The Characterization of Linear Polyethylene SRM 1475. IX. Number Average Molecular Weight of Fractions by Membrane Osmometry

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The number average molecular weights of a series of fractions of linear polyethylene have been determined using a high speed membrane osmometer. The M_n values of the fractions, which were prepared by an elution technique, were used in GPC calibration and subsequent characterization of linear polyethylene SRM 1475. The molecular weights, measurement techniques, and the precision of the measurements are presented.

Key words: Concentration dependence; linear polyethylene; membrane; number average molecular weight; osmometer; osmotic pressure; virial coefficient.

1. Introduction

In the course of the characterization of the linear polyethylene Standard Reference Material 1475 described in this series of papers [1],[1] the molecular weight distribution was determined [2] by gel permeation chromatography. The gel permeation chromatograph was calibrated with linear polyethylene fractions obtained [3] by a column elution technique. These fractions were characterized for use in the calibration procedure by determining their number- and weight-average molecular weights. Determination of the weight-average molecular weights from light-scattering studies is described elsewhere [4]. In the present paper, we report the determination of the number-average molecular weights, M_n, ranging from about 8,000 to about 350,000, from osmotic pressure measurements.

2. Experimental Procedure

2.1. Apparatus

Osmotic pressure measurements were made with a Hewlett-Packard Mechrolab Membrane Osmometer, Model 502[2]. This instrument, which has been described elsewhere [5], consists essentially of a photocell for detecting liquid flow across a semipermeable membrane, monitored by the motion of a bubble in a capillary tube, and a servomechanism for balancing the osmotic pressure by varying the liquid level on the solvent side of the membrane. It is characterized by rapid response time (of the order of a few minutes with a suitable membrane), negligible solvent transfer across the membrane [6], and small sample volume (about 0.3 ml).

2.2. Membranes

The semipermeable membranes employed were gel cellophane membranes, type 450D, obtained from Arro Laboratories, Inc. When received, they were swollen in an isopropanol-water solution. The following procedure was used to condition them to 1-chloronaphthalene, the solvent used in this work: 24 hours in 50 percent ethanol solution; rinsing with ethanol; 48 hours in ethanol; 24 hours in a 1:1 mixture of ethanol and acetone; 24 hours in a 1:1 mixture of acetone and toluene; rinsing with toluene; 24 hours in toluene; rinsing with 1-chloronaphthalene; heating (with an infrared lamp) in 1-chloronaphthalene under reduced pressure for a minimum of 1 hour, to drive off dissolved gases.

2.3. Procedure

Polyethylene solutions were made up by weight in distilled Fisher reagent grade 1-chloronaphthalene, in concentrations ranging from 0.5 to 12 g/l. Osmotic pressure measurements were made by first placing pure solvent in both sides of the osmometer and recording the level on the solvent side, then flushing out and filling the sample side with one of the solutions and recording the new solvent level. Several measurements were made for each solution. The reference solvent height was checked between solutions by flushing and refilling the sample side with pure solvent. The osmotic pressure for each solution is then given directly as the hydrostatic pressure

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[1] Figures in brackets indicate the literature references at the end of this paper.

[2] Certain commercial equipment, instruments, or materials are identified in this paper in order to adequately specify the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the material or equipment identified is necessarily the best available for the purpose.

difference between solvent and solution. All measurements were made at a temperature of 130 °C.

3. Results and Discussion

In order to obtain values of M_n from the variation of osmotic pressure with solution concentration, we start with the familiar virial expansion, expressed in one of the two equivalent forms:

$$\pi/c = RT\left[\frac{1}{M_n} + A_2 c + A_3 c^2 \ldots\right],$$
$$= (\pi/c)_0\left[1 + \Gamma_2 c + \Gamma_3 c^2 + \ldots\right], \quad (1)$$

where π is the osmotic pressure of a solution of concentration c (weight per unit volume), relative to that of pure solvent, R and T are the gas constant and absolute temperature, respectively, the A's and Γ's are the virial coefficients, and the subscript zero denotes the limit of zero concentration.

According to eq (1), M_n is obtained directly from the zero-concentration intercept of a plot of π/c versus c. Such plots are shown in figure 1 for three typical fractions, PE 7, PE 120, and PE 350. Although the plot for PE 7, the lowest molecular-weight fraction, is essentially linear, the plots for the higher molecular-weight fractions show distinct curvature, and extrapolation to zero concentration presents a problem. In principle, the extrapolation may be performed by fitting π/c to a polynomial in c, thus determining some of the virial coefficients higher than the second. In the present case, however, the precision of the data and the concentration range spanned do not appear to warrant the determination of more than two parameters. We therefore resort to the approximate relationship $\Gamma_3 = \frac{1}{4}\,\Gamma_2^2$, which is frequently found to give
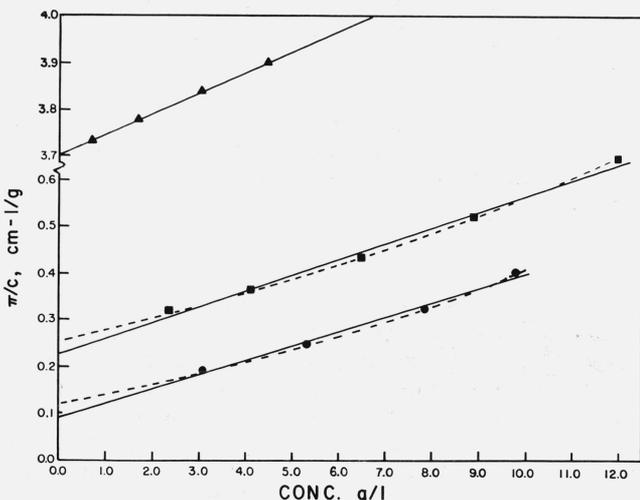
satisfactory results for polymer solutions in good solvents at sufficiently low concentrations [5, 7]. With the aid of this relation, and neglecting terms beyond the third virial coefficient, eq (1) may be rewritten in the form:

$$(\pi/c)^{1/2} = (\pi/c)_0^{1/2}(1 + \tfrac{1}{2}\,\Gamma_2 c). \quad (2)$$

To the extent that the approximations implied in obtaining eq (2) are justified, a plot of $(\pi/c)^{1/2}$ versus c should yield a straight line with a zero-concentration intercept of $(RT/M_n)^{1/2}$ and a slope of $(RT/M_n)^{1/2}\Gamma_2/2$. Figure 2 shows the data of figure 1 replotted as $(\pi/c)^{1/2}$ versus c. The plot is clearly much more nearly linear than that of figure 1. We have therefore used a linear least-squares analysis to fit $(\pi/c)^{1/2}$ to a linear function of concentration, according to eq (2). The dashed lines in figure 1 are plots of eq (2), using the parameters obtained from the least-squares analysis. It is clear that for the higher molecular-weight fractions, use of a simple linear plot would introduce significant errors into the limiting zero-concentration value of π/c, and therefore of M_n.

The results of the least-squares analyses are shown in table 1. The standard deviations for the values of M_n range from about 0.1 percent for PE 7 to 2–4 percent for the higher molecular-weight fractions. For the lower molecular-weight fractions, accuracy is limited by the diffusion of solute through the membrane, as discussed by Staverman et al. [8, 9] and by Tung [10]. From observation of the drift in hydrostatic pressure over periods of an hour or more, we conclude that errors arising from this source are much smaller than the reproducibility of the measurements, even for the lowest molecular-weight fractions reported here. The accuracy of the M_n values for the high molecular-weight fractions is limited primarily by uncertainties arising from the use of the approximate eq (2) to fit the data. In the absence of information on the behavior of the higher virial coefficients, it is very difficult to estimate the uncertainty introduced by the use of eq (2). It is our feeling, however, that for all the fractions, the errors in M_n from all sources are unlikely to exceed 10 percent.

FIGURE 1. *Plots of π/c versus c, where π is osmotic pressure and c is concentration, for solutions of three fractions of linear polyethylene, PE 7 ($\triangle$), PE 120 ($\square$), and PE 350 ($\bigcirc$), in 1-chloronaphthalene.*
The solid lines are the results of linear least-squares fits of π/c versus c; the dashed lines are the results of linear least-squares fits of $(\pi/c)^{1/2}$ versus c.
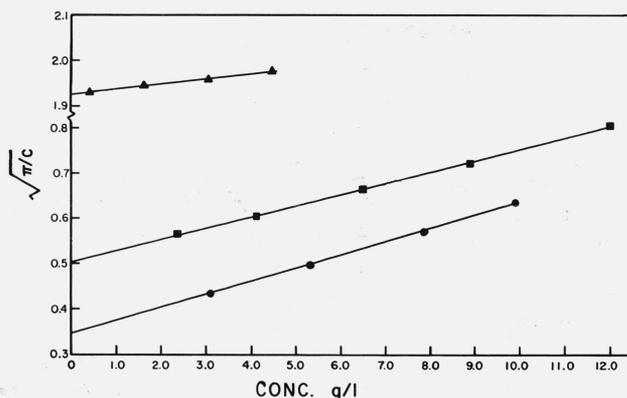
FIGURE 2. *The data of figure 1, replotted as $(\pi/c)^{1/2}$ versus c.*
The solid lines are the results of linear least-squares fits of the data in this form, and are equivalent to the dashed lines in figure 1.