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

The Molecular Structure of Polyethylene. IX. Weight-average Molecular Weight and Intrinsic Viscosity of Linear Polyethylene[1]

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The weight-average molecular weight ($\bar{M}_w$) of linear polyethylene was measured with a recording angular dissymmetry meter. The relation between $\bar{M}_w$ and the intrinsic viscosity ($[\eta]$) in α-chloronaphthalene at 125° is $[\eta] = 4.3 \times 10^{-4}\bar{M}_w^{0.67}$ dl./g. Solutions of some samples of linear polyethylene gave severely distorted Zimm plots. Zimm plots linear in the angle coördinate were obtained after elevated temperature filtration or ultracentrifugation of the solutions.

Introduction

The intrinsic viscosity ($[\eta]$) of a heterogeneous linear polymer is a function of the viscosity–average molecular weight ($\bar{M}_v$). This average molecular weight is approximated better by the weight-average ($\bar{M}_w$) than by the number-average molecular weight ($\bar{M}_n$). The difference between $\bar{M}_v$ and $\bar{M}_w$ can be calculated in the few cases where the molecular weight distribution is known.

The approximate relation between $\bar{M}_w$ and $[\eta]$ does not hold for branched polymers. In fact, the amount of long chain branching is determined from the ratio of the intrinsic viscosity of a branched polymer to that of the linear variety with the same weight-average molecular weight.[3]

The present study was undertaken to establish the relation between $[\eta]$ and $\bar{M}_w$ for linear polyethylene by accurate light scattering measurement. It was facilitated by the availability of linear polyethylene over a wide molecular weight range and by the recent improvements in the light scattering technique.[3b]

Experimental

Samples.—Polyethylene sample[4] 92 was made by a high pressure free radical method.[5] The other samples were prepared by low pressure syntheses for linear polyethylene using either a Ziegler type initiator[6] or a supported metal oxide catalyst.[7,8]

Light Scattering.—Measurement was made with an automatically recording photoelectric dissymmetry meter using the method described previously.[3b] Data were plotted in the usual way as a Zimm plot.

Optical Clarification.—Clarification was necessary for solutions of all samples of linear polyethylene prior to light scattering measurement. Unclarified solutions were contaminated with particulate matter resulting in pronounced curvature of the Zimm plots toward the angle coördinate axis, especially at small angles. The distortion exceeded by far the maximum curvature attributable to wide molecular weight distribution.[3b,9–11]

Most of the samples of linear polyethylene were clarified adequately by high temperature filtration. The filtering device[12] is shown in Fig. 1. A "Selas" FO-54 porous filter candle (Selas Corporation of America, Philadelphia, Pa.) with a maximum pore radius of 0.6 μ was sealed directly to an inner glass tube. The closed system prevented contamination from the atmosphere. Filtration could be accelerated by applying an external pressure. Solutions of two samples of polyethylene (samples 92 and 93) were clarified only by elevated temperature ultracentrifugation.[3b] The amount of particulate matter was less than 2-3%.

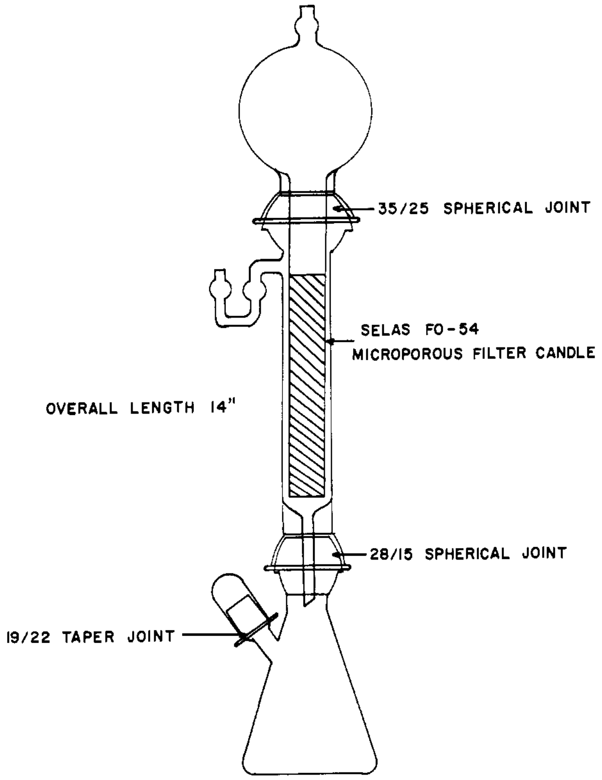

Fig. 1.—Filtration apparatus.

Viscosity Measurement.—Intrinsic viscosity was measured in either Ostwald-Fenske or Ubbelohde suspended level viscometers.[3a] The viscometers had a negligible kinetic energy correction. Solvent in both light scattering and viscosity measurements was α-chloronaphthalene (α-ClN) at 125°. The same solution was used for both determinations.

Results

Table I lists $\bar{M}_w$ and $[\eta]_{\alpha\text{-ClN},125°}$ as well as second virial coefficient (A_2), z-average root-mean-square end-to-end distance $\sqrt{\overline{r_z^2}}$, and the number of methyl groups per hundred carbon atoms (CH_3/100 C) for the samples.[13]

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[1] Presented at the 130th National Meeting of the American Chemical Society, Atlantic City, New Jersey, September 19, 1956.

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[3] (a) F. W. Billmeyer, Jr., THIS JOURNAL, **75**, 6118 (1953); (b) L. T. Muus and F. W. Billmeyer, Jr., *ibid.*, **79**, 5079 (1957).

[4] Sample designation is consistent with that in other papers of this series.

[5] R. A. Hines, W. M. D. Bryant, A. W. Larchar and D. C. Pease, *Ind. Eng. Chem.* **49**, 1071 (1957).

[6] K. Ziegler, Belgian Patent 533,362 (1955).

[7] A. K. Roebuck and A. Zletz, U. S. Patent 2,692,258 (1954).

[8] Phillips Petroleum Co., Belgian Patent 530,617 (1955).

[9] B. H. Zimm, *J. Chem. Phys.*, **16**, 1099 (1948).

[10] H. Benoit, *J. Polymer Sci.*, **11**, 507 (1953).

[11] H. Benoit, A. M. Holtzer and P. Doty, *J. Phys. Chem.*, **58**, 635 (1954).

[12] We wish to acknowledge the assistance of R. G. Nester, R. J. McCarter and V. Kokle in development of this filter.

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

TABLE I

MOLECULAR PARAMETERS OF LINEAR POLYETHYLENES

Sample	CH_3/100 C	$\bar{M}_w$	$A_2 \times 10^4$, ml. mole g.$^{-2}$	$(\overline{r_z^2})^{1/2}$, Å.	$[\eta]_{\alpha\text{-ClN},125°}$, dl./g.[c]
86	0.4	48,000	12.4	*ca.* 800	0.59
87	.5	95,000	11.9	*ca.* 700	1.03
88	.1	135,000	8.9	*ca.* 900	1.30
89	.3	287,000	6.9	*ca.* 1100	1.94
90	.1	950,000	9.7	1900	4.56
91	.2	5,600,000	2.7	4900	11.6
92	.03	100,000[a] (120,000)[b]	10.3[a] (12.1)[b]	*ca.* 400[a] (*ca.* 400)[b]	0.89[a] 0.90[b]
93	.43	110,000[a] (105,000)[b]	11.7[a] (8.1)[b]	*ca.* 700[a] (*ca.* 500)[b]	1.05[a] 1.20[b]

[a] Top solution polymer. [b] Bottom solution polymer. [c] Uncorrected for shear rate.

The data in parentheses for samples 92 and 93 are for polymer from the bottom solution in the ultracentrifugation. The Zimm plots were not linear in the angle coördinate, and the weight-average molecular weights are approximate only. Comparison of these approximate weight-average molecular weights with the accurate ones for the top solution polymer suggests that little, if any, fractionation occurred during ultracentrifugation. The intrinsic viscosities support this conclusion. In contrast, fractionation was observed in the ultracentrifugation of branched polyethylenes with weight-average molecular weights much higher than those of samples 92 and 93.[3b]

The absence of appreciable chain branching was confirmed by infrared determination of the number of methyl groups. The methyl group content in Table I is considerably lower than that for commercial free radical polyethylene.[13]

The dependence of $[\eta]_{\alpha\text{-ClN},125°}$ on $\bar{M}_w$ is given by the equation

$$[\eta]_{\alpha\text{-ClN},125°} = 4.3 \times 10^{-4}\,\bar{M}_w^{0.67}\text{dl./g.} \qquad (1)$$

A previous estimate by Billmeyer[3] is in fair agreement with eq. 1.

The relation between $\bar{M}_w$ and A_2 in α-chloronaphthalene at 125° follows the expression

$$A_2 = 0.06\bar{M}_w^{-0.35}\ \text{ml. mole g.}^{-2} \qquad (2)$$

The exponent in eq. 2 is in accord with that for other linear polymers, such as polymethyl methacrylate.[14]

For most of the samples, the ratio $A_2\bar{M}_w/[\eta]$ is in the range 1.0–1.6 reported for other linear polymers in good solvents.[15–17] The sole exception is sample 89 for which A_2 appears to be high.

Comparison of eq. 2 with that for branched polyethylene[3b] indicates that the second virial coefficient of linear polyethylene is higher than that of a branched sample of the same weight-average molecular weight, in agreement with the reduction in molecular size due to branching.

The molecular weight is in general too low to produce appreciable dissymmetry of scattered light. Accordingly, the molecular size determination is not highly accurate. The approximate relation between $(\overline{r_z^2})^{1/2}$ and $\bar{M}_w$ is

$$(\overline{r_z^2})^{1/2} \cong 2.2\bar{M}_w^{0.5} \qquad (3)$$

and is indicative of internal consistency of the light scattering data.

Discussion

Two equations were previously suggested to relate $[\eta]$ of free radical polyethylene to $\bar{M}_n$ rather than $\bar{M}_w$. Ueberreiter, *et al.*,[18] proposed the following equation for fractions of an experimental free radical polymer dissolved in decalin at 70°

$$[\eta]_{\text{decalin},70°} = 3.87 \times 10^{-4}\,\bar{M}_n^{0.74}\ \text{dl./g.} \qquad (4)$$

Furthermore, Harris[19] suggested the relation

$$[\eta]_{\text{xylene},\,75°} = 1.35 \times 10^{-3}\,\bar{M}_n^{0.63}\ \text{dl./g.} \qquad (5)$$

for a number of unfractionated samples of commercial free radical polyethylene and a single polymethylene. Equations of type 4 and 5 reflect a probable cancellation of the effects of long chain branching and molecular weight distribution on the intrinsic viscosity. The approximate equation for linear polymers

$$[\eta]_{\text{linear}} = K\bar{M}_w^{a}$$

can be written as

$$[\eta]_{\text{branched}} = K\left[\frac{[\eta]_{\text{branched}}}{[\eta]_{\text{linear}}}\left(\frac{\bar{M}_w}{\bar{M}_n}\right)^{a}\right]\bar{M}_n^{a} \qquad (6)$$

According to Beasley,[20] $\bar{M}_w/\bar{M}_n$ increases with increasing long chain branching. However, the ratio $[\eta]_{\text{branched}}/[\eta]_{\text{linear}}$ decreases under the same conditions.[3,21,22] For a particular type of polyethylene, the bracketed term in (6) may be essentially constant leading to identity with equations of type 4 and 5. The interpretation suggests that eq. 4 and 5 are invalid for fractions of commercial free radical polyethylene, in accord with observations by Trementozzi.[23]

Recently, Duch and Kuchler[24] suggested the following relation between the intrinsic viscosity in tetralin at 120° and $\bar{M}_w$ of linear polyethylene by light scattering measurement

$$[\eta]_{\text{tetralin},\,120°} = 2.36 \times 10^{-4}\,\bar{M}_w^{0.78}\text{dl./g.} \qquad (7)$$

For branched polyethylene, the intrinsic viscosity in tetralin is 1.28 times that in α-chloronaphtha-

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(14) E. F. Cassassa, Thesis, Massachusetts Institute of Technology, Cambridge, Mass., 1953.

(15) A. R. Shultz, THIS JOURNAL, **76**, 3422 (1954).

(16) S. N. Chinai, P. C. Scherer and D. W. Levi, *J. Polymer Sci.*, **17**, 117 (1955).

(17) S. N. Chinai, J. D. Matlack, A. L. Resnick and R. J. Samuels, *J. Polymer Sci.*, **17**, 391 (1955).

(18) K. Ueberreiter, H.-J. Orthman and G. Sorge, *Makromol. Chem.*, **8**, 21 (1952).

(19) I. Harris, *J. Polymer Sci.*, **8**, 353 (1952).

(20) J. K. Beasley, THIS JOURNAL, **75**, 6123 (1953).

(21) B. H. Zimm and W. H. Stockmayer, *J. Chem. Phys.*, **17**, 1301 (1949).

(22) W. H. Stockmayer and M. Fixman, *Ann. N. Y. Acad. Sci.*, **57**, 334 (1953).

(23) Q. A. Trementozzi, *J. Polymer Sci.*, **23**, 887 (1957).

(24) E. Duch and Kuchler, *Z. Elektrochem.*, **60**, 218 (1956).

lene.[3] Assumption of this proportionality factor also for linear polyethylene converts eq. 7 into

$$[\eta]_{\alpha\text{-ClN},\ 125°} = 1.84 \times 10^{-4}\ \bar{M}_w{}^{0.78}\text{dl./g.} \qquad (8)$$

Equation 1 is probably more accurate than 8 in view of the uncertainties in Duch and Kuchler's light scattering measurement.[25]

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[25] Equation 1 was later supported by the relation

$$[\eta]_{\text{decalin},\ 135°} = 6.77 \times 10^{-4}\ \bar{M}_w{}^{0.67}\text{dl./g.} \qquad (9)$$

suggested for linear polyethylene by Francis, *et al.*[26]

For branched polyethylene, the intrinsic viscosity in decalin is 1.48 times that in α-chloronaphthalene.[3] Equation 9 converts into

$$[\eta]_{\alpha\text{-ClN},125°} = 4.6 \times 10^{-4}\ \bar{M}_w{}^{0.67}\text{dl./g.} \qquad (10)$$

in excellent agreement with (1).[27]

[26] P. S. Francis, R. C. Cooke, Jr., and J. H. Elliott, presented at the 130th National Meeting of the American Chemical Society, Atlantic City, N. J., September 19, 1956.

[27] Note added in proof (May 27, 1957). Recently, Tung[28] proposed the following relation based on osmotic data on fractions of linear polyethylene

$$[\eta]_{\text{tetralin},\ 130°} = 5.10 \times 10^{-4}\ \bar{M}_n{}^{0.725} \qquad (11)$$

Conversion to α-chloronaphthalene at 125° gives

$$[\eta]_{\alpha\text{-ClN},\ 125°} = 4.0 \times 10^{-4}\ \bar{M}_n{}^{0.725} \qquad (12)$$

For molecular weights in the range 20,000–100,000, eq. 2 leads to results about half those from eq. **1**. The discrepancy probably reflects heterogeneity of Tung's fractions ($\bar{M}_w/\bar{M}_n \sim 2$).

[28] L. H. Tung, *J. Polymer Sci.*, **24**, 333 (1957).

WILMINGTON, DELAWARE

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WASHINGTON]

Alkenylboranes. I. Preparation and Properties of Some Vinyl- and Propenylboranes[1,2]

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Dimethylvinyl-, methyldivinyl- and trivinylborane, dimethylpropenyl- and methyldipropenylborane were prepared from dimethylbromoborane and vinylsodium or propenyllithium, respectively. The products in each case were separated by fractional condensation and the vinyl derivatives were separated more effectively by gas partition fractometry. The structures were demonstrated to be as claimed through identity of the hydrocarbons formed in the reaction with silver ammonium ion. Acidity of the vinylboranes toward ammonia was diminished as would be expected if the vacant boron orbital participated in the pi-electron system belonging to the alkenyl substituents. Relative acidity was found to account for the several products obtained in the preparative reaction, for absence of reaction of trivinylborane with oxygen and the slow autoöxidation of methyldivinylborane.

Compounds such as dimethoxyborane, dimethylaminoborane and borazole are stable as monomers, presumably because dimerization is prevented through internal dative bonding, which serves as an alternative to formation of three-center bonds in the dimers. This inspires the question concerning other sources from which electrons might be drawn into the vacant orbital of boron, and there comes to mind the intriguing possibility that in such structurally favorable cases as the alkenylboranes the phenomenon might cause the vacant boron orbital to participate in the carbon pi-electron system. The resulting mesomerism would be depicted by canonical forms involving a shift in the unsaturation from Δ^{C-C} to Δ^{C-B}. Synthesis of suitable compounds becomes even more interesting when the vinylboranes are seen to be isoelectronic with allyl carbonium ion, and the possibility arises of observing with stable substances the properties attributed to unstable species.

The acidity of vinylboranes and the behavior of related hydrogen compounds with respect to dimerization should test the validity of the structural hypothesis; while observations of spectra and their comparison with predictions of molecular orbital computations should serve to evaluate any similarity with allyl carbonium ion. The latter program is outside the scope of the work reported here, and observations from this and other studies[3] makes improbable the existence of the vinyldiboranes. Accordingly this paper presents the syntheses of some completely substituted alkenylboranes, an efficient method for their separation, a chemical proof of their structure, a preliminary measure of their acidity, and some related chemical reactions.

The preparative method selected to involve the fewest unknown reactions was that in which a suitable carbanion displaced halide ion from a boron halide. Two such reagents were available, vinylsodium[4] and propenyllithium.[5] A weakly acidic boron halide was needed to avoid polymerization of the olefins, and for this purpose dimethylbromoborane[6] was chosen. Though a single product might have been expected from each organoalkali compound, there was obtained in addition to the dimethylalkenylboranes both the methyldialkenylboranes, and the trialkenylboranes.

The products were separated by fractional condensation and in the case of the vinylboranes also by gas partition fractometry, a method so superior as to be greatly preferred.

Experimental

Analytical Methods.—The bomb combustion method used for elementary analysis of organoboron compounds was essentially that described by McKennon. The sample

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[2] Based on doctoral theses submitted to the Graduate School, University of Washington by Theran D. Parsons, 1953, and Morris Bernard Silverman, 1956.

[3] F. G. A. Stone and H. J. Emeleus, *J. Chem. Soc.*, 2755 (1950).

[4] A. A. Morton, *et al.*, THIS JOURNAL, **72**, 3785 (1950).

[5] E. A. Baude, J. A. Coles and C. J. Timmons, *J. Chem. Soc.*, 2000 (1950); *Nature*, **166**, 58 (1950).

[6] F. L. McKennon, Dissertation, University of Chicago Libraries, 1936.