

Orofino and Fox.<sup>30</sup> (Equation 6 ( $p = 3$ ) was also obtained by these authors.)

### Conclusion

In summary, we are forced to conclude that no definitive evidence for the unique applicability of any of the eq. 2-4 has yet been exhibited on the basis of combined viscometric and absolute molecular weight data alone. This inadequacy may be traced directly to failure of any of the theories to describe adequately the data for low molecular weight ( $M < 10^5$ ) systems. This uncertainty makes analysis of data restricted to good solvents to determine the thermodynamic parameter  $B$  and/or the chain extension parameter  $A^3$  hazardous since the values obtained depend directly on the extrapolation procedure employed which in turn depends on which of the eq. 2-4 are used.

Similarly, attempts to extrapolate  $[\eta]$  vs.  $M$  correlations to molecular weights higher than those explicitly studied are liable to yield erroneous results unless the correct set of relations is used. That is, any of the relations 2-4 could very well fit a given set of data in a good solvent over a restricted molecular weight

(30) T. A. Orofino and T. G. Fox, Aeronautical Systems Division Report ASD-TR 61-22, Part I, United States Air Force, Wright-Patterson Air Force Base, Ohio.

range (with a different value of  $BA^{-3}$  for each relation to be sure) with acceptable precision, but still yield quite different correlations at higher (or lower) molecular weights. Indeed,  $[\eta]$ - $M$  data on the system polystyrene-benzene<sup>19</sup> correlate with either eq. 2 ( $p = 5/2$ ) or with eq. 4 with about the same precision over the molecular weight span  $10^4 < M < 2 \times 10^6$ , although the values of  $BA^{-3}$  so obtained differ by a factor of 3. These calculated  $[\eta]$  vs.  $M$  curves differ considerably, however, by the time  $M$  is ca.  $10^7$ .

It is suggested that the most reliable evaluation of viscosity-molecular weight relationships may involve examination of  $[\eta]$ - $M$  data as a function of temperature for systems where there is *a priori* knowledge of the thermodynamic parameter  $B$  (as well as  $A^3$ ) as a function of temperature, that is, knowledge of  $\psi_1$  and  $\theta$ . Further, it is suggested that examination of the Mark-Houwink-Sakurada coefficient  $\nu$  at high molecular weight (high  $\alpha_\eta$ ) should provide a basis for a reasonable choice between at least some of the relations 2-4.

**Acknowledgment.**—We acknowledge the assistance of R. E. Kerwin on some of the numerical calculations required at certain stages of this evaluation. This study was supported in part by the Research and Technology Division, Air Force Materials Laboratory, under Contract No. AF 33(657)-10661.

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

## The Molecular Structure of Polyethylene. XV. Comparison of Number-Average Molecular Weights by Various Methods<sup>1</sup>

By F. W. BILLMEYER, JR., AND V. KOKLE

RECEIVED APRIL 2, 1964

Number-average molecular weight was determined for samples of both linear and branched polyethylenes by at least two of the thermodynamic methods of osmometry, cryoscopy, and ebulliometry, the kinetic method of thermoelectric differential vapor pressure, and the chemical method of end-group analysis. Within the known limitations of each technique, the agreement among methods was excellent, the results of three different methods often falling within a range of less than 5%.

### Introduction

Measurement of the molecular weight of high polymers has been a subject of great scientific and technological importance ever since the macromolecular nature of these compounds was proved in the early 1920's. Very few new techniques for these measurements have been developed since that time, however, the latest of these with a thermodynamic basis being the light scattering method of Debye<sup>2</sup> yielding information on particle size as well as the weight-average molecular weight and second virial coefficient. More recently, a kinetic method has been proposed<sup>3</sup> for the determination of the number-average molecular weight, and several older techniques have been improved or applied for the first time to random-coil polymers.

This paper considers several methods for determining the number-average molecular weight in application

at elevated temperature to branched and linear polyethylene. These techniques include osmometry, cryoscopy (as described in paper XIII of this series<sup>4</sup>) and ebulliometry,<sup>5</sup> the above-mentioned thermoelectric differential vapor pressure method,<sup>3</sup> and the chemical method of end-group analysis by infrared spectroscopy. The purpose of this research was to define the range of applicability of each of the above methods and to demonstrate the validity of the results of kinetic and chemical methods in application to the polyethylene system. This involves comparisons among the results of the various methods; other comparisons of this type were presented in paper XI of this series<sup>6</sup> for number-average molecular weights determined by osmometry and cryoscopy and in paper XIV<sup>7</sup> for weight-average molecular weights determined by light scattering and by Archibald ultracentrifugation.

(1) Previous papers in this series are published in *J. Am. Chem. Soc.*, **75**, 6110 (1953); **79**, 5079 (1957); **81**, 3219 (1959); *J. Polymer Sci.*, **62**, 251 (1961); **A1**, 1921 (1963); and an article in press; and *J. Phys. Chem.*, **67**, 2728 (1963).

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TABLE I  
 NUMBER-AVERAGE MOLECULAR WEIGHT OF POLYETHYLENE BY VARIOUS METHODS

Method	Solvent	T, °C.	Sample						
			75	76	77	99	99H	99L	101
Osmometry	Xylene	105	(30,300)	(26,600)	(31,400)	...	40,100 40,800 40,800	...	...
Cryoscopy	Hexamethylbenzene	165.5	10,700	13,300	19,100	7400 <sup>a</sup> 8860	...	3450 3250 3250	11,800
Ebulliometry	Toluene	111	10,900	...	...	...	...	...	...
	<i>n</i> -Octane	125	11,400	...	18,400	...	...	...	...
Thermoelectric DVP	<i>n</i> -Decane	100	10,900 <sup>b</sup>	16,100 <sup>b</sup>	18,600 <sup>b</sup>	...	...	3504	...
	<i>o</i> -Dichlorobenzene <sup>c</sup>	130	...	...	...	8600	38,400	3507	11,900
End groups by infrared	...	...	...	...	...	8100	37,400	4800	11,700

<sup>a</sup> Average of several experiments (paper XIII). <sup>b</sup> Calibration with octacosane. <sup>c</sup> Calibration with tristearin.

### Experimental

**Samples.**—Polyethylene samples 75, 76, and 77 are branched high-pressure Fawcett-type<sup>8</sup> polyethylenes. Samples 99 and 101 are essentially linear polyethylenes made in low pressure syntheses.

**Osmometry.**—Osmotic pressure measurements were made using Stabin osmometers<sup>9</sup> with 450 gauge undried cellophane membranes, following the technique described in paper XI.<sup>8</sup> The solvent was reagent grade xylene (mixed isomers), and the operating temperature was 105°.

**Cryoscopy.**—Cryoscopic measurements were made using the apparatus and techniques described in paper XIII.<sup>4</sup> The solvent was hexamethylbenzene (m.p. 165.5°). Nucleation of the solvent in the cryoscopic tube was controlled by the addition of 0.3% finely divided CdI<sub>2</sub>. Octacosane (mol. wt. 395) and pentatricontane (mol. wt. 493) were used as calibration standards.

**Ebulliometry.**—Ebulliometric measurements were performed by M. Ezrin of the Monsanto Chemical Co. (to whom we are indebted for the results) using an ebulliometer of the Schön and Schulz type<sup>10</sup> as modified by Ezrin and Claver.<sup>5</sup> The solvents were toluene (b.p. 111°) and *n*-octane (b.p. 125°).

**Thermoelectric Differential Vapor Pressure Lowering.**—Measurements were carried out in a Mechrolab Model 302 vapor pressure osmometer (Mechrolab, Inc., Mountain View, Calif.). The solvents and operating temperatures were *n*-decane at 100° for the branched polyethylene samples and sample 99L, and *o*-dichlorobenzene at 130° for the linear polyethylenes. Octacosane (mol. wt. 395) and tristearin (mol. wt. 891.5) were used as calibration standards.

**Infrared Spectroscopy.**—The molar concentration of the vinyl group, RCH=CH<sub>2</sub>, was determined by infrared spectroscopy using pressed film samples, a Perkin-Elmer Model 21 spectrometer (Perkin-Elmer Corp., Norwalk, Conn.) with NaCl optics, and the techniques described in paper II.<sup>11</sup> The functional group absorption coefficient for the vinyl band at 11.00 μ was taken as 50.3 following Anderson and Seyfried.<sup>12</sup> From this value it follows that

$$\bar{M}_n = 123,000dt/K \quad (1)$$

where  $d$  is density (g./cm.<sup>3</sup>),  $t$  is thickness (cm.), and  $K$  is absorbance at 11.00 μ corrected for background. The latter correction is made with respect to a straight base line drawn between absorption minima at approximately 10.59 and 11.53 μ.

**Viscometry.**—Dilute solution viscosity was measured in  $\alpha$ -chloronaphthalene at 125° by the technique described in paper III.<sup>13</sup> Results are reported as the inherent viscosity at a polymer concentration of 0.5 g./dl.

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(12) J. A. Anderson, Jr., and W. D. Seyfried, *Anal. Chem.*, **20**, 998 (1948). See also R. J. deKoch and P. A. H. M. Hol, *Polymer Letters*, **2**, 339 (1964).

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**Fractionation.**—Fifty grams of sample 99 was dissolved in approximately 1.5 l. of distilled xylene (mixed isomers). The solution was poured onto approximately 6 kg. of No. 11 glass beads (150–250-μ diameter, Potters Bros., Inc., Carlstadt, N. J.) preheated to 130° in a resin kettle in an oil bath. The polymer was precipitated onto the beads by slow cooling (5°/hr.) to room temperature. The coated beads were then placed, on top of a layer of clean beads, in a fractionation column placed in a temperature-controlled oil bath.

The column was filled with xylene and the apparatus heated to about 85°. At this point, continuous extraction was initiated with the column temperature being raised about 1°/hr. through control of the bath temperature. A total of 15 l. of eluent was collected in a 9-hr. period over the temperature range 86.3–94.4°. The final temperature was chosen on the basis of preliminary experiments to give approximately 50% of the polymer in the eluent. This polymer constituted the low molecular weight fraction 99L. An additional 4 l. of xylene eluent was collected after the column had remained at 94.4–94.7° for 4 hr., but this eluent failed to show turbidity on cooling to room temperature and thus must have contained very little polymer.

The column temperature was then raised to 137° with the collection of 15 l. of eluent containing the high molecular weight fraction 99H.

The fractions were recovered by concentration of the eluent to ca. 2.5 l. through vacuum evaporation of solvent with a nitrogen bleed with mild heating, followed by re-solution at elevated temperature and precipitation in an excess of cold distilled methanol. The precipitates were exhaustively washed with methanol and, finally, vacuum-dried to constant weight at 68°.

### Results

Table I lists the number-average molecular weights of the polyethylene samples discussed in this paper, as determined by the methods outlined above. In the case of the thermoelectric differential vapor pressure method, two results are given when the two calibration standards disagreed slightly. It is felt that this discrepancy results from slight impurity of one or the other calibration substance. Occasionally, results from several successive experiments are listed to illustrate the reproducibility of the method. (Cryoscopy of sample 99 is discussed further in paper XIII.<sup>4</sup>)

Data pertinent to the fractionation of sample 99 are listed in Table II. Recovery (99.7%) was essentially complete, and the inherent viscosities of the fractions added, in proportion to their weight fractions, to the viscosity of the whole polymer, both as measured prior to fractionation and as reconstituted from the fractions.

### Discussion

**Thermoelectric Differential Vapor Pressure Lowering.**—The basis of the thermoelectric method<sup>3,5</sup> is the meas-

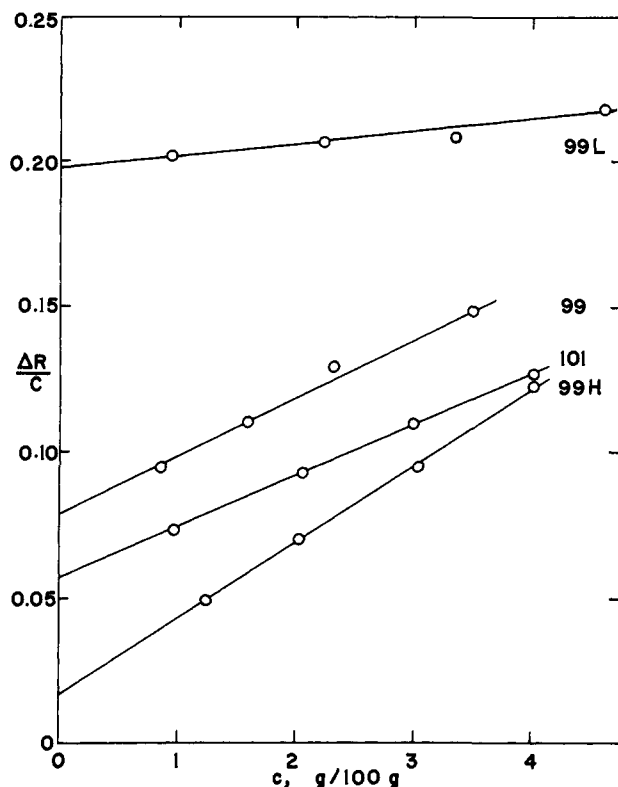


Fig. 1.—Reduced difference in resistance,  $\Delta R/c$ , plotted against polymer concentration for thermoelectric differential vapor pressure lowering of solutions of the designated polyethylene samples in *o*-dichlorobenzene at 130°.

TABLE II  
FRACTIONATION OF POLYETHYLENE SAMPLE 99

Sample	% of polymer	Inherent viscosity, dl./g.
99L	43.77	0.4994
99H	55.93	1.5443
Whole polymer, obsd.	99.70 <sup>a</sup>	1.108, 1.110
Whole polymer, calcd.	(100.0)	1.086
Whole polymer, obsd. on reconstituted fractions	...	1.110, 1.109

<sup>a</sup> Per cent recovery.

urement of the small temperature difference resulting from different rates of solvent evaporation from droplets of pure solvent and polymer solution maintained in an atmosphere of solvent vapor. As pointed out by Burge,<sup>14</sup> the important assumption to be tested is that this temperature difference is proportional to the difference of chemical potential between the pure solvent and the solvent in the solution. This propor-

(14) D. E. Burge, *J. Phys. Chem.*, **67**, 2590 (1963).

tionality relates the thermodynamic properties of the solution to the temperature difference established by transport processes. If it is approached at high dilution, molecular weights found by extrapolation to zero concentration will be valid; if it holds over the entire concentration range, the second virial coefficient can also be obtained. The first requirement appears to be met adequately for both linear and branched polyethylene under the conditions of this research. We have no independent values for the second virial coefficient of polyethylene in *o*-dichlorobenzene, but the apparent second virial coefficient from the thermoelectric method for sample 75 in decane solution at 100°,  $4.0 \times 10^{-4}$  ml. mole g.<sup>-2</sup>, may be compared with that for an essentially identical polymer, sample 94, measured by light scattering using the same solvent and temperature,  $1.6 \times 10^{-4}$  ml. mole g.<sup>-2</sup> (paper XI<sup>6</sup>). The agreement is reassuring but hardly conclusive.

Typical data from the thermoelectric method are shown in Fig. 1.

**End Group Analysis.**—The validity of the interpretation of vinyl group absorbance at 11.00  $\mu$  as an analysis for end groups is restricted to those polymers for which it can be established, through considerations of synthesis conditions, that one and only one such group appears per molecule. Samples 99 and 101 were made in such a manner. The relatively poor agreement between the infrared and other methods in the case of sample 99L may be attributed to the concentration of species for which the above statement is not true in the low molecular weight fraction of this polymer.

**Osmometry.**—As discussed in paper XI,<sup>6</sup> osmotic results for unfractionated branched polyethylenes, given in parentheses in Table I, are grossly in error due to diffusion of low molecular weight species through the osmotic membrane. Even in sample 99H, largely free of low molecular weight species, there is the suggestion that the osmotic results are too high, although osmotic heights were not observed to change with time in these measurements.

**Fractionation.**—The fractional extraction of sample 99 may have been carried out, in part, below the crystalline melting point. If so, fractionation may not have occurred entirely according to molecular weight. This was of no consequence to us, since the experiment was not designed to obtain a sharp separation or information on molecular weight distribution, and the results in Table I are unaffected.

Values of  $\bar{M}_n$  for sample 99 calculated from the number-average molecular weights for fractions range between 7000 and 9500, depending on the value of  $\bar{M}_n$  chosen for sample 99L.