra showed no resolution at all between the resonances of C-β and C-5.

We therefore conclude that—at least for the purpose of identification of ethylene–1-olefin copolymers—hexyl can be distinguished from longer branches at 67.9 MHz by looking at the resonance at 26.3 ppm (internal octamethylcyclotetrasiloxane reference) or at −2.7 ppm (main methylene peak reference). A careful choice of experimental conditions (see Experimental Section) is, however, necessary.

We wonder if at the higher fields now available (carbon-13 resonance up to 125 MHz) it will be possible to elaborate specific assignments for carbons of even longer branches. Both the increase in the dispersion of the chemical shifts and in the sensitivity, which may allow the application of modern resolution enhancement techniques, should make it worthwhile to try.

Experimental Section

The 67.9-MHz carbon-13 spectra were obtained at 120 °C with a Bruker HX-270 spectrometer operating in the quadrature detection mode and equipped with a Bruker Aspect 2000 computer; for the 25.2-MHz spectra, a Varian XL-100/15 spectrometer equipped with a Varian 620 L computer and an interactive disk unit was used. Sample concentration was 40% (w/v) in a solvent mixture made up to 65% hexachlorobutadiene and 35% (v/v) 1,1-dideuteriotetrachloroethane, which has a high boiling point and displays good solvent properties for polyethylene; moreover, it provides the internal lock which is an essential requisite for good spectral resolution. Internal tetrachloroethane should therefore be preferred to internal perdeuteriobenzene or to any

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external lock. The use of hexachlorobutadiene, which bears quaternary carbons only, will minimize solvent signal intensities; it should therefore be preferable to trichlorobenzene. Ten-millimeter sample tubes have been used at 67.9 MHz (12 mm at 25.2 MHz), which are preferable to larger diameters at least for the normal-bore 270-MHz magnet.

The chemical shifts have been internally referenced to both the major methylene and the octamethylcyclotetrasiloxane resonances. The maximum deviation between the values of chemical shifts of a single carbon atom determined in two spectra obtained from two different copolymers amounted to 0.010 ppm. The spectrum in Figure 1 was obtained after the accumulation of 10 000 scans.

Pulse widths of 90° (=24 μs) and pulse delays of 14 s were applied in order to allow for the determination of the 1-olefin concentration of the copolymer. The digital resolution amounted to 0.472 Hz/point, corresponding to a spectral width of 8000 Hz and a data length of 32 K. A data length of 16 K, however, will suffice in order to observe the splitting between the C-5 and C-8 resonances.

The ethylene–octene copolymer was prepared at 85 °C by suspension polymerization, using the catalyst system $Mg(OEt)_2$–$TiCl_4$–$AlEt_3$ and an apparatus already described.[6] The polymerization was started with ethylene and hydrogen only; octene was fed into the reaction vessel after 5 min and was held constant over the whole period.

The copolymer thus obtained was characterized by a viscosity-average molecular weight of 70 000 and an ethylene/1-olefin molar ratio of 99.4:0.6.

Acknowledgment. Thanks is due Dr. L. Böhm for the synthesis of the copolymer and Professor Dr. H. Cherdron for permission to publish this paper.

References and Notes

(1) Randall, J. C. *J. Polym. Sci.* **1973**, *11*, 275.
(2) Cudby, M. E. A.; Bunn, A. *Polymer* **1976**, *17*, 345.
(3) Randall, J. C. *J. Appl. Polym. Sci.* **1978**, *22*, 585.
(4) Bovey, F. A.; Schilling, F. C.; McCrackin, F. C.; Wagner, H. L. *Macromolecules* **1976**, *9*, 76.
(5) Axelson, D. E.; Levy, G. C.; Mandelkern, L. *Macromolecules* **1979**, *12*, 41.
(6) Böhm, L. L. *Polymer* **1978**, *19*, 553.
(7) The nomenclature used in this note is the same as in the references and is now generally accepted.

Promotion of Photo-cross-linking of Polysiloxanes by Oxygen

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Polysiloxanes are remarkably resistant to near-ultraviolet light and intense exposures may be required to detect cross-linking. Delman et al., relying on infrared analysis, reported the formation of cross-links after exposing a complex poly(dimethylsiloxane) system in air to wavelengths >281 nm.[1] Siegel et al. investigated the insolubilization of a poly(dimethyldiphenylsiloxane) of low molecular weight (480) resulting from exposure, under vacuum, to 254-nm radiation.[2]

The present report gives more extensive results on the photogelation of polysiloxanes with repeat units I–IV.

$$\underset{\text{I}}{-OSi(CH_3)_2-} \qquad \underset{\text{II}}{-OSi(CH_3)(C_6H_5)-}$$

$$\underset{\text{III}}{-OSi(C_6H_5)_2-} \qquad \underset{\text{IV}}{-OSi(H)(CH_3)-}$$

Experimental Section

Polysiloxanes were obtained from Polysciences, Inc.; the supplier's descriptions of these polymers are quoted in Table I. Two further samples of poly(dimethylsiloxane), from the same source, were analyzed by gel permeation chromatography (Springborn Laboratories) to determine number- and weight-average molecular weights, M_n and M_w, respectively. Both polymers approximated to a most-probable distribution by reference to the criterion[3] that $M_w/M_n = 2$; for one sample $M_w = 83\,800$ and $M_n = 47\,100$ ($M_w/M_n = 1.8$) and for the other $M_w = 39\,000$ and $M_n = 22\,800$ ($M_w/M_n = 1.7$).

Electronic absorption spectra were run, using cells of 1-cm path length, in a Perkin-Elmer 402 spectrophotometer.

In some experiments polymers were exposed in layers of thickness 1.0 cm, in air, directly to ultraviolet radiation. In other experiments, samples were exposed in tubes (diameter 0.4 cm.; wall thickness 0.1 cm) made of sodium glass or quartz. Samples sealed under vacuum were first rigorously degassed by freeze–thaw cycles.

Two ultraviolet sources were used, a medium-pressure Hg lamp (200 W, Hanovia) and a bank of seven low-pressure Hg lamps (each of 18 W, General Electric). The energy incident on samples or tubes was measured by two ultraviolet meters, calibrated by the National Bureau of Standards to monitor wavelengths in the short (230–270 nm) or long (300–400 nm) ranges.

The gel point was detected, approximately, by periodically tilting the samples, which were viscous fluids, until flow was no longer evident. In certain cases the depth of the gel layer (d) was measured.

Results and Discussion

Polysiloxanes with phenyl groups eventually become yellow on exposure to the medium-pressure lamp (Table I). This observation can be rationalized by adoption of a suggestion made by Rabek and Rånby, with respect to polystyrene,[4,5] that a triplet state of the phenyl group rearranges to give a colored product such as a fulvene derivative. In extension of this view, the observed retardation of yellowing in air could be attributed to triplet-state quenching by oxygen. However, it should be mentioned that such observations about retardation by air appear to differ from previous reports on yellowing in both a poly(dimethyldiphenylsiloxane)[2] and polystyrene.[6]

The most important discovery in Table I is that photogelation is promoted by the presence of air. Therefore, despite the small sensitivity of polysiloxanes to near-ultraviolet light, it is worth compromising with difficulties inherent in estimating a quantum yield for cross-links. To this end the low-pressure lamps were selected as a rough[7] but conveniently intense source of 254-nm radiation. Polymers containing phenyl groups (cf. Figure 1) and also poly(methylhydrosiloxane) were judged inconvenient for such studies because of "skin" effects. Neither was the poly(dimethylsiloxane) of highest molecular weight studied because, in agreement with previous reports,[8,9] it was found to contain impurities which appear to be phenyl groups (cf. Figure 1A–C). Two poly(dimethylsiloxanes) of lower molecular weight were not objectionable in this extreme sense, although absorption in the range 250–300 nm still appears anomalous by reference to the dimethylsiloxane repeat unit.[10-12] Only a part of this anomalous absorption is attributable to the presence of oxygen, which was found to result in marked effects only at lower wavelengths (Figure 2). Incidentally, the influence of oxygen on ultraviolet absorption is much more pronounced than previously reported for other polymers,[13,14] presumably because of the higher solubility of oxygen in poly(dimethylsiloxanes).

The number of quanta absorbed per gram, N_q, up to the gel point was calculated from eq 1 in which t is the time to gelation, I_0 the incident intensity, k Lambert's absorp-

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