JOURNAL OF THE
AMERICAN CHEMICAL SOCIETY

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VOLUME 79 OCTOBER 9, 1957 NUMBER 19

PHYSICAL AND INORGANIC CHEMISTRY

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

The Molecular Structure of Polyethylene. VI. Molecular Weight from Dissymmetry of Scattered Light[1]

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RECEIVED DECEMBER 10, 1956

Weight-average molecular weight of branched polyethylene is determined by light scattering measurement with a recording angular dissymmetry meter. The molecular weight distribution is wide for branched polyethylene. Weight-average molecular weight is in the range 350,000-615,000 for samples with number-average molecular weight about 30,000. For some samples of branched polyethylene, Zimm plots linear in the angle coördinate are obtained only after removal of a small fraction of particulate matter. Elevated temperature ultracentrifugation is efficient for this removal. Fractionation in molecular weight of the soluble portion occurs during ultracentrifugation.

Introduction

Paper III[2] of this series reported weight-average molecular weight of long chain branched polyethylene by light scattering. Measurement was made with a photoelectric turbidimeter allowing observation of the scattered light intensity only in the direction transverse to the incident light beam. Correction for angular dissymmetry was estimated by employing molecular dimensions calculated from viscosity measurement.

Precise characterization of polyethylene by light scattering requires determination of the angular distribution of light scattered from a polyethylene solution. Long chain branching and molecular weight distribution are both known to affect the shape of the projection of the reciprocal intensity surface.[3-5]

Optical clarification presents a major complication in the examination of many samples of polyethylene by the light scattering method. The presence of large scattering particles results in low reciprocal intensities of scattered light, particularly at angles of observation close to the incident beam. Such particles must be removed before the projection of the reciprocal intensity surface can be interpreted in terms of the properties of dissolved polyethylene molecules.

Experimental

Samples.—Three samples of polyethylene, designated[6] 10, 13 and 49, were used. They are commercial Fawcett-type[7] (branched, high-pressure, free-radical) polyethylenes.

Angular Dissymmetry Meter.—The photoelectric turbidimeter[5b] records automatically the intensity of scattered light as a continuous function of the angle of observation. The angular range extends from 20 to 150 degrees with a resolution of five degrees. The scattering cell is a right cylinder with a plane window for the incident beam and a black glass block for its complete absorption after passing through the solution. The scattering cell is placed in a heating chamber. The maximum use temperature is 150°. The temperature is automatically controlled within 0.2°.

Cornell Standard Polystyrene is used for calibration of the angular dissymmetry meter. The excess transverse turbidity of a solution of 0.750 g. of the Standard Polystyrene in 100 ml. of 2-butanone is taken as 10.5×10^{-3} cm.$^{-1}$; that of 0.500 g. Standard Polystyrene in 100 ml. of toluene as 1.31×10^{-3} cm.$^{-1}$. Both calibrations are made with plane polarized light of wave length 5461 Å. and vertical electric vector. These turbidities are in good agreement with the so-called "high values" in the literature.[8,9]

Optical Clarification.—Wide variation is observed in the appearance of the projection of the reciprocal intensity surface of light scattered from solutions of polyethylene. Some samples dissolved in α-chloronaphthalene give solu-

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[1] Presented at the 129th National Meeting of the American Chemical Society, Dallas, Texas, April 11, 1956. Papers I-V of this series are published in THIS JOURNAL, **75**, 6110, 6113, 6118, 6123, 6127 (1953).

[2] F. W. Billmeyer, Jr., *ibid.*, **75**, 6118 (1953).

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

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

[5] (a) H. Benoit, A. M. Holtzer and P. Doty, *J. Phys. Chem.*, **58**, 635 (1954); (b) F. W. Billmeyer, Jr., and C. B. deThan, THIS JOURNAL, **77**, 4763 (1955).

[6] Sample designation is consistent with the other papers in this series.

[7] E. W. Fawcett, R. O. Gibson and M. W. Perrin, U. S. Patent 2,153,553 (1939).

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

[9] D. K. Carpenter and W. R. Krigbaum, *J. Chem. Phys.*, **24**, 1041 (1955).

tions with linear or almost linear patterns when the light scattering data are plotted in the form of a Zimm plot. This type of plot is based on an angular intensity distribution $P^{-1}(\theta)$ given as a function of the angle of observation (θ) by the equation

$$P^{-1}(\theta) = 1 + \bar{u}_z/3 \qquad (1)$$

where $\bar{u}_z$ is defined as

$$\bar{u}_z = [(4\pi/\lambda')\sin(\theta/2)]^2\overline{s_z^2} \qquad (2)$$

in terms of the wave length of light in the solution (λ'), and the z-average root-mean-square radius of gyration $\sqrt{\overline{s_z^2}}$.

On the other hand, light scattering measurements on other samples of branched polyethylene result in Zimm plots distorted in the direction of low reciprocal intensities at angles close to the incident beam.

A likely source for the low angle distortion is particulate matter with dimensions larger than the wave length of light.

Both filtration and centrifugation[2,10,11] were employed for removal of particulate matter from solutions of branched polyethylene.

Filtration.—Filtration was made in α-chloronaphthalene solution at 125° using "Selas" FD-54 porous filter candles (Selas Corporation of America, Philadelphia, Pa.) with a pore diameter as small as 1.2 μ. This treatment was unsuccessful for samples of branched polyethylene containing particulate matter as indicated by distorted Zimm plots for filtered as well as unfiltered solutions.

Ultracentrifugation.—The centrifugation was carried out at constant temperature in the range 100–120° for 4–5 hours with a "Spinco" Model L Preparative Ultracentrifuge (Spinco Division, Beckman Instruments, Inc., Belmont, California). The average centrifugal acceleration was 40,000 times that of gravity. The solvent was either n-octane or n-decane, both with density lower than amorphous polyethylene at 100–120°.

The top portion of the solution in the stainless steel centrifuge tubes was removed by suction into an electrically heated hypodermic syringe immediately after centrifugation. The bottom solution was poured out of the tubes. Finally, the tubes were immersed in xylene at 100° to recover a small residue, containing mainly particulate matter, sticking to the bottom of the tubes. The polymer from the top and the bottom solution was isolated by evaporation of the hydrocarbon solvent *in vacuo*.

In one experiment, the entire soluble portion of polyethylene sample was isolated without separation into top and bottom solution.

Light Scattering Measurement.—Light scattering measurement was made in redistilled α-chloronaphthalene at 125° with vertically polarized light of wave length 5461 Å. The refractive index increment[2] was taken as 0.191 ml./g.

Viscosity.—Viscosity was measured in α-chloronaphthalene at 125° for four polymer concentrations by the technique described in Paper III.[2]

Results

Some samples of branched polyethylene gave linear or essentially linear Zimm plots without any previous optical clarification. Figure 1 presents the light scattering data for a polyethylene, sample 49, belonging to this class. In Table I are listed the data for sample 49.

TABLE I

MOLECULAR PARAMETERS FOR POLYETHYLENE SAMPLE 49

Weight-average mol. wt. ($\bar{M}_w$)	350,000
Number-average mol. wt. ($\bar{M}_n$)	32,000[a]
Intrinsic viscosity ($[\eta]$), dl./g.	0.75
Long chain branching index	17
Huggins' parameter (k')	0.52
Second virial coefficient (A_2), ml. mole g.$^{-2}$	5.3×10^{-4}
z-Average root-mean-square radius of gyration, Å.	410

[a] Paper VIII of this series.[12]

Light scattering measurements on unclarified solutions of other samples of branched polyethylene, for example samples 10 and 13, give severely distorted Zimm plots (Fig. 2). The distortion is in the direction of low reciprocal intensities at small angles. The apparent second virial coefficient decreases drastically at small angles resulting in a somewhat less pronounced curvature of the locus of zero concentration data. Zimm plots of this type were shown in a recent publication.[13]

The effect of ultracentrifugation is shown in Fig. 3 for the polymer from the bottom solution of sample 10. The Zimm plot is essentially linear with $\sin^2(\theta/2)$ in contrast to that from the unclarified solution (Fig. 2). The Zimm plot for the polymer from the top solution also shows a high degree of linearity with $\sin^2(\theta/2)$. Ultracentrifugation removes the spurious dependence on angle of the second virial coefficient. A similar change in appearance of the Zimm plots is observed for sample 13. Table II lists the data from the experiments. Samples 10 and 13 both have number-average molecular weight 34,000 as determined by osmometry.[2]

TABLE II

ULTRACENTRIFUGATION AND LIGHT SCATTERING EXPERIMENTS WITH BRANCHED POLYETHYLENE SAMPLES 10 AND 13

	Sample 10	Sample 13
Polymer fractionation, %		
Top soln.	63.8	62.1
Bottom soln.	30.6	33.4
Residue	3.7	2.7
Loss (by difference)	1.9	1.8
Total soluble polymer	94.4	95.5
Weight-average mol. wt.		
Polymer from top soln.	155,000	340,000
Polymer from bottom soln.	1,580,000	940,000
Total polymer (calcd.)	615,000	550,000
Intrinsic viscosity, dl./g.		
Polymer from top soln.	0.77	0.69
Polymer from bottom soln.	.87	.83
Total polymer (calcd.)	.81	.74
Original sample	.80	.76
Long chain branching index		
Polymer from top soln.	6	18
Polymer from bottom soln.	40	34
Total polymer (calcd.)	17	24
Huggins' parameter (k')		
Polymer from top soln.	0.39	0.45
Polymer from bottom soln.	.45	.50
Original polymer	.43	.44
Second virial coefficient (A_2), ml. mole g.$^{-2}$		
Polymer from top soln.	6.1×10^{-4}	9.0×10^{-4}
Polymer from bottom soln.	1.6×10^{-4}	3.0×10^{-4}
z-Average root-mean-square radius of gyration, Å.		
Polymer from top soln.	300	340
Polymer from bottom soln.	930	610

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(10) G. V. Schulz, H.-J. Cantow and G. Meyerhoff, *J. Polymer Sci.*, **10**, 79 (1953).

(11) W. B. Dandliker and J. Kraut, THIS JOURNAL, **78**, 2380 (1956).

(12) C. E. Ashby, J. S. Reitenour and C. F. Hammer, *ibid.*, **79**, 5086 (1957).

(13) L. D. Moore, Jr., *J. Polymer Sci.*, **20**, 137 (1956).

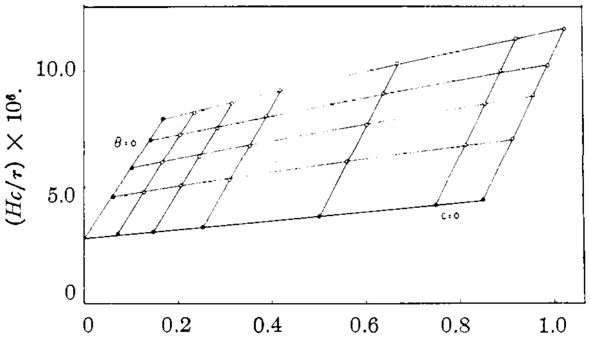

Fig. 1.—Zimm plot of polyethylene sample 49.

The polymer weight balance (Table II) shows that the centrifugation was carried out with a very small loss of material. A maximum of 5% of the original sample weight is removed as particulate matter in the ultracentrifugation experiment. However, this amount is sufficient to affect the Zimm plot over its entire angular range. The distorted Zimm plots from unclarified solutions of samples 10 and 13 may be extrapolated to $\bar{M}_w \cong 5{,}000{,}000$ and $\bar{M}_w \simeq 1{,}200{,}000$, respectively. These weight-average molecular weights are extreme compared to those (615,000 and 550,000) calculated in Table II for about 95% of the original polymer in samples 10 and 13.

In the last experiment, sample 10 was centrifuged without a following separation into top and bottom solution. The residue was determined as 4.7%, the polymer loss as 1.3%. The Zimm plot from this experiment was also linear with $\sin^2 (\theta/2)$. The weight-average molecular weight is 465,000, in fair agreement with that of 615,000 listed in Table II. The discrepancy may, at least in part, reflect some difficulty in reproducing the separation of a high molecular weight tail in sample 10 from the particulate matter.

The calculation of the long chain branching index is based on a comparison of the intrinsic viscosity of a branched and a linear polyethylene having the same weight-average molecular weight.[2,14,15]

The intrinsic viscosity of linear polyethylene in α-chloronaphthalene at 125° is derived from the equation[16]

$$[\eta] = 4.3 \times 10^{-4} \bar{M}_w^{0.67} \qquad (3)$$

The long chain branching indices in Tables I and II are calculated as the weight-average number of trifunctional branch points per molecule, applying the relation between h^3 and g suggested by Stockmayer and Fixman[17] and eq. 5 in Paper III[2] relating g and the weight-average number of branch points n_w.

Branching indices calculated in this way should be considered relative measures of the amount of long chain branching in polyethylene rather than representative of the true weight-average number of branch points. Several assumptions in the derivation are probably unrealistic for polyethylene.[18] Furthermore, no correction is made for the effect of molecular weight distribution on the variations in the ratio of viscosity-average to weight-average molecular weight.[19]

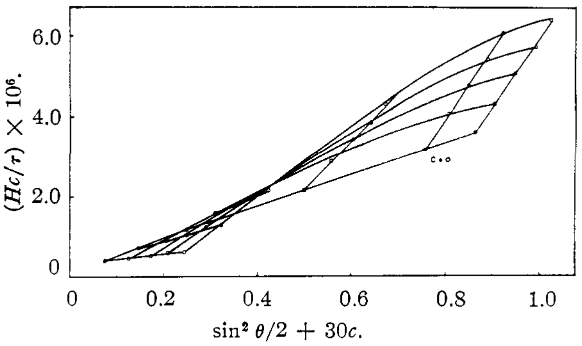

Fig. 2.—Zimm plot from unclarified solution of polyethylene sample 10.

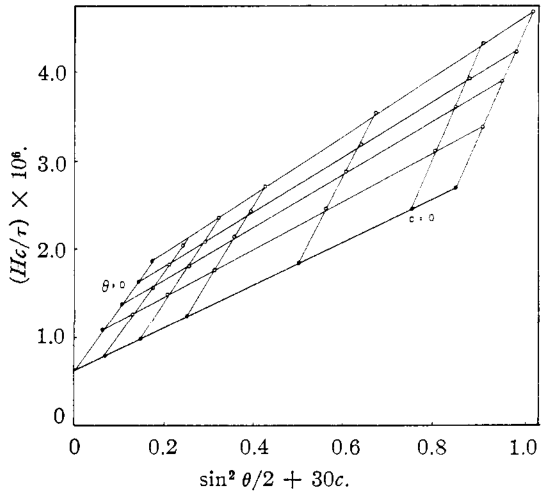

Fig. 3.—Zimm plot of bottom solution polymer from polyethylene sample 10.

Discussion

The molecular weight distribution is quite wide for samples 10, 13 and 49, since $\bar{M}_w/\bar{M}_n$ is in the range 11–18. In addition to removal of particulate matter, ultracentrifugation results in some fractionation. The ratio of weight-average molecular weight of the top solution polymer to that of the bottom solution polymer is ten for sample 10 and slightly less than three for sample 13. The ratios reflect the wide molecular weight distribution.

The second virial coefficient and the z-average root-mean-square radius of gyration depend upon both molecular weight and long chain branching index. The second virial coefficient decreases with increase of both molecular weight and long chain branching. The z-average root-mean-square radius of gyration also increases with increasing molecular weight, but it decreases with increasing long

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

[15] C. D. Thurmond and B. H. Zimm, *J. Polymer Sci.*, **8**, 477 (1952).

[16] J. T. Atkins, L. T. Muus, C. W. Smith and E. T. Pieski, THIS JOURNAL, **79**, 5089 (1957) (paper IX of this series).

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

[18] See the discussion in references 2, 14 and 17.

[19] S. W. Hawkins in P. Morgan, editor, "Plastics Progress 1955, Papers and Discussions at the British Plastics Convention, 1955," Philosophical Library, New York, N. Y., 1956.

chain branching. The number of samples of branched polyethylene examined so far is too limited to separate the effect of long chain branching from that of molecular weight. For the samples examined, long chain branching increases with increasing weight-average molecular weight (Tables I and II).

Taken as functions of molecular weight only, the second virial coefficient (A_2) and the z-average root-mean-square radius of gyration $\sqrt{\overline{s_z^2}}$ may be represented by the equations

$$A_2 = 0.14\bar{M}_w^{-0.75} \text{ ml. mole g.}^{-2} \quad (4)$$

$$\sqrt{\overline{s_z^2}} = 0.5\bar{M}_w^{0.50}\text{Å}. \quad (5)$$

The effect of long chain branching is reflected in both equations. In the first equation, long chain branching results in an exponent numerically larger than that for linear polymers, such as polymethyl methacrylate.[6,20]

In the second equation, the effect of long chain branching is to give an exponent smaller than that for polymethyl methacrylate.[5b]

It is noteworthy that Zimm plots essentially linear with $\sin^2(\theta/2)$ are obtained from samples of branched polyethylene with a known wide molecular weight distribution and a rather high weight-average molecular weight. Wide molecular weight distribution combined with high weight-average molecular weight may lead to curvature toward the angle coördinate axis of the locus of zero concentration points.[3-5] On the other hand, long chain branching may result in curvature in the opposite direction.[3] A linear Zimm plot is likely when the effects of both molecular weight distribution and long chain branching are small.

The curvature due to molecular weight distribution may be small as seen from the calculations of Zimm[3] and of Benoit and his co-workers.[5a] Their calculations assume the distribution function suggested by Schulz[21] for randomly coiled unbranched molecules. Application of this distribution function to eq. 1 indicates a smooth curvature for the locus of zero concentration points in the reciprocal intensity plot. The curvature is away from the angle coördinate axis for $\bar{M}_w/\bar{M}_n < 2$, in the opposite direction for $\bar{M}_w/\bar{M}_n > 2$. An increase in the width of the distribution from $\bar{M}_w/\bar{M}_n = 3$ to $\bar{M}_w/\bar{M}_n = 21$ results in a drastic reduction in the rate with which $P^{-1}(\theta)$ approaches its asymptote.[5]

The Schulz–Zimm weight distribution function is assumed representative of the actual distribution in typical long-chain branched polyethylenes, although its initial vertical slope for $\bar{M}_w/\bar{M}_n > 2$ and its limit of $\bar{M}_z/\bar{M}_w \leqslant 2$ are probably unrealistic features for this polymer.[22] The function $P^{-1}(\theta)$ was calculated for samples of linear polyethylene with $\bar{M}_n = 28{,}000$ and $56{,}000$ and $\bar{M}_w/\bar{M}_n = 21$ ($\bar{M}_w = 588{,}000$ and $1{,}176{,}000$). The calculations apply to measurement with 5461 Å. light in α-chloronaphthalene at 125°. The root-mean-square length of a monomer unit in polyethylene was estimated as 4.9 Å. following the usual procedure.[3,24]

For both samples the locus of zero concentration points was found to have only a slight curvature toward the angle coördinate axis. Weight-average molecular weights can be determined with confidence from the best straight lines through the experimental points. The z-average root-mean-square end-to-end distances calculated from these lines are low by 3 and 5%, respectively, for the samples with $\bar{M}_w = 588{,}000$ and $\bar{M}_w = 1{,}176{,}000$.

Conclusions

1. Zimm plots linear in the angle coördinate were obtained for both whole polymers and ultracentrifuge fractions of branched polyethylene with weight-average molecular weight in the range 350,000–1,500,000.

2. The molecular weight distribution of branched polyethylene is wide, as evidenced by ratios of weight-to number-average molecular weight in the range 11–18.

3. For some samples of branched polyethylene, a small fraction of particulate matter must be removed before light scattering measurement. Elevated temperature ultracentrifugation proved effective for the removal.

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(20) E. F. Casassa, Thesis, Massachusetts Institute of Technology, Cambridge, Massachusetts, 1953.

(21) G. V. Schulz, *Z. physik. Chem.*, **B43**, 25 (1939).

(22) The distribution function suggested by Beasley in Paper IV of this series[23] is not applicable for our purpose, since $\bar{M}_z/\bar{M}_w = 3(1 - 2\beta)/2(1 - 3\beta)$ goes to infinity when the branching parameter β approaches 1/3, corresponding to $\bar{M}_w/\bar{M}_n = 4$.

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

(24) W. J. Taylor, *J. Chem. Phys.*, **16**, 257 (1948).