[Contribution from the Polychemicals Department, E. I. du Pont de Nemours and Company, Inc.]

The Molecular Structure of Polyethylene. VIII. Number-average Molecular Weight by Cryoscopy[1]

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The number-average molecular weight of polyethylene is determined by cryoscopy. The freezing point depression of a solution of polyethylene in hexachlorobenzene is measured using a thermistor as temperature sensing element. The precision of the freezing point depression is approximately 1×10^{-4}°. The reproducibility is ±10% over the molecular weight range 5,000–50,000. The number-average molecular weight of polyethylene obtained from cryoscopy correlates well with that from osmotic measurement when diffusion of low molecular weight species is low. There is no simple correlation between the number-average molecular weight of polyethylene and either solution viscosity or melt viscosity (melt index).

Introduction

Measurement of the number-average molecular weight of polyethylene has been made by osmometry,[2] ebullioscopy[2b,3] and cryoscopy.[2c] The osmotic technique commonly used for measuring number-average molecular weight was shown[4] in Paper III of this series to be complicated for several samples of polyethylene by diffusion of low molecular weight species through the osmotic membrane. The ebullioscopic method appears[3c] to be limited by the tendency of a polyethylene solution to froth or foam.

This paper describes an improved cryoscopic technique for measuring the number-average molecular weight of polyethylene. The method is free from the difficulties encountered in osmometry and ebullioscopy. The molecular weight by this technique is compared to that from osmometry and discussed for fractionated and extracted samples.

The number-average molecular weight is important in kinetic calculations and in correlating with polymer properties. It has been tempting to seek simple relations between the number-average molecular weight and more readily measured quantities such as solution or melt viscosity. Such relations might not be expected to have wide validity for a polymer with a complex molecular structure such as polyethylene. The cryoscopic method gives data against which the validity of several of these relations is tested.

Experimental

Samples.—The polyethylene samples used in this paper are Fawcett-type[5] (branched, high-pressure, free-radical) polyethylenes. Some of the samples are characterized further in Paper VII of this series.[6]

Cryoscopic Apparatus.—Thermistors are well suited for the detection of small differences in temperature. The Western Electric 14A thermistor used in this work consists of manganese, nickel and cobalt oxides formed into a bead about 1 mm. diameter. The bead together with lead wires is sealed into a soft glass sheath.

The thermistor is used as one leg of a bridge circuit. Opposite the thermistor is a five decade precision resistance box of 1000 ohms. A Brown Electronik Recorder modified by addition of a bridge circuit to read approximately 0.01° full span records the resistance and the change in resistance as a function of temperature.

The cryoscopic tube is a 32 mm. "Pyrex" cylinder, 9.5" long, with a standard taper grind. An indentation at the bottom serves as a bearing for a rotating stirrer. The tube is wrapped with 19 feet of Glass-Ohm wire. It is held by a rubber stopper inside a 53 mm. diameter × 8" long glass jacket. The jacket provides a stagnant air space to help control heat transfer. The cap to the cryoscopic tube has openings for the thermistor and the agitator shaft, and an inlet tube for purified nitrogen.

Hexachlorobenzene is used as the solvent. Commercial material is purified by three recrystallizations from benzene followed by drying in a circulating air oven. The high freezing point of hexachlorobenzene (230°) ensures that the solid phase on freezing is solvent only.

Freezing Point Determination.—One hundred grams of purified hexachlorobenzene is introduced into the cryoscopic tube suspended in an oil-bath at 220 ± 0.5°. The solvent is melted by the heater. The thermistor is inserted and the solvent allowed to freeze. The freezing point is recorded on the upper part of the recorder chart. The solvent is melted and frozen several times to establish the freezing point of the pure solvent. A 0.5-g. sample of polyethylene is now added. The freezing point depression for the solution is determined by repetition of the heating and cooling cycle to ensure complete solution of the polymer. The freezing point depression is measured with several increments of polymer. A calibration is finally made by adding known amounts of tristearin (molecular weight 891).

The freezing point depression of hexachlorobenzene was calibrated with terphenyl (molecular weight 230) as well as tristearin. In typical calibrations, the molar freezing point depression per 100 grams of solution, expressed in recorder chart divisions, was found as 4.88 and 4.98×10^{-5} for terphenyl, and 4.96, 5.12 and 5.26×10^{-5} for tristearin.

To calculate the number-average molecular weight, the quantity $\Delta D/c$ is plotted against c, where ΔD is the freezing point depression in recorder chart divisions, and c is the polymer concentration per 100 g. solution. Typical data are shown in Fig. 1. Number-average molecular weights are calculated from the intercepts of the plots at $c = 0$

$$\bar{M}_n = [891(\Delta D_T/c)_{c=0}]/[(\Delta D_P/c)_{c=0}]$$

where the subscript T denotes tristearin and P polyethylene.

The second virial coefficients from Fig. 1 are in the range $1\text{–}2 \times 10^{-3}$ ml. mole. g.$^{-2}$.

The freezing point depression is read to one chart division, equivalent to approximately 1×10^{-4}°. The reproducibility is about ±10% over the molecular weight range from 5,000 to 50,000.

Melt and Solution Viscosity.—Melt viscosity is measured in terms of melt index[7] by ASTM Method D 1238–52.

Solution viscosity is measured in α-chloronaphthalene at 125°. Solution viscosity is expressed as inherent viscosity

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[1] Presented at the 129th National Meeting of the American Chemical Society, Dallas, Texas, April 11, 1956.

[2] (a) M. S. Muthana and H. Mark, *J. Polymer Sci.*, **4**, 527 (1949); (b) I. Harris, *ibid.*, **8**, 353 (1952); (c) K. Ueberreiter, H.-J. Orthmann and G. Sorge, *Makromol. Chem.*, **8**, 21 (1952); (d) S. H. Pinner and J. V. Stabin, *J. Polymer Sci.*, **9**, 575 (1952); (e) McCrae, quoted by 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.

[3] (a) H. Morawetz, *J. Polymer Sci.*, **6**, 117 (1951); (b) N. H. Ray, *Trans. Faraday Soc.*, **48**, 809 (1952); (c) H. Smith, quoted by 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.

[4] F. W. Billmeyer, Jr., This Journal, **75**, 6118 (1953).

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

[6] W. L. Peticolas and J. M. Watkins, This Journal, **79**, 5083 (1957).

[7] J. P. Tordella and R. E. Jolly, *Modern Plastics*, **31**, no. 2, 146 (October, 1953).

at concentration 0.1 g./100 ml. It is within 1–2% of intrinsic viscosity.

Osmometry.—Number-average molecular weight by osmometry was measured by F. W. Billmeyer, Jr., using the technique described in Paper III.[4]

Results

Comparison of Osmometry and Cryoscopy.—Table I lists number-average molecular weights from osmometry and cryoscopy.[8] The osmotic results are higher than those from cryoscopy. The difference is attributed to diffusion of low molecular weight species through the osmotic membrane.

TABLE I

NUMBER-AVERAGE MOLECULAR WEIGHT FOR POLYETHYLENE

Sample	$\bar{M}_{os}$(osmometry)	$\bar{M}_n$(cryoscopy)
32	50,000	45,000
6	37,000	31,000
4	31,000	25,000
31	28,000	21,000

Fractionated Sample.—Table II compares the cryoscopic molecular weight for a whole polymer with those of three crude fractions of the sample obtained by the technique described in Paper III.[4] The molecular weight calculated for the whole polymer is in good agreement with that observed for the original sample.

TABLE II

NUMBER-AVERAGE MOLECULAR WEIGHT FOR POLYETHYLENE SAMPLE 63 AND ITS FRACTIONS

Sample	% in Fraction	$\bar{M}_n$ (cryoscopy)
Top fraction	29	32,000
Middle fraction	27	22,000
Bottom fraction	44	12,000
Whole polymer (obsd.)		18,000
Whole polymer (calcd.)		20,000

Extracted Samples.—Table III shows the cryoscopic molecular weight of eight polyethylenes before and after extraction of less than one per cent. of the sample with diethyl ether. Extraction results in a substantial increase in number-average molecular weight, whereas the change in melt index is small, less than 0.5 unit. Infrared examination indicates that the extracted material is essentially low molecular weight polyethylene.

TABLE III

CHANGE IN NUMBER-AVERAGE MOLECULAR WEIGHT OF POLYETHYLENE ON EXTRACTION WITH DIETHYL ETHER

	$\bar{M}_n$ (cryoscopy)	
Sample	Before extraction	After extraction
49	32,000	58,000
50	26,000	80,000
69	17,000	31,000
70	20,000	44,000
71	21,000	35,000
72	16,000	24,000
73	27,000	45,000
74	32,000	58,000

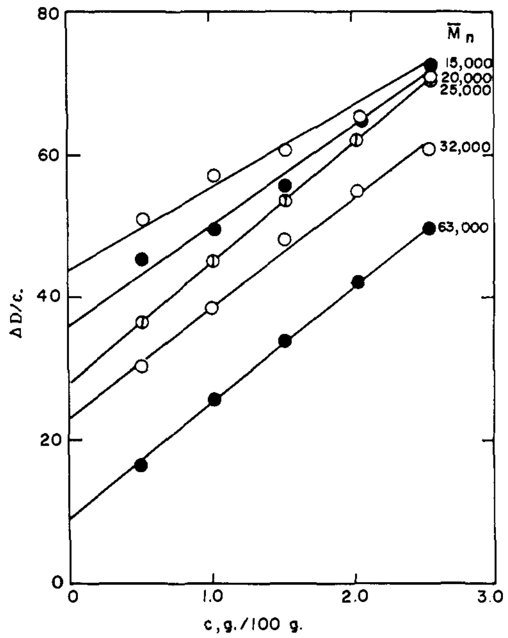

Fig. 1.—Freezing point depression–concentration plots for typical polyethylenes.

Discussion

Applicability of the Cryoscopic and Osmotic Techniques.—The cryoscopic method probably gives the true number-average molecular weight of polyethylene. The osmotic technique, on the other hand, is complicated by the diffusion of low molecular weight species through the osmotic membrane. As shown by the extraction experiments, many samples contain small amounts of low molecular weight material with a pronounced influence on the number-average molecular weight.

The number-average molecular weight by cryoscopy is defined as

$$(\bar{M}_n)\text{cryoscopy} = \left(\sum_{i=1}^{\infty} M_iN_i\right)\Big/\left(\sum_{i=1}^{\infty} N_i\right)$$

where N_i is the number of moles of species i with molecular weight M_i. In contrast, the number-average molecular weight by osmometry is given by

$$(\bar{M}_n)\text{osmometry} = \left(\sum_{i=j}^{\infty} M_iN_i\right)\Big/\left(\sum_{i=j}^{\infty} N_i\right) > (\bar{M}_n)\text{cryoscopy}$$

assuming that species lower in molecular weight than the jth diffuse through the membrane. It is an experimental fact that many commercial samples of polyethylene contain a significant amount of low molecular weight material. Accordingly, the number-average molecular weight by cryoscopy is lower than that by osmometry.

The effect of diffusion is illustrated in Fig. 2. Comparison is made between cryoscopic and osmotic data from this paper as well as between ebullioscopic measurements by Smith[3c] and osmotic results by McCrae.[2e] The estimated error of the data from this paper is shown by a rectangle. The error in Smith's data is taken as the spread in molecular weight observed in different solvents and indicated in Fig. 2 by points connected with dashed lines.

Molecular Weight Distribution.—The ratio of weight-average to number-average molecular weight, $\bar{M}_w/\bar{M}_n$, is often used as a measure of the breadth of the molecular weight distribution. Table

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[8] Sample designations are the same as those in other papers of this series.

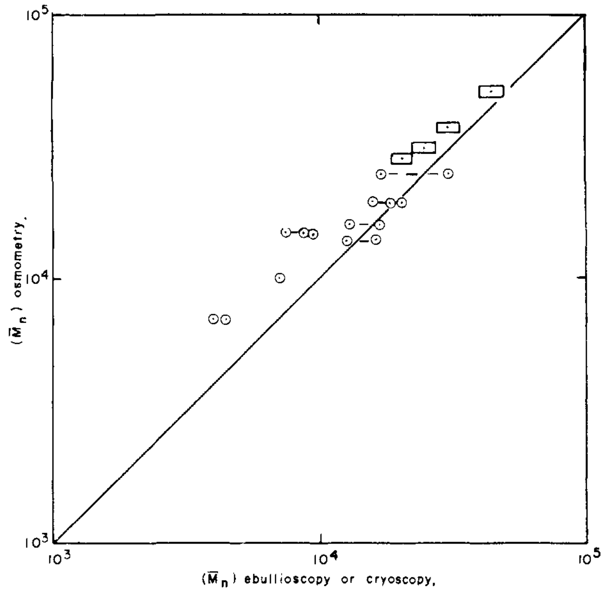

Fig. 2.—Comparison of number-average molecular weight of polyethylene by osmometry with that by cryoscopy and ebullioscopy: ⊡, this paper; ⊙, Smith[3c] and McCrae.[2e]

IV lists $\bar{M}_w/\bar{M}_n$ obtained by combining the cryoscopic number-average molecular weights from this paper with weight-average molecular weights determined by the techniques of papers VI[9] and VII.[6] The wide molecular weight distribution and the sample-to-sample variation in distribution breadth are typical of commercial branched polyethylene.

Table IV

Weight- and Number-average Molecular Weight for Polyethylene

Sample	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
4	25,000	200,000	8
6	31,000	440,000	14
31	21,000	145,000	7
32	45,000	1,000,000	22
49	32,000	350,000	11
50	26,000	900,000	35
52	28,000	600,000	22
66	50,000	450,000	9
68	54,000	350,000	6

Inherent Viscosity.—Table V suggests no simple relation between number-average molecular weight from cryoscopy and inherent viscosity. Such relations[2b,2c] were proposed for a limited series of samples, but are not substantiated by our data. Further discussion is presented in Papers III,[4] VI[9] and IX.[10]

Table V

Number-average Molecular Weight by Cryoscopy and Solution and Melt Viscosity of Typical Polyethylenes

Sample	$\bar{M}_n$	η_i	Melt index
49	32,000	0.75	2.1
50	26,000	.75	2.0
52	28,000	.78	2.1
64	33,000	1.00	0.3
65	18,000	0.77	3.7
66	50,000	.76	2.0
67	48,000	.72	3.0
68	54,000	.76	2.2

This result shows that solution viscosity should be used only with extreme caution for the determination of number-average molecular weight of polyethylene.

Melt Viscosity.—The data listed in Table III show that relatively large changes in number-average molecular weight take place at almost constant melt index on extraction. Together with the melt indices in Table V, these data show that the empirical relationship given in Paper V[11] between melt index and number-average molecular weight is not substantiated for our samples.

This result, together with the work in Paper VII,[6] shows that the melt viscosity of polyethylene is more directly related to its weight-average molecular weight. The use of melt viscosity to estimate number-average molecular weight of a particular sample is in general unwarranted.

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[9] L. T. Muus and F. W. Billmeyer, Jr., This Journal, **79**, 5079 (1957).

[10] J. T. Atkins, L. T. Muus, C. W. Smith and E. T. Pieski, *ibid.*, **79**, 5089 (1957).

[11] C. A. Sperati, W. A. Franta and H. W. Starkweather, Jr., *ibid.*, **75**, 6127 (1953).