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.

Acknowledgments.—The authors wish to thank C. E. Day and the staff of the infrared laboratory for making many of the measurements required for the successful completion of this study. The heating cell used was designed and constructed by R. Roberts.

Grateful acknowledgment is made to the following individuals for specific assistance during the course of the work: to J. T. Rundquist for supplying samples of polymethylene and the synthetic polymeric hydrocarbon with *n*-amyl branches; to R. C. Schreyer for supplying samples of hydrogenated polyethylenes, and to Miss Mary T. Dunleavy for making the statistical computations.

Wilmington, Delaware

(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]

By F. W. Billmeyer, Jr.

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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

(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).

others[8] has shown that the intrinsic viscosity of a branched molecule is lower than that of a linear molecule of the same molecular weight. This explained why these broad distributions were not noticed in earlier viscosity measurements, and suggested the technique described in this paper for measuring long chain branching in polyethylenes.

Experimental

Light Scattering.—Light scattering measurements were carried out, following the usual techniques, with a photoelectric turbidimeter built in this Laboratory. This turbidimeter measures at a 90° angle only. It is equipped with a small air oven which can be operated at temperatures up to 125°. The instrument is calibrated with a "Vitrolite" reflectance standard and gives turbidity values in good agreement with other laboratories.[9]

No solvents have been reported for polyethylene at room temperature, but it is soluble in many liquids at temperatures above 70°. Most of the light scattering experiments were made with α-chloronaphthalene solutions at 125°. C.P. grade α-chloronaphthalene was obtained from the Fisher Scientific Company and was not redistilled before use. It was freed from dust by filtration through a Selas grade 015 porous porcelain filter candle with a rated maximum pore diameter of 1.4 μ.

The refractive index increment for polyethylene in α-chloronaphthalene was 0.199 at 90°[10] and 0.191 at 125°.[11] Several samples of polyethylene gave the same molecular weights at both temperatures.

A few measurements were made using o-dichlorobenzene and cetane as solvents at 125°. Precise values of the refractive index increments for these solvents were not available; rough estimates of this quantity led to molecular weights agreeing within 30% in all the solvents used.

The polyethylene solutions for light scattering were not filtered. It was found that coarse filter media did not cause a reduction in turbidity. As successively finer media were used, no change occurred until the filter clogged and removed an appreciable amount of polymer from the solution. The reduction in turbidity and the fraction of polymer removed under these conditions could not be reproduced in successive experiments. Because of this lack of reproducibility, and because most polyethylenes were found relatively free from dust, dirt and other foreign impurities, filtration was deemed unnecessary.

Corrections for angular dissymmetry of scattering should be made for many of the samples. Lack of suitable equipment has forced us to apply a calculated correction, based on the mean square distance $\bar{r}^2$ between the ends of the molecules, calculated from Flory's expression[12]

$$(\bar{r}^2)^{3/2} = [\eta]M/\phi \qquad (1)$$

where Flory's value of $\phi = 2.1 \times 10^{21}$ ($[\eta]$ in deciliters/gram and $\sqrt{\bar{r}^2}$ in cm.) is assumed to be correct.

The angular dissymmetry of light scattering depends upon the polydispersity of the system as well as the average values of M and $\bar{r}^2$. Since this is not known in detail, the dissymmetry correction has been based on the angular dependence of scattering for a polydisperse system having the exponential type molecular weight distribution[13]

$$P^{-1}(\theta) = 1 + \frac{(U)_w}{2};\; U = 16\pi^2 \frac{\bar{r}^2}{\lambda^2} \sin^2(\theta/2) \qquad (2)$$

In view of the high polydispersity of the samples, it is anticipated that this procedure will lead to an undercorrection in most cases.

A few typical light scattering results are shown in Fig. 1 and Table I. The trend in values of μ, the Flory–Huggins interaction constant calculated from the slope of the $H(c/\tau) - c$ curve, is due to branching as will be explained later. Values of $\sqrt{\bar{r}^2}$ were calculated from eq. 1 and used to correct the molecular weights for angular dissymmetry.

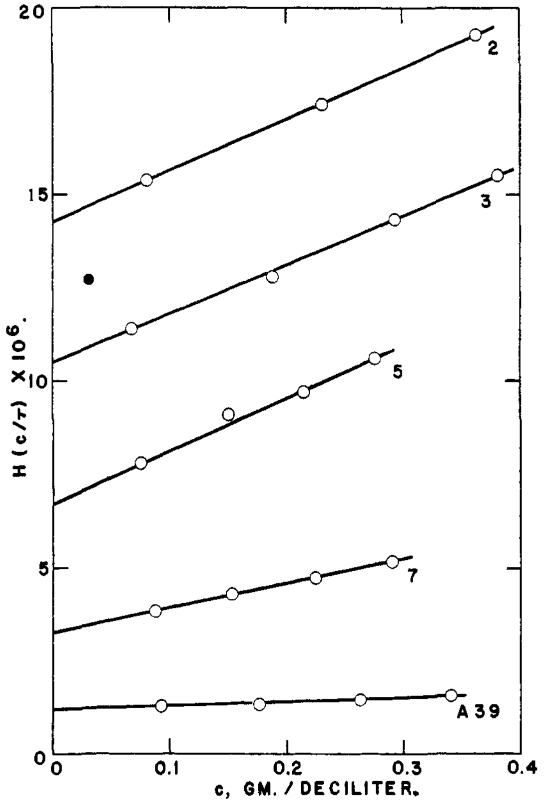

Fig. 1.—Light scattering data for typical polyethylenes.

TABLE I

LIGHT SCATTERING DATA FOR TYPICAL POLYETHYLENES

Sample	M_w (obsd.)	μ	$[\eta]$	$\sqrt{\bar{r}^2}$, Å.	M_w (cor.)
2	71,000	0.429	0.629	280	74,000
3	93,000	.443	.510	290	98,000
5	145,000	.436	.845	400	160,000
7	300,000	.473	.707	480	340,000
A39[a]	820,000	.496	.478	605	1,000,000

[a] Sample A39 was also measured by Muthana and Mark.[2a]

Osmometry.—The osmotic pressures of polyethylene solutions in xylene at 90° were measured in modified Zimm–Myerson[14] osmometers, with 600 gage gel cellophane membranes. Membrane life at 90° was over one month. With whole polymer samples, the equilibrium head decreased with time, presumably due to diffusion of polymer through the membrane, although in no case could polymer be detected in the solvent compartment. To correct for this diffusion, the osmotic height was measured with time and extrapolated linearly back to the time of filling the osmometer. It was found convenient to make this extrapolation and the subsequent $\pi/c - c$ extrapolation by plotting π/c vs. $(t + kc)$, where t is time and k is a constant chosen for convenience in plotting. Figure 2 shows a typical osmotic plot by this method. Duplicate points, as well as points at different

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(8) (a) B. H. Zimm and W. H. Stockmayer, *J. Chem. Phys.*, **17**, 130 (1949); (b) C. D. Thurmond and B. H. Zimm, *J. Polymer Sci.*, **8**, 477 (1952); (c) W. H. Stockmayer, J. T. Clarke and R. O. Howard, presented at 121st National meeting of the American Chemical Society, Buffalo, New York, March, 1952.

(9) B. A. Brice, M. Halwer and R. Speiser, *J. Opt. Soc. Am.*, **40**, 768 (1950).

(10) Measured by J. B. Nichols, Chemical Department, E. I. du Pont de Nemours & Co., on a Brice differential refractometer [B. A. Brice and M. Halwer, *ibid.*, **41**, 1033 (1951)].

(11) Measured in this Laboratory on a differential refractometer similar to that of P. P. Debye [*J. Applied Phys.*, **17**, 392 (1946)].

(12) P. J. Flory and T. G. Fox, THIS JOURNAL, **73**, 1904 (1951). Flory has pointed out (private communication) that a better parameter would be the mean square radius of the molecules (*i.e.*, the mean square distance of the segments from the center of gravity), since the concept of end to end distance cannot be applied unambiguously to branched molecules. This substitution would not change the numerical results.

(13) B. H. Zimm, *J. Chem. Phys.*, **16**, 1099 (1948).

(14) B. H. Zimm and I. Myerson, THIS JOURNAL, **68**, 911 (1946).

concentrations, represent results with different osmometers. The μ-values for polyethylenes in xylene are 0.35–0.38. These are in agreement with Harris' results,[2d] but not with those of Muthana and Mark,[2a] who found μ-values over 0.50. No deviations from a linear relationship between π/c and c could be detected over the concentration range used.

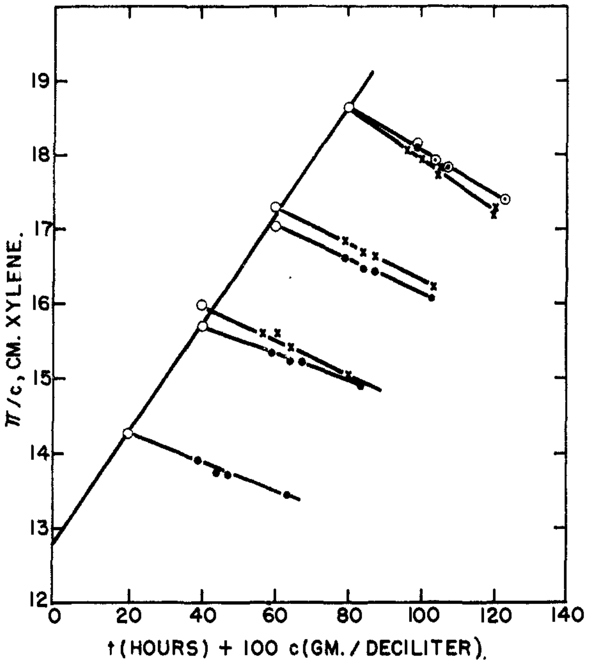

Fig. 2.—Simultaneous extrapolation in time and concentration of osmotic data for a typical polyethylene.

Viscometry.—Viscosities were measured on solutions of polyethylenes in α-chloronaphthalene at 125°. For some polymers viscosities were also measured on tetralin solutions at 125°, on xylene solutions at 85°, and on decalin solutions at 70°. Ubbelohde viscometers were so modified that successive dilutions could be made in the viscometers. All solutions were filtered through 200-mesh stainless steel filters. Concentration units were grams per deciliter. No kinetic energy or shear rate corrections were applied; efflux times for solvents were above 100 seconds in all cases. Intrinsic viscosities were estimated from plots of reduced or inherent viscosities against concentration. In most cases the plots of reduced viscosity showed some upward curvature, but in all cases the plots of inherent viscosity were straight lines. More weight was given to these points in determining the intrinsic viscosity.

Within the precision of the experiments intrinsic viscosities obtained in tetralin at 125° and in xylene at 85° were identical. Intrinsic viscosities in α-chloronaphthalene were 0.78 times those in tetralin or xylene, reflecting the lower solvent power of α-chloronaphthalene. Viscosities in decalin were 1.15 times those in xylene or tetralin.

Fractionations.—The fractionation experiments discussed here were not designed for a detailed study of molecular weight distribution, but to provide partially fractionated materials to confirm the abnormal breadth of the molecular weight distributions of polyethylenes. Polymers were divided into three fractions by successive additions of a non-solvent, dibutyl phthalate, to solutions of 2 g. of polyethylene per 100 cc. of α-chloronaphthalene at 125°. After the addition of a predetermined volume of non-solvent, the solutions were heated to 150–160°, where all of the polymer dissolved. They were then allowed to cool slowly back to 125° over a period of several hours. After 24 hours at 125°, the solution was poured away from the swollen polymer phase. The latter was dissolved in a small volume of xylene and precipitated in finely divided form by pouring the solution into cold methanol. After the removal of two fractions in this way, the lowest molecular weight polymer was isolated from the remaining liquid by pouring it into a large volume of cold methanol. The precipitates were washed with methanol and vacuum dried for 24 hours at 60°.

The Long Chain Branching Index

Thurmond and Zimm[8b] have recently shown that in the absence of the excluded volume effect the viscosities of a branched and an unbranched polymer of the same molecular weight are related by a ratio g such that

$$g^{3/2} = [\eta](\text{branched})/[\eta](\text{linear}) \qquad (3)$$

Values of g for several types of branched systems have been computed by Zimm and Stockmayer[8a] as a function of the weight-average number of branch points per molecule.[15] This number (hereafter referred to as the branching index, n) may be calculated from experimental data as follows: The light scattering molecular weight and intrinsic viscosity of a branched polymer are measured. The intrinsic viscosity of a linear polymer of the same molecular weight and same chemical type is then determined (either by experiment or by calculation from the viscosity–molecular weight law for the linear polymers). The two intrinsic viscosities are used to calculate g and thence the branching index.[16]

Properties of an Unbranched Polymer Analog of Polyethylene.—Linear polyethylene analogs called polymethylenes have been prepared[1d,4,17] from diazomethane, but data on these materials are not at hand. In lieu of studying these polymers we have assumed that one polymethylene of this type reported on by Harris had a weight-to-number average molecular weight ratio equal to two. This is not an unreasonable assumption, for the unusually broad distributions in polyethylenes result from branching mechanisms which are absent in polymethylenes. It was also assumed that the exponent in the viscosity–molecular weight equation is the same for polymethylenes as Harris found for polyethylenes, and that it is the same for solutions of polyethylenes in α-chloronaphthalene as in xylene. These assumptions lead to an approximate viscosity–molecular weight equation for polymethylenes

$$[\eta] = 8 \times 10^{-4}\bar{M}_w^{0.63} \qquad (4)$$

It should be noted that this equation has not been tested experimentally.

Effect of Excluded Volume.—Although α-chloronaphthalene is a poorer solvent for polyethylene than is xylene or tetralin, the excluded volume effect is not completely absent in this system. The magnitude of the resulting error in the branching index is not known but is not considered serious.[8b]

Choice of Branching Function g.—The form of g depends upon molecular weight distribution, and none of the available functions is correct for polyethylenes with their very broad distributions. We have used the function[8a] giving the weight average number n_w of trifunctional branch points in a

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(15) This term is defined by Zimm and Stockmayer, ref. 8a. The phrase "branches per molecule" is taken to mean "branch points per molecule" throughout this paper.

(16) A refinement of this calculation was discussed by W. H. Stockmayer and M. Fixman, Conference on Branched Molecules, New York Academy of Science, Jan. 9, 1953.

(17) (a) G. H. Buckley, L. H. Cross and N. H. Ray, *J. Chem. Soc.*, 2714 (1950); (b) G. H. Buckley and N. H. Ray, *ibid.*, 3701 (1952); (c) L. C. Leitch, P. E. Gagnon and A. Cambron, *Can. J. Research*, **B28**, 256 (1950).

system having the exponential distribution of molecular weights

$$g = \frac{6}{n_w}\left[(1/2)\left(\frac{2+n_w}{n_w}\right)^{1/2} \ln\left(\frac{(2+n_w)^{1/2}+n_w^{1/2}}{(2+n_w)^{1/2}-n_w^{1/2}}\right) - 1\right] \quad (5)$$

Since this relation is not exact, branching indices are not the weight-average number of branch points per molecule, but an unspecified lower average, dependent upon the molecular weight distribution of the sample. (They are therefore designated n instead of n_w.)

Effect of Short Branches.—Stockmayer (private communication, 1947) has calculated the function g for a monodisperse system with equally spaced short branches

$$g = \frac{1}{s+1}\left[1 + s(1 - 2f + 2f^2 - 2f^3) + s^2(-f + 4f^2 - f^3)\right] \quad (6)$$

where s is the number of branches per molecule and f is the fractional length of a branch. This model is an obvious oversimplification, but it indicates that the reduction in viscosity due to branches four carbon atoms long (on a polyethylene of degree of polymerization 2,000) is about 1/100 as great per branch as that indicated by the long chain branching index.

Results

Chain branching data[18] for several typical polyethylenes (selected from over 150 studied) are shown in Tables II and III. In these tables M_w is the weight-average molecular weight from light scattering, corrected for dissymetry; M_n the number-average molecular weight either measured by osmotic pressure or calculated from intrinsic viscosities[2d]; $[\eta]$ the intrinsic viscosity in α-chloronaphthalene at 125°; and n the branching index defined above. Limitations of the present data and theories are such that the branching indices are not exact numbers of branch points per molecule.

Structural Variations in Polyethylenes.—Sperati[19] has used number-average molecular weight, short chain branching and long chain branching as three independent structural parameters of polyethylenes. It is interesting to compare the molecular properties of samples in which one or two of these parameters are varied while the others remain roughly constant. The samples in Table II are selected on this basis. Density is included as a measure of short chain branching.[19] Due to sample limitations examples of the exact structural variations desired could not always be selected.

Fractionated Polymers.—Chain branching data for several polymers and their fractions are summarized in Table III. The letters H, M and L in the sample designation indicate the high, middle and low molecular weight fractions, respectively. It is very unlikely that a crude three-part fractionation could yield fractions with such a wide range of molecular weights, unless the molecular weight distributions of the parent polymers were very broad indeed. Within a given polymer the degree of long chain branching increases with increasing molecular weight. This is predicted from the kinetics of a branching mechanism[7] based on chain transfer to polymer. That is, the larger the molecule, the higher is its probability of branching. This effect must, of course, be differentiated from the comparisons of branching among different polymers shown in the previous table.

TABLE II

STRUCTURAL VARIATIONS IN POLYETHYLENE

Sample	M_w	M_n	$[\eta]$	Density	n
Long chain branching varying					
21	190,000	34,000	0.73	0.915	4.4
26	305,000	34,000[a]	.72	.914	7.9
10	430,000	34,000[a]	.73	.917	10.6
9	560,000	31,000	.71	.918	13.6
Short chain branching varying					
19	72,000	4,400	.21	.941	12.7
20	43,000	2,700	.19	.918	9.4
1	38,000	2,600	.15	.890	11.2
Number-average mol. wt. varying					
23	155,000	15,000	.46	.914	8.3
13	340,000	34,000[a]	.74	.916	8.4
25	370,000	49,000	.92	.917	6.6
Long and short chain branching varying					
28	80,000	42,000[a]	.82	.936	0.7
27	140,000	36,000	.84	.929	2.3
15	305,000	40,000[a]	.77	.914	7.1
Long chain branching and M_n varying					
17	260,000	38,000	.80	.920	5.8
11	380,000	34,000[a]	.75	.921	9.1
A38	580,000	11,600[b]	.52	.921	20.3
Short chain branching and M_n varying					
14	340,000	7,800	.32	.927	24
29	600,000	19,000	.56	.935	20
A41	1,800,000	38,000[b]	1.02	.921	21

[a] Osmotic pressure measured in this Laboratory. All osmotic molecular weights not otherwise marked were calculated from intrinsic viscosities.[2d] [b] Osmotic pressure measured by Muthana and Mark.[2a] Their molecular weights and μ-values do not agree well with those of Harris[2d] or our own values. Other samples studied by Muthana and Mark were:

A39	1,000,000	16,700[b]	0.48	0.924	39.0
A40	650,000	26,200[b]	0.85	0.911	12.6
A42	480,000	37,000[b]	1.11	0.931	6.3

TABLE III

LONG CHAIN BRANCHING OF POLYETHYLENE FRACTIONS

Sample	%	M_w	$[\eta]$	n
10	100	430,000	0.73	10.6
10H	18	2,100,000	1.30	17.8
10M	40	175,000	0.81	3.5
10L	42	30,000	.32	2.2
11	100	380,000	.75	9.1
11H	42	830,000	1.06	11.2
11M	13	74,000	0.58	1.9
11L	45	33,000	.43	1.0
26	100	305,000	.72	7.9
26H	38	650,000	1.105	8.7
26M	22	96,000	0.61	3.0
26L	40	31,000	0.35	2.0

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(18) Most of the experimental data were obtained by Mr. J. T. Atkins.

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

Discussion

Validity of the Branching Index.—It is clear that numerical values of the long chain branching index for polyethylenes are based upon many assumptions and approximations, *viz.*, the angular dissymmetry correction, the presence of an appreciable excluded volume effect, the assumed properties of linear polyethylene analogs, the dependence of g on distribution of molecular weights, etc. Numerical values of the branching index are only approximate. It seems likely that the present calculations tend to underestimate rather than overestimate the degree of long chain branching in polyethylenes.[20]

Other Measures of Branching. μ-Values.—Figure 3 shows the correlation between the branching indices for 70 polyethylenes and their μ-values in α-chloronaphthalene at 125°. Examination of data for samples having different degrees of branching at constant weight-average molecular weight, and for samples having constant branching index but differing in molecular weight, shows that μ-values increase with branching index largely independent of molecular weight. Deviations from the average line in Fig. 3 do not appear to correlate with number-average molecular weight or with short chain branching.

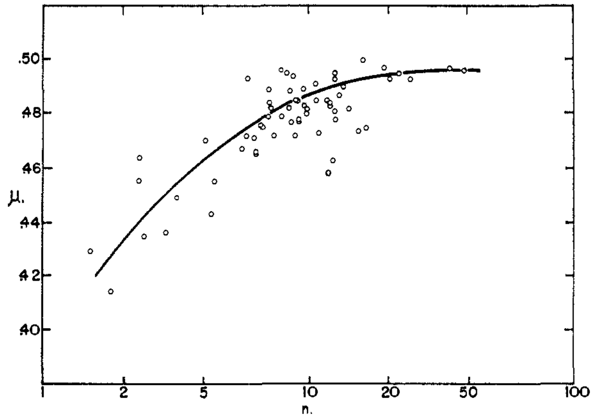

Fig. 3.—Correlation between long chain branching index and μ-value for polyethylenes.

Huggins' k'.—The k'-values calculated from viscosity–concentration measurements in α-chloronaphthalene at 125° ranged between 0.5 and 0.7 with a slight trend toward higher values for more highly branched polymers. This measurement does not have adequate precision to be useful for measuring chain branching of polyethylenes.

Conclusions

(1) In addition to its short chain branches,[3] a polyethylene molecule has a small number of much longer branches. On a weight average basis there are usually 8 to 10 long branches per molecule. These branches occur predominantly on the large molecules.

(2) As a result of the formation of long branches, the distribution of molecular weights in polyethylenes is very broad. Weight-to-number average molecular weight ratios as high as 10 or 20 to 1 are not uncommon.

(3) The intrinsic viscosity of a polyethylene solution has been found[2d] in some cases to be a rough measure of its number-average molecular weight. This unusual relationship is the coincidental result of the simultaneous increase in weight-average molecular weight due to the branching reaction, and reduction in intrinsic viscosity from that of linear homologs due to the presence of branched molecules.

(4) Long chain branching in polyethylenes can most readily be detected by comparing weight-average molecular weights with other parameters. For most cases, the best measure of long chain branching now available is based upon the measurement of light scattering molecular weight and intrinsic viscosity.

(5) Other quantities which have been suggested as measures of long chain branching, such as the μ-values from light scattering or osmometry, or the k'-values from the slope of viscosity-concentration curves, lack either theoretical basis or sensitivity.

Acknowledgment.—The author is deeply indebted to W. H. Stockmayer for aid in the development of the measurement of long chain branching.

WILMINGTON, DELAWARE

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[20] Unpublished experiments by W. H. Stockmayer and R. O Howard on polyvinyl acetate substantiate this conclusion. They find that eq. 5 underestimates branching in polyvinyl acetate in the presence of a broad distribution of molecular weights by a factor of three or four (see ref. 16).