[CONTRIBUTION FROM THE POLYCHEMICALS DEPARTMENT, E. I. DU PONT DE NEMOURS AND COMPANY, INC.]

The Molecular Structure of Polyethylene. II. Determination of Short Chain Branching[1]

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Infrared studies have shown the presence of methyl groups in polyethylene far in excess of terminal group requirements. Comparison with the accepted bimolecular mechanism of branching, involving transfer between a growing chain and completed polymer, indicates that there are too many methyl groups to be explained in this way. However, a unimolecular mechanism based on *intra*molecular transfer can account for this large excess. Infrared procedures have been refined to provide reliable measures of methyl and ethyl groups through absorption bands at 7.25 and 11.18 μ, respectively. Preliminary observations were also made in the 13–14 μ region on bands related to branching. Corrections were applied for overlapping absorptions due to methylene and vinylidene, and for intensity changes in passing from solid to liquid. The following conclusions were reached: (1) No appreciable number of pendant methyl side chains are present. The methyl and ethyl groups are parts of longer chains most of which are believed to contain four carbons. (2) Methyl groups in unfractionated polyethylenes studied range from 0.2 to 4.6 per hundred carbon atoms. (3) Predominance of short chains over long chains leads to a larger crystallite size and a degree of crystallinity in better accord with X-ray results. The general structural picture of the polymer has been revised to conform with these findings.

Introduction

The presence of side chains in polyethylene was established in 1940 by Fox and Martin[2] as a result of detailed studies of the infrared spectrum of this polymer in the three μ region. These investigators demonstrated the presence of methyl groups far in excess of terminal group requirements for a linear paraffin hydrocarbon.

Since no clear indication of the length of methyl-terminated branches was available, it is natural that the answer should have been sought in the kinetics of polymerization. As early as 1937 Burk[3] pointed out the possibility of both unimolecular and bimolecular branching reactions. Flory[4] in the same year developed the bimolecular branching mechanism systematically. This mechanism in its present form is based on chain transfer of a growing free radical with a completed polymer molecule. When applied to the polymerization of ethylene, this mechanism predicts the formation of a few very long branches as shown by Beasley.[5] Roedel[6] in 1944 conceived the idea of an *intra*molecular chain transfer reaction capable of producing a large number of short chain branches. Roedel's mechanism of short chain branching is in harmony with the high concentration of methyl groups usually found in polyethylenes.

Infrared absorption is probably the most promising approach to a solution of the identity of short branches in polyethylenes. Downing[7] made a valuable contribution by pointing out the specificity of the absorption at 11.2 μ for ethyl groups, either singly or at the ends of long alkyl chains. Bryant[8] utilized Downing's measurements to emphasize the importance of branching and to establish its relationship to crystallinity. In the meantime, Thompson and Torkington[9] showed that methyl groups could be measured by an infrared band at 7.25 μ. Thus, in 1947, three distinct but reasonably concordant infrared measures of branching were in hand. Recently, Cross, Richards and Willis[10] made a careful study of the infrared bands at 7.25 and 11.2 μ. They found a linear relationship between methyl content and the absorptions of liquid normal paraffin hydrocarbons, including molten polyethylenes. Their closer examination disclosed disadvantages associated with both spectral regions. Measurement of methyl groups at 7.25 μ was impaired by the presence of nearby bands at 7.31 and 7.39 μ, apparently due to methylene. However, this effect could be minimized by careful graphical resolution of the spectra. Richards found that use of the 11.2 μ band (now attributed to ethyl groups) was complicated by an absorption at 11.27 μ due to the vinylidene type of unsaturation.

In the present investigation we have concentrated our major effort on the methyl and ethyl group absorptions at 7.25 and 11.2 μ, respectively, but have also done some exploratory work with infrared bands in the 13–14 μ region bearing on the problem of branching.

Experimental

The infrared records used in the present work were obtained in our laboratories using a group of three model 21 Perkin–Elmer double-beam spectrometers. Sodium chloride prisms were used for the range 2 to 15 μ, while a calcium fluoride prism covered the range up to about 8 μ at higher resolution. The heated specimen cell for the study of molten polymers was an improvement of a design described by Richards and Thompson.[11]

In some instances, compensation spectra were produced by placing a suitably selected reference specimen in the reference beam of the spectrometer and thus effectively cancelling out unwanted bands present in both the reference and test specimens. This method was used to determine the position and intensity of overlapping bands.

Since overlap corrections were used extensively in this study, it became necessary to establish band positions as accurately as possible by superposition of the known spectra

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(1) Presented at the 123rd National Meeting of the American Chemical Society, Los Angeles, Cal., March 16, 1953.

(2) J. J. Fox and A. E. Martin, *Proc. Roy. Soc.* (*London*), **A175**, 208 (1940).

(3) R. E. Burk, H. E. Thompson, A. J. Weith and I. Williams, "Polymerization," Reinhold Publ. Corp., New York, N. Y., 1937, p. 140.

(4) P. J. Flory, THIS JOURNAL, **59**, 240 (1937).

(5) J. K. Beasley, *ibid.*, **75**, 6123 (1953).

(6) (a) M. J. Roedel, private communication; (b) THIS JOURNAL, **75**, 6110 (1953).

(7) J. R. Downing, Chemical Department, E. I. du Pont de Nemours and Company, Inc., private communication.

(8) W. M. D. Bryant, *J. Polymer Sci.*, **2**, 547 (1947).

(9) J. W. Thompson and P. Torkington, *Trans. Faraday Soc.*, **41**, 248 (1945).

(10) L. H. Cross, R. B. Richards and H. A. Willis, *Disc. Faraday Soc.*, **No. 9**, 235 (1950).

(11) R. E. Richards and H. W. Thompson, *Trans. Faraday Soc.*, **41**, 183 (1945).

of water vapor and ammonia gas.[12] For example, when it was desired to place a water vapor spectrum over the recorded spectrum of a polyethylene, the recorder drum was driven in the reverse direction without disengaging the drive. When the beginning of the region to be verified was reached, the sample beam was blanked off and moist air was permitted to enter the reference beam. A test signal of constant amplitude was applied in place of the output of the darkened thermocouple to keep the recording circuit in balance. Except for these details, the calibration spectrum was recorded in the usual way. This procedure was particularly useful in measuring very low concentrations of the methyl group where the 7.25 μ band was too weak to be located visually. The wave lengths found for various hydrocarbon absorption peaks are listed in Table I.

TABLE I

INFRARED BANDS OF POLYETHYLENE AND REFERENCE HYDROCARBONS

Absorbing group	Wave length, μ	Calibration substance	Standard wave length, μ
$RCH{=}CH_2$[a]	11.00	NH_3	11.206, 11.257
$RR'C{=}CH_2$[b]	11.27		
$RCH{=}CHR'$ (*trans*)	10.37		
$-C_2H_5$ (melt, solid)	11.18		
$-CH_3$ (melt, solid)[c]	7.25	H_2O	7.162, 7.269
$-CH_2-$ (melt, solid)[d]	7.31		7.335, 7.460
	7.39		
$RCH{=}CH_2$	6.09	H_2O	5.983, 6.107
$RR'C{=}CH_2$	6.08		

In addition to polyethylene the following reference hydrocarbons were used: [a] 1-Octadecene. [b] Limonene. [c] *n*-Tetracosane. [d] Polymethylene.

The polyethylenes studied were selected from a large group on the basis of their methyl content and the amount of olefinic unsaturation present. The unsaturation was varied further by catalytic hydrogenation of a few polyethylenes, either partly or in some cases almost completely removing the olefinic bands originally present. Three Eastman paraffin hydrocarbons, *n*-octadecane, *n*-tetracosane and *n*-octacosane were used to establish the relation between absorbence and the methyl content for the molten materials. Measurements on the three reference hydrocarbons in the crystalline state revealed no correlations useful for the study of solid polyethylenes. The latter problem was solved by measuring the absorbences of solid polyethylenes already evaluated in terms of methyl groups by the melt procedure.

Two polymeric hydrocarbons formed by the decomposition of diazoparaffins[13,14] were employed in this study. A polymethylene from diazomethane, almost free of methyl groups, was used as a reference substance to correct for methylene absorptions in the vicinity of the methyl band at 7.25 μ. A polymeric hydrocarbon containing *n*-amyl branches, obtained by decomposition of a mixture of diazomethane and diazo-*n*-hexane,[14b] was required to establish a calibration for ethyl groups at the ends of hydrocarbon chains.

Films of optimum thickness for the band under investigation were compression-molded in a Preco press at 160° and shock-cooled in ice-water. Shock-cooling reduced the size of spherulites in the preparations, thus reducing the losses of infrared energy due to scattering. Thickness was measured either by an interference method or directly using micrometer calipers.

Results

Infrared data for the solid films and melts are expressed as the specific absorption coefficients, *K'*, per centimeter length, *l*, for a concentration of one gram per milliliter of the absorbing material, according to the equation

$$K' = (1/dl)\log_{10} I_0/I \qquad (1)$$

where *d* is the density ($d^{t/4}$) and $\log_{10} I_0/I$ is the absorbence read from the charts after correction for background absorption. No correction was made for the finite resolving power of the instrument relative to the bands studied. Linear equations 2 and 3 represent the best lines drawn through the origin in plots of specific absorption coefficient at 7.25 μ *vs.* the stoichiometric number of methyl groups per hundred carbon atoms for the three low molecular weight reference hydrocarbons

$$CH_3/100C = 0.113\,K'_{7.25}\text{ (cor.) (95\% confidence limits } \pm 1.060) \qquad (2)$$

93.5% explainable variation in $CH_3/100C$

$$CH_3/100C = 0.150\,K'_{7.25}\text{ (cor.) (95\% confidence limits } \pm 2.305) \qquad (3)$$

93.1% explainable variation in $CH_3/100C$

The *K'* values in equation 2 were measured using a calcium fluoride prism in the spectrometer, while those of equation 3 were obtained with a sodium chloride prism. The absorption coefficient for polymethylene at 7.25 μ was subtracted from each *K'* value before use in the above equations. Figure 1 shows the well-defined peak in the spectrum of a polyethylene at 7.25 μ, but no indication of an absorption peak at this wave length for the polymethylene. The methyl end-group concentration of the latter was estimated at less than 0.1 per hundred carbon atoms. The correction actually represents the overlap by the 7.31 and 7.39 μ methylene bands. The use of the specific absorption coefficient, *K'*, permitted comparison of measurements on molten polyethylenes at 140°, with those for the liquid normal paraffin hydrocarbons at 70°. The methyl contents of 14 poly-

TABLE II

METHYL CONTENT OF POLYETHYLENES FROM ABSORPTION BAND AT 7.25 μ

Polymer designation[a]	Data for melts		Data for solids	
	K'(uncor.)[b]	CH_3/100	*K'* (uncor.) av.[c]	CH_3/100C
23	51.2, 51.7, 51.3, 46.1, 47.6	4.64	58.1	4.55
15	38.9, 38.4	3.33	44.7	3.32
A40	34.0, 34.9, 33.5	2.81	40.4	2.81
10	34.6, 35.0	2.88	41.2	2.99
33	33.6, 34.3	2.79	38.7	2.81
34	37.0, 35.5, 32.2, 33.3	2.86	39.9	2.87
35	35.1, 36.3, 36.3	3.01	41.3	3.01
11	30.4, 28.5	2.27	34.1	2.35
27	17.7, 17.6, 18.0, 18.5, 21.2, 20.4	1.07	19.8	1.04
36	18.8	1.07	19.6	1.03
37	18.4, 19.2	1.06	20.0	1.04
43	11.1, 11.9	0.21	11.5	0.35
44	11.9, 11.9	0.25	10.5	0.19
45	....	..	42.4	3.11
46(hydrogenated)	39.8, 40.4, 39.2	3.44	46.2	3.45
47(partly hydrogenated)	....	..	42.6	3.13
48(partly hydrogenated)	....	..	42.9	3.15

[a] The polymer designation identifies the samples discussed in paper III of this series. [b] Calcium fluoride prism. [c] Sodium chloride prism.

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[12] R. A. Oetgen, Chao-Lan Kao and H. M. Randall, *Rev. Sci. Instr.*, **13**, 515 (1942).

[13] L. C. Leitch, P. E. Gagnon and A. Cambron, *Can. J. Research*, **28B**, 256 (1950).

[14] (a) G. D. Buckley, L. H. Cross and N. H. Ray, *J. Chem. Soc.* 2714 (1950); (b) G. D. Buckley and N. H. Ray, *ibid.*, 3701 (1952).

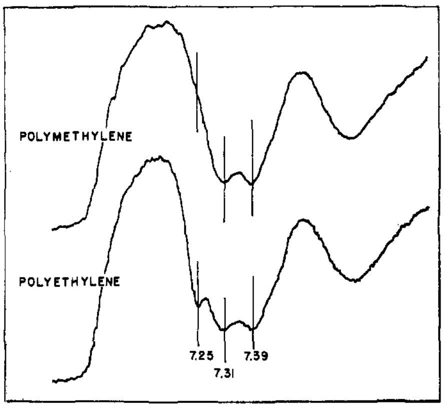

Fig. 1.—Infrared spectra of polymethylene and a polyethylene in the 7μ region (molten condition, 140°).

ethylenes measured in the molten condition at 140° are shown in column three of Table II. The absorbences taken from the recorded spectra were calculated to the corresponding K' values and these in turn were converted to methyl groups per hundred carbon atoms with the aid of equation 2.

In practice, the plot of K' *vs.* methyl content for solid polyethylenes at room temperature shown in Fig. 2 is more convenient than a relation based on the molten materials at an elevated temperature. Unfortunately, the low molecular weight reference hydrocarbons could not be used for this calibration since their absorbences in the crystalline condition are not comparable with those of solid polyethylenes. Polymorphism and unpredictable differences in crystalline orientation in the reference hydrocarbons are probable causes of this difficulty. It was necessary, therefore, to compare K' values for solid polyethylenes with the methyl contents found for the same polyethylenes in the molten condition, the latter serving as secondary standards. The methyl contents read from the smooth curve in Fig. 2 are shown in the last column of Table II. It will be seen that the agreement is excellent. A constant correction of 8.6 units, due mainly to methylene absorption, was subtracted from K' to bring the curve through the origin.

Comparison of the corrected K' values for polyethylenes at 7.25 μ in the solid and molten conditions showed that the specific absorption coefficient for the solid is roughly 1.6 times that for the liquid. This is also brought out by a comparison of the slope of the line for solid polyethylenes in Fig. 2 with that of equation 3 for the molten hydrocarbons. (Both sets of measurements were made using a sodium chloride prism.)

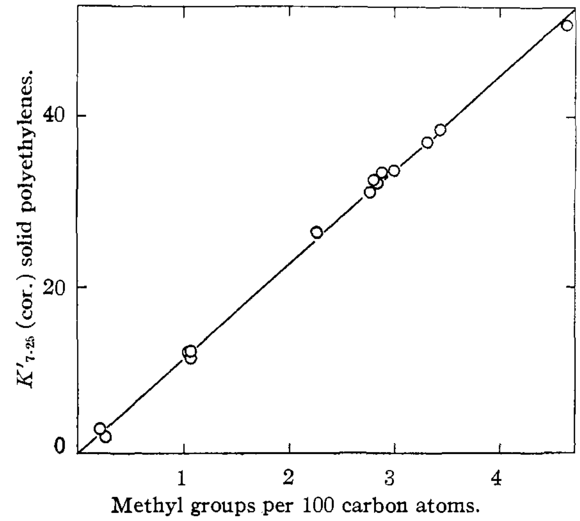

Fig. 2.—Relationship between specific absorption coefficient of solid polyethylenes and methyl content of some polymers in the molten condition. $K'_{7.25}$ measured at room temperature with sodium chloride prism.

Standardization of the ethyl group absorption at 11.18μ by means of the low molecular weight reference hydrocarbons was not possible since a change in band position from 11.24 to 11.18 μ was observed on passing from these compounds to high molecular weight polyethylenes. A reduction in band intensity by about a factor of two accompanied this change. However, the branched polymeric hydrocarbon having only *n*-amyl side chains, synthesized from diazomethane and diazo-*n*-hexane, had its absorption peak at 11.18 μ, hence was sufficiently high in molecular weight to serve as a standard for ethyl groups in polyethylene. The polymer is almost completely amorphous due to extensive branching hence it will relate to polyethylenes in the molten condition. The number of branches per hundred carbon atoms was obtained from the methyl group content, since the ratio of comonomers used was known only approximately. From its structure the number of methyl groups in this polymer must equal the number of ethyl groups. Although this constitutes our only clear-cut standardization for ethyl groups, a definite proportionality between methyl and ethyl groups in solid polyethylenes has been demonstrated independently, as will be shown below. This comparison cannot be made directly since most polyethylenes exhibit a strong absorption band at 11.27 μ due to vinylidene unsaturation. It will be seen from Fig. 3 that the bands for ethyl and vinylidene lie so close together that resolution would be impossible without independent knowledge of the intensity of one or the other band. Yet the coincidence is not close enough to permit a strictly additive treatment. The mechanics of band addition was studied by hydrogenating the vinylidene groups in suitable

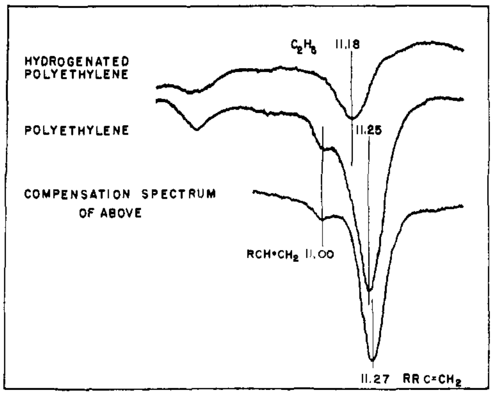

Fig. 3.—Comparative infrared spectra of polyethylene before and after hydrogenation, showing location of bands due to ethyl groups and two types of olefinic unsaturation (solid polymers, 11 μ region).

polyethylenes to various degrees, ending with the practical removal of this type of unsaturation. It was found that the 11.18 μ band due to the ethyl group had only 75% of its peak intensity at 11.25 μ, the wave length usually associated with the composite band, while the 11.27 μ band for vinylidene unsaturation differed only negligibly from the peak value at this wave length. Because the base of an infrared band is roughly constant in extent, regardless of the peak height, the ethyl band correction applies over the entire range of peak heights.

It is apparent, therefore, that if an independent measure of the vinylidene group could be found, it would be possible to obtain a measure of the ethyl group by the above method of peak resolution applied to the composite band at 11.25 μ without the need for hydrogenation or other chemical means of removing unsaturation. Such an independent measure of vinylidene groups actually exists to a large degree in an olefinic absorption band at 6.08 μ. This band also measures vinyl and, to a lesser extent, other types of olefinic unsaturation. A correction for the vinyl band, though small, is readily applied through its absorption at 11.00 μ. It was found experimentally, using selected polyethylenes including some of abnormally high vinyl content, that the vinyl band is 4.1 times as strong at 11.00 μ as at 6.08 μ, and vinylidene at 11.27 μ is 3.83 times as intense as at 6.08 μ.[15] The following sample calculation shows how $K'_{11.18}$ for the ethyl group in polyethylene no. 15 is obtained from the composite absorption, $K'_{11.25}$:

$$\begin{aligned}
\text{Total } K'_{6.04} &= 1.08 \\
K'_{11.00} &= 0.24 \qquad \text{obsd. val.} \\
\text{Total } K'_{11.25} &= 5.10 \\
K'_{11.00}/4.1 &= 0.06 \\
\text{Corrected } K'_{6.08} &= 1.02 \\
K'_{11.27}(\text{calcd.}) &= \text{cor. } K'_{6.08} \times 3.83 \\
&= 3.91 \\
K'_{11.25}-K'_{11.27} &= 1.19 \\
K'_{11.18}(\text{ethyl groups}) &= (K'_{11.25}-K_{11.27})/0.75 \\
&= 1.59
\end{aligned}$$

This procedure permits the calculation of $K'_{11.18}$, the specific absorption coefficient, for the band due to ethyl groups for the entire series of polyethylenes investigated. These results are less precise than the values found after complete hydrogenation of the vinylidene band because of the many operations and corrections required.

It is now possible to explore the proportionality that we have said exists between the concentration of methyl and ethyl groups in polyethylenes. A statistical evaluation of the data for $K'_{7.25}$ (cor.) and $K'_{11.18}$ (calcd.) shows that these results are related in a linear fashion according to the equation

$$K'_{7.25}(\text{cor.}) = 29.4\ K'_{11.18} - 6.53\ (95\%\ \text{confidence limits}\ \pm 8.87) \quad (4)$$

$$\text{Coefficient of determination, } r^2 = 0.911$$

A value for the ratio $K'_{7.25}$ (cor.)/$K'_{11.18}$ of 24.0 that is probably more precise was obtained by a direct comparison of absorption coefficients for two hydrogenated polyethylenes, essentially free of vinylidene unsaturation. All of these calculations refer to solid polyethylenes.

The only reasonable explanation for the proportionality existing between the methyl and ethyl absorptions is that both represent different aspects of the same branching phenomenon: methyl groups terminating chains of methylene groups, the two end-most carbon atoms of each forming an ethyl group. Support for this proposed one-to-one relationship between methyl and ethyl groups comes from the measurements on the polymeric hydrocarbon having only *n*-amyl branches. The slope of the straight line drawn through this one point in a plot of $K'_{11.18}$ *vs.* ethyls per hundred carbon atoms (Fig. 4) for the liquid state (lower line) is compared with that of the average straight line derived from $K'_{11.18}$ for the solid polyethylenes on the assumption of the equivalence of methyl and ethyl. The slope of the line for the solid polymers is found to be greater by a factor of 1.6 than that of the line for molten material, in agreement with a similar comparison of $K_{7.25}$ (methyl group absorption) in the solid and molten conditions presented above. If we are willing to assume *a priori,* that the methyl and ethyl group absorptions have the same intensity ratios on passing from the liquid to the solid state, then the upper line in Fig. 4 can be derived independent of our assumption of a one-to-one ratio between the two structures. The coefficient of determination between methyl and ethyl group concentrations for solid polyethylenes, r^2, equals 0.912 in agreement with equation 4.

There appears to be no experimental evidence for the presence of pendant methyl groups attached directly to the side of the polyethylene chains since these would be detected along with other methyl groups but would not contribute to the number of ethyl groups found. It is concluded that substantially all methyls must be attached to longer alkyl chains with at least one methylene intervening. This is important because neither of the two branching mechanisms advanced in the present series of papers predicts the formation of pendant methyl side chains.

Qualitatively, some additional structural information is available in the 13 to 14 μ region of the spectrum. It is known that bands near 12.9, 13.5 and 13.9 μ in liquid or dissolved long chain paraffin hydrocarbons can be correlated with the presence of ethyl, *n*-propyl and *n*-butyl or longer alkyl groups.[16] McMurry and Thorton,[17] in their correlation of available infrared spectra for hydrocarbons, suggest that the number of consecutive methylene groups is the important feature associated with these bands, whether they are present in side chains or in segments between branches in a principal chain. They also show that it is possible to distinguish absorption bands for chains of methylene groups up to five (*e.g.*, a *n*-hexyl branch) on the short wave length side of the limiting 13.9 μ band. Our own observations on molten poly-

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(15) A weak *trans*-vinylene band at 10.37 μ makes no contribution at 6.08. Even assuming this is matched by an equal concentration of *cis*-vinylene structure, the absorbence at 6.08 μ would, at most, be only about $^1/_{15}$ as great as the *trans*-vinylene band at 10.37, (estimated from hydrocarbon spectra in the A.P.I. collection) or a negligible quantity for all of the polyethylenes studied.

(16) S. Ställberg-Stenhagen, E. Stenhagen, N. Sheppard, G. B. B. M. Sutherland and A. Walsh, *Nature*, **160**, 580 (1947).

(17) H. L. McMurry and V. Thorton, *Anal. Chem.*, **24**, 318 (1952).

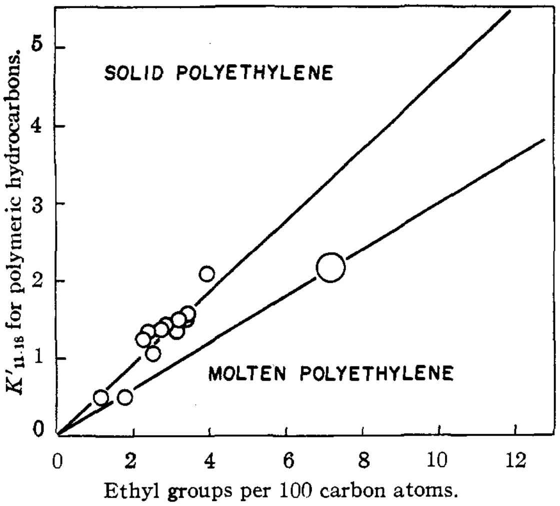

Fig. 4.—Calibration curves relating the specific absorption coefficient, $K'_{11\cdot 18}$, and ethyl content: ○, synthetic polymeric hydrocarbon (amorphous) containing 7.05 *n*-amyl branches per 100 C; ○, solid polyethylenes assuming ethyl ≈ methyl; upper straight line derived from lower assuming factor 1.6 converting K' from molten to solid state.

meric hydrocarbons,[18] illustrated by Fig. 5, show only the 13.9 μ peak resolved but suggest others at shorter wave lengths. Resolution on the basis of bilateral symmetry led to a residual peak near 12.9 and possibly one at 13.5 μ. Qualitatively the more branched polyethylenes had the larger components at each of the three locations, and the normal C_{18}-, C_{24}- and C_{28}-paraffin hydrocarbons showed a comparable behavior. We believe that small segments of the appropriate length in a long unbranched chain can vibrate to produce some absorption at 12.9 and 13.5 μ, although less than in a suitably branched chain. Thus at present, general rather than specific structural information on polymeric hydrocarbons is obtained from these bands.

The question of the probable length of short chain branches is best answered as follows: The branches are longer than methyl. Ethyl branches by the short chain branching mechanism are probably excluded on a configurational basis. The postulated mechanism favors a normal butyl branch, but does not exclude C_3 or C_5. Much longer branches by this mechanism should be infrequent. For example, a polyethylene with one branch in 30 carbon atoms could not on the average have more than 29 carbon atoms per branch, but this would be absurd on steric grounds. A more reasonable upper limit would be 15 carbon atoms. Assuming a mechanism no more favorable than long chain branching, the number of 15 carbon branches would be too few to detect by infrared methods.

Branching in Relation to Polymer Structure.—It is of interest to consider the extent to which the more detailed knowledge of branching may have affected our general conception of the polyethylene structure. A number of years ago one of the authors[8] fitted together existing information on X-ray crystal structure, crystallinity, crystal optics, infrared absorption, molecular weight and reaction kinetics to obtain a crude but integrated picture of the physical structure of polyethylene. This picture, still moderately reliable by present standards, nevertheless lacked certain features now regarded as essential. The distinction between long and short chain branching was not made, thus leading to apparent inconsistencies in the X-ray, infrared and kinetic findings. Although the relationship between branching and crystallinity was recognized, the disordering influence of methyl groups *per se*, was at first overemphasized. Richards[19] later showed that isolated methyl groups are too small to destroy crystalline order in a polymer. Hence almost the whole disordering effect must be associated with other features of branching. A means of estimating the crystallinity of polyethylene from the relative areas under the amorphous and principal crystalline X-ray diffraction peaks was published by Matthews, Peiser and Richards.[20] Somewhat lower values for the crystallinity of polyethylenes were found by Bryant, Tordella and Pierce[21] who refined the X-ray method. They found a practically linear relationship between crystallinity and density. Recently infrared bands have been found that relate directly to the crystallinity and amorphous content of polyethylene.[19]

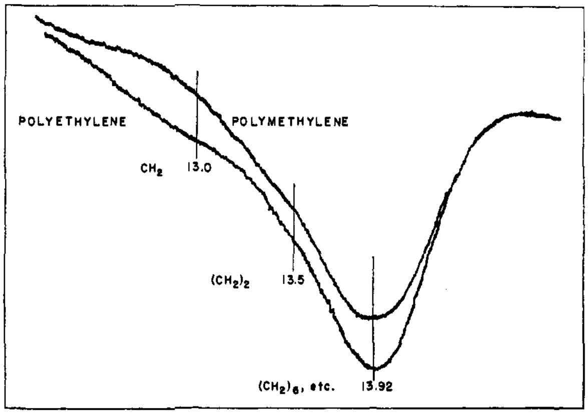

Fig. 5.—Infrared spectra of molten polymethylene and polyethylene in the 13–14 μ region. Both specimens approximately 0.015 cm. thick.

All of these studies have served to establish firmly the relationship between crystallinity and the methyl or ethyl group content. In other words, alkyl side chains (terminated by methyl groups) introduce disorder and thus reduce the fraction of polyethylene chain segments capable of crystallizing.[8-10] The inverse relationship between short chain branching expressed as methyls per hundred carbon atoms and density (*i.e.*, crystallinity) is brought out clearly in the last paper of this series.[22]

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(18) Polymethylene, about five polyethylenes, and the three reference hydrocarbons, *n*-octadecane, *n*-tetracosane and *n*-octacosane were included in this study. Records were made for 0.015 cm. layers. The materials were maintained molten at 140° to eliminate a 13.7 μ band due to crystallinity. The outstanding feature in all was a strong band at about 13.92 μ. This large peak was not symmetrical and could be resolved into at least two additional bands.

(19) R. B. Richards, *J. Appl. Chem.*, **1**, 370 (1950).

(20) J. L. Matthews, H. S. Peiser and R. B. Richards, *Acta Cryst.*, **2**, 85 (1949).

(21) W. M. D. Bryant, J. P. Tordella and R. H. H. Pierce, Jr. Chicago Meeting, American Chemical Society, September 1950; to be submitted for publication.

(22) C. A. Sperati, W. A. Franta and H. W. Starkweather, Jr., THIS JOURNAL, **75**, 6127 (1953).

Examination of a Hirschfelder model for a branched polyethylene suggested that the permanent disorder attending branching may extend about four carbon atoms in each direction beyond the carbon atom bearing the branch. For a polyethylene containing one butyl branch for 30 carbon atoms, one would calculate

$$\text{Crystallinity } (\%) = \frac{(30 - 1 - (3 \times 4))\,100}{30} = 56.7 \quad (5)$$

It is assumed that methyl groups are included in the crystalline portion. This result is in close agreement with our value of 57.1% for the crystallinity estimated from X-ray diffraction[21] and the figure 61.0% obtained by Parks and Mosley from thermal measurements.[23] However, other X-ray results[20,24] lead to crystallinities ranging from 70 down to 40% for comparable polyethylenes. A previous calculation[8] was unsatisfactory because the disordering effect of the branch upon the main chain was neglected.

Our assumption that short chain branches are mainly *n*-butyl groups clarifies an inconsistency encountered in an earlier research,[8] where chain branching appeared to set an upper limit of about 16 Å. for the average linear dimensions of crystallites in polyethylenes. Substituting *n*-butyl groups for the longer side chains and slightly reducing the number of methyl groups per hundred carbon atoms in accord with the present findings, bring the average size of crystallites into line with the lower limit set by the broadening of X-ray diffraction peaks, or about 20–50 Å.

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WILMINGTON, DELAWARE

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[23] G. S. Parks and J. R. Mosley, *J. Chem. Phys.*, **17**, 691 (1949).

[24] S. Krimm and A. V. Tobolsky, *J. Polymer Sci.*, **7**, 57 (1951).

[CONTRIBUTION FROM THE POLYCHEMICALS DEPARTMENT. E. I. DU PONT DE NEMOURS AND COMPANY, INC.]

The Molecular Structure of Polyethylene.
III. Determination of Long Chain Branching[1]

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A new method for the quantitative estimation of chain branching is developed and applied to polyethylenes. The light scattering molecular weight and intrinsic viscosity of a branched polymer are compared with those calculated for a linear but otherwise identical sample. The method is sensitive only to long branches. Some polyethylenes have from 4 to 34 such branches per molecule, on a weight-average basis. Their molecular weight distributions are extremely broad; weight-to-number average molecular weight ratios as high as 20:1 are often found. Experiments with fractionated polyethylenes confirm these conclusions.

Introduction

Previous workers[2] studying molecular weight and its distribution in polyethylenes have utilized only number average molecular weights and intrinsic viscosities of whole polymers and fractions. The results of such studies, together with estimates of total chain branching from infrared absorption,[3] can be interpreted in terms of a relatively simple molecular structure. For example, molecular weight distributions are reported[2e,g] to be relatively narrow, with weight-average molecular weights estimated to be not greater than two to three times the number averages. The effects of chain branching have been ascribed mainly to its influence on the crystallinity of the solid polymer.[4] Only in a few communications[5] has the simplicity of this structure been questioned.

A more complex structure was suspected when in 1949 light scattering measurements in this Laboratory showed that most polyethylenes have much higher weight-average molecular weights, and therefore much broader molecular weight distributions, than had been anticipated. Roedel's concepts[6] of the origins of chain branching in polyethylenes offered an explanation of these facts, since a branching mechanism based on chain transfer to polymer should give a broad molecular weight distribution—as later verified theoretically by Beasley.[7] The work of Zimm, Stockmayer and

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[1] Presented at the 123rd National meeting of the American Chemical Society, Los Angeles, Cal., March 16, 1953.

[2] (a) M. S. Muthana and H. Mark *J. Polymer Sci.*, **4**, 527 (1949); (b) V. Desreux and M. C. Spiegels, *Bull. soc. chim. Belges*, **59**, 476 (1950); (c) H. Morawetz, *J. Polymer Sci.*, **6**, 117 (1951); (d) I. Harris, *ibid.*, **8**, 353 (1952); (e) K. Ueberreiter, H. J. Orthmann and G. Sorge, *Die Makromol. Chem.*, **8**, 21 (1952); (f) S. H. Pinner and J. V. Stabin, *J. Polymer Sci.*, **9**, 575 (1952); (g) F. Bebbington, E. Hunter and R. B. Richards, presented at the XIIth International Congress of Pure and Applied Chemistry. New York, September, 1951.

[3] W. M. D. Bryant and R. C. Voter, THIS JOURNAL, **75**, 6113 (1953).

[4] R. B. Richards, *J. Applied Chem.*, **1**, 370 (1951).

[5] (a) I. L. Hopkins, W. O. Baker and J. B. Howard, *J. Applied Phys.*, **21**, 206 (1950); (b) W. O. Baker, W. P. Mason and J. H. Heiss, *J. Polymer Sci.*, **8**, 129 (1952).

[6] M. J. Roedel, THIS JOURNAL, **75**, 6110 (1953).

[7] J. K. Beasley, *ibid.*, **75**, 6123 (1953).