JOURNAL OF POLYMER SCIENCE VOL. XIX, PAGES 353-358 (1956)

On the Determination of Methyl Content in Polyethylenes*

E. J. SLOWINSKI, JR.,† H. WALTER, and R. L. MILLER, *Plastics Division, Monsanto Chemical Co., Springfield 2, Mass.*

INTRODUCTION

An idealized polyethylene molecule would have a very simple structure:

$$CH_3—(CH_2—CH_2)_n—CH_3$$

The methyl content of this molecule, then, would be very small (for commercial polymers of $\bar{M}_n$ approximately 30,000, the methyl content would be less than 0.1%). However, the infrared studies of Fox and Martin[1] showed that polyethylene molecules are branched. Estimates of the amount of branching have recently been made by Rugg and his co-workers[2] and by Bryant and Voter.[3] Other structural units (such as unsaturation[4]) have also been shown to be present.

It is of importance to be able to determine the degree of branching quantitatively since many physical properties of polyethylene are dependent on the presence of these structural units. For example, as Richards[5] pointed out, the amount of crystalline material present increases as the degree of branching decreases.

EXPERIMENTAL

Normal Octapentacontane. Nonacosyl alcohol, prepared by the method of Jones,[6] was used as starting material. 20 g. of this alcohol, 6 g. of iodine, and 1 g. of red phosphorus were reacted at 150–220° C. for five hours. The reaction mixture was dissolved in 1000 cc. of ether and filtered. 21 g. of crude nonacosyl iodide was obtained after evaporation of the ether (78% yield). 16 g. of the iodide was recrystallized from petroleum ether and 14.5 g. recovered (m.p. 63 °C.).

The recovered iodide was fused with 1 to 1.5 g. of freshly pressed sodium ribbon. The reaction was carried out in a test tube heated to 160 °C. at the start and regulated at 135 °C. for 4 hours. Occasional stirring was done with a glass rod. As predicted,[7] the reaction mixture turned blue with a few purple specks.

---

* Presented in part before the Symposium on Molecular Structure and Spectroscopy at Ohio State University, Columbus, Ohio, June 13–17, 1955.

† Industrial Leave Fellow, September, 1953, to September, 1954.

After the alloted time, the reaction mixture was allowed to cool before being transferred into absolute ethanol. After one or two hours, water was added to dispose of any free sodium metal. The crude octapentacontane was filtered off and purified as follows: (*1*) recrystallized twice from butyl acetate,[8] (*2*) leached with boiling water, (*3*) recrystallized from ethanol, and (*4*) recrystallized twice from petroleum ether. After drying, the octapentacontane melted at 94–95°C. On remelting, the melting point was 97°C. on a Fisher-Johns melting point apparatus (predicted melting point, 97°C.[8]).

Hexatriacontane. This compound was obtained from J. D. Cotman.[9]

Octacosane was Eastman Kodak White Label material recrystallized once.

SAMPLES

The hydrocarbons were contained in an approximately 0.004″ standard sealed liquid cell with rock salt windows. The exact spacing of the cell could be determined, when necessary, from a measurement of the interference fringes.

The polymer samples were prepared by placing a film of material, approximately 0.004″ thick between two optically flat rock salt windows and mounting in a suitable holder.

All samples, both hydrocarbon and polymer, were preheated to *ca.* 150°C. on a hot plate before insertion in an oven designed for the spectrometer.[10]

SPECTRA

The spectra were obtained in the 7 to 7.6 μ region on a Perkin-Elmer Model 21 double-beam spectrometer equipped with a rock salt prism. Because of the dependence of band intensities in solid films on the amount of crystalline material present[11] (because of crystalline interactions), it was decided to measure the methyl contents on molten samples. For this purpose, a temperature (150°C.) was used that was above the melting point of the highest melting material available (140°C.). The spectrometer was set at its fastest response time, the slit varied from 80–90 microns over the scan, and the scanning time for the region was ten minutes.

DISCUSSION AND RESULTS

The methyl groups in polyethylene are exhibited in two distinct regions of the infrared spectrum—the 3 μ stretching region and the 7 μ bending or deformation region. For this work, the 7 μ region was employed because of the better resolution of the instrument used and because of the greater intensity of the methyl band relative to the adjacent methylene bands in this region. Figure 1 shows this region for a typical polyethylene. The 1378 cm.$^{-1}$ band is associated with the degenerate deformation of the CH_3 group. The 1370 and 1353 cm.$^{-1}$ bands are associated with deformations of the CH_2 groups.

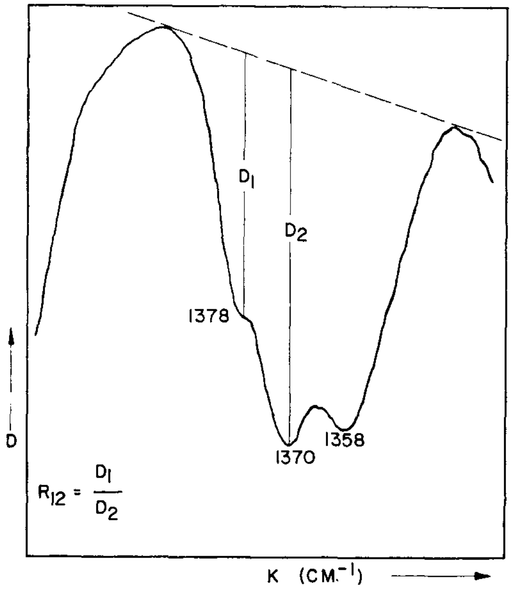

Fig. 1. The 7 to 7.5 μ region of a typical polyethylene.

The optical density of the 1378 cm.$^{-1}$ band, then, is a measure of the number of methyl groups in the material: the two should be related by a Lambert-Beer expression:

$$\log (I_0/I)_1 = D_1 = K_1^1 C_1 \rho l + K_2^1 C_2 \rho l \qquad (1)$$

where ρ is the density and l the thickness of the molten film, C_1 and C_2 are the number of methyl and methylene groups, respectively, and K_1^1 and K_2^1 are the extinction coefficients at 1378 cm.$^{-1}$ of the 1378 (methyl) and 1370 (methylene) cm.$^{-1}$ bands, respectively. In order to eliminate the necessity of making an accurate measurement of the thickness of each sample, the ratio of the optical density of the 1378 cm.$^{-1}$ band (D_1) to that of the 1370 cm.$^{-1}$ band (D_2) was used ($D_2 = K_2^2 C_2 \rho l$, where K_2^2 is the extinction coefficient of the 1370 cm.$^{-1}$ methylene band at 1370 cm.$^{-1}$). Therefore:

$$R_{12} \equiv D_1/D_2 = (K_1^1/K_2^2)(C_1/C_2) + (K_2^1/K_2^2) \qquad (2)$$

the second term in equation (2) resulting from the overlap of the two bands.

If the Lambert-Beer Law holds in this case, equation (2) requires that a linear relationship exist between R_{12} and C_1/C_2. In previous determinations of methyl content,[1-3] this was assumed to be true but not proved. It proved necessary to extrapolate from the methyl contents used for calibration (*ca.* 8%) to the methyl contents found in polymers (0–3%). The authors decided, therefore, to prepare a hydrocarbon whose methyl content was approximately the same as that found in the polymers. For this reason, the preparation of the hydrocarbon, octapentacontane ($C_{58}H_{118}$), was undertaken. With the series of hydrocarbons available—octacosane ($C_{28}H_{58}$), hexatriacontane ($C_{36}H_{74}$), and octapentacontane ($C_{58}H_{118}$)—this linear relationship is proved to exist, as is shown in Figure 2. From this

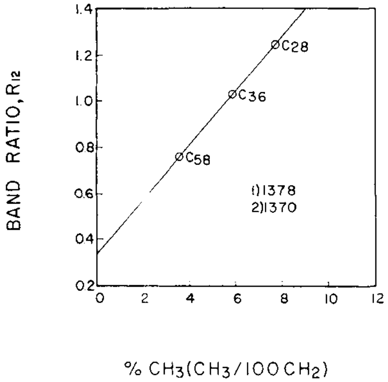

Fig. 2. Calibration curve for the degree of branching of polyethylenes.

calibration curve, then, the methyl contents of a number of polyethylenes, both commercial and experimental, were determined.

The densities of these polymers were also determined in order to relate crystallinity, as measured by density, to methyl content. This is shown in Figure 3. Bryant and Voter,[3] in their attempt to relate these same quantities, obtained a linear relationship between them. Their work, how-

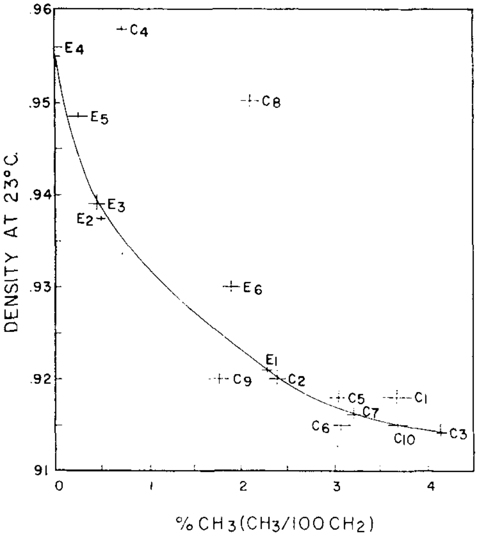

Fig. 3. Variation of density with degree of branching for various polyethylenes.

ever, extended over a limited density range only (0.90 to 0.93 g./cc.). It is seen from Figure 3 that the relationship between crystallinity and density is much more complex. In general, though, the crystallinity is seen to be determined, to a great extent, by the degree of branching. It is thought, in those samples which do not conform to the smooth curve of Figure 3, that other structural factors, such as unsaturation, are important. In Figure 3, C and E indicate commercial and experimental samples, respectively.

The dependence of molecular weight on branching was also investigated. A whole polymer was fractionated and the average molecular weight of the fractions determined.[12] Measurement of the methyl contents of some of the fractions showed that, over the molecular weight range of 10,000 to 100,000, the molecular weight increased with decreasing branching. This is in agreement with Rugg's[2] work on the variation of methyl content in whole polymers of varying average molecular weight. Last, a relation between the mechanical properties of polyethylene and the degree of branching is shown in Figure 4, where the logarithm of the dynamic shear modulus is plotted versus methyl content to show a rough correlation between them.

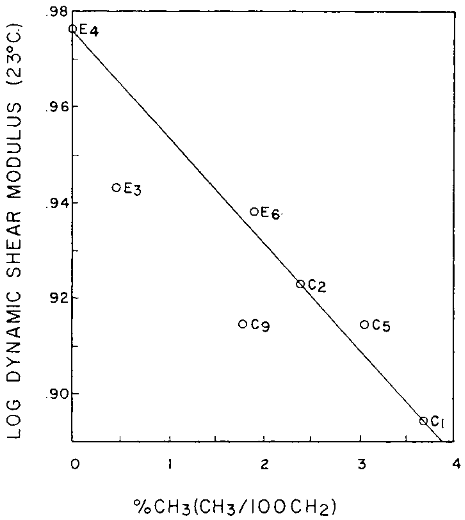

Fig. 4. **Variation of dynamic shear modulus with degree of branching for various polyethylenes.**

In summary, it has been shown that the methyl content of ethylene polymers can be measured quantitatively by standard infrared techniques, and that the presence of these structural features has a direct influence on other physical properties.

References

1. Fox, J. J., and Martin, A. E., *Proc. Roy. Soc. London,* **A175,** 208 (1940).
2. Rugg, F. M., Smith, J. J., and Wartman, L. H., *J. Polymer Sci.,* **11,** 1 (1953).

3. Bryant, W. M. D., and Voter, R. C., *J. Am. Chem. Soc.*, **75**, 6113 (1953).
4. Thompson, H. W., and Torkington, P., *Proc. Roy. Soc. London*, **A184**, 3 (1945).
5. Richards, R. B., *J. App. Chem.*, **1**, 370 (1951).
6. Jones, R. G., *J. Am. Chem. Soc.*, **69**, 2353 (1947).
7. Hell, C., and Hagle, C., *Ber.*, **22**, 504 (1889).
8. Carothers, W. H., *J. Am. Chem. Soc.*, **52**, 5279 (1930).
9. Cotman, J. D., *Ann. N. Y. Acad. Sci.*, **57**, 417 (1953).
10. Claver, G. C., unpublished work.
11. Cross, L. H., Richards, R. B., and Willis, H. A., *Disc. Faraday Soc.*, **9**, 235 (1950).
12. Trementozzi, Q. A., to be published.

Synopsis

A method for the quantitative determination of the degree of branching (methyl content) in ethylene polymers is described. This method involves the use of a calibration curve prepared from hydrocarbons of known methyl content. Because of the importance to the calibration of having hydrocarbon with a methyl content roughly that of the polymers to be measured, the hydrocarbon, n-$C_{58}H_{118}$, was prepared and its synthesis is given. The methyl contents of a series of polyethylenes, both commercial and experimental, were determined, and the results correlated with some physical properties of the polymers. A quantitative relationship was shown between the crystallinity of a polymer, as measured by the density, and the degree of branching. Qualitative relationships between molecular weight and branching and between mechanical properties and branching were also shown.

Résumé

Une méthode pour la détermination quantitative du degree de ramification (contenance de méthyl) dans des polymères de ethylene est décrit. Cette méthode emploie une courbe de calibration, quelle est preparé pour des carbures dont la contenance de méthyl est connue. Parce qu'il est important pour cette calibration à avoir un carbure avec une contenance de méthyl approximative à celle des polymères mesurés, le carbure, n-$C_{58}H_{118}$, etait preparé et la synthese du même est décrit. Les contenances de méthyl d'une serie de polyethylene, commercialle et experimentale, etaient déterminées, et les résultats sont correlés avec quelques proprietées physicales des polymères. Une relation quantitave était trouvée entre la crystallinité d'une polymère, measurée par la densité, et le degreé de ramification. Des relations qualitative entre le poid moleculère et la ramification et entre les proprietères mechanique et la ramification étaient décrites ainsi.

Zusammenfassung

Eine Methode für die quantitative Bestimmung des Grades der Verzweigung (Methyl-Gehalt) in Äthylen-Polymeren ist beschreiben. Diese Methode ist verbunden mit der Anwendung einer Eichkurve, die für Kohlenwasserstoffe von bekanntem Methyl-Gehalt aufgestellt wurde. Da es wichtig ist für die Eichung einen Kohlenwasserstoff zu haben, dessen Methyl-Gehalt ungefähr dem des zu messenden Polymeren entspricht, wurde der Kohlenwasserstoff, n-$C_{58}H_{118}$, dargestellt und seine Synthese beschrieben. Die Methyl-Gehalte einer Serie von Polyäthylenen, sowohl handelsüblich als im Versuchsmasstab, wurden bestimmt, und die Ergebnisse wurden auf einige physikalische Eigenschaften der Polymeren bezogen. Ein quantitativer Zusammenhang zwischen der Krystallinität eines Polymeren, bestimmt durch die Dichte, und dem Grade der Verzweigung wurde gefunden. Qualitative Zusammenhänge zwischen dem Molekulargewicht und Verzweigung und zwischen mechanischen Eigenschaften und Verzweigung werden aufgezeigt.

Received July 11, 1955