

Molecular Weight Distribution and Swell Properties of Some Low-Pressure Polyethylenes

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Synopsis

The molecular weight distribution of some low-pressure homopolymers of ethylene intended for use in blown bottles have been determined by using a modified sand column technique. A correlation is indicated between the *Z*-average molecular weight \bar{M}_z and the postextrusion swelling of the resin as measured by the weight of a bottle blown from that polymer.

INTRODUCTION

An earlier publication from this laboratory¹ showed how the shear sensitivity of a series of low-pressure polyethylenes, as measured by the so-called flow ratio I_{10}/I_2 , appeared to correlate with the *Z*-average molecular weight \bar{M}_z . The fractionations at that time were carried out by using essentially the sand column method of Francis et al.² with some modifications. Subsequently, the sand column method was modified further in order to reduce the number of man-hours required per fractionation. These modifications and some data concerning molecular weight distribution and swell characteristics of a series of bleach-bottle-grade polyethylenes are the subject of this report.

In spite of the advent of gel permeation chromatography,³ the sand column technique is still a useful procedure. First, it provides fractions that can be further characterized, e.g., by differential thermal analysis.⁴ Second, it can handle certain polymers that because of an excessively high molecular weight tail cannot be run by present techniques on a GPC. The polymers reported here belong to such a group.

EXPERIMENTAL

Fractionation and Characterization

The fractionations were carried out by using an upflow column technique similar to that described by Shyluk⁵ for polypropylene. A diagram of the apparatus is shown in Figure 1. A stirred sample preheater was mounted on top of the main column, both of which are heated with refluxing octane (bp 124.5°C). The sand in the main column was supported on a glass

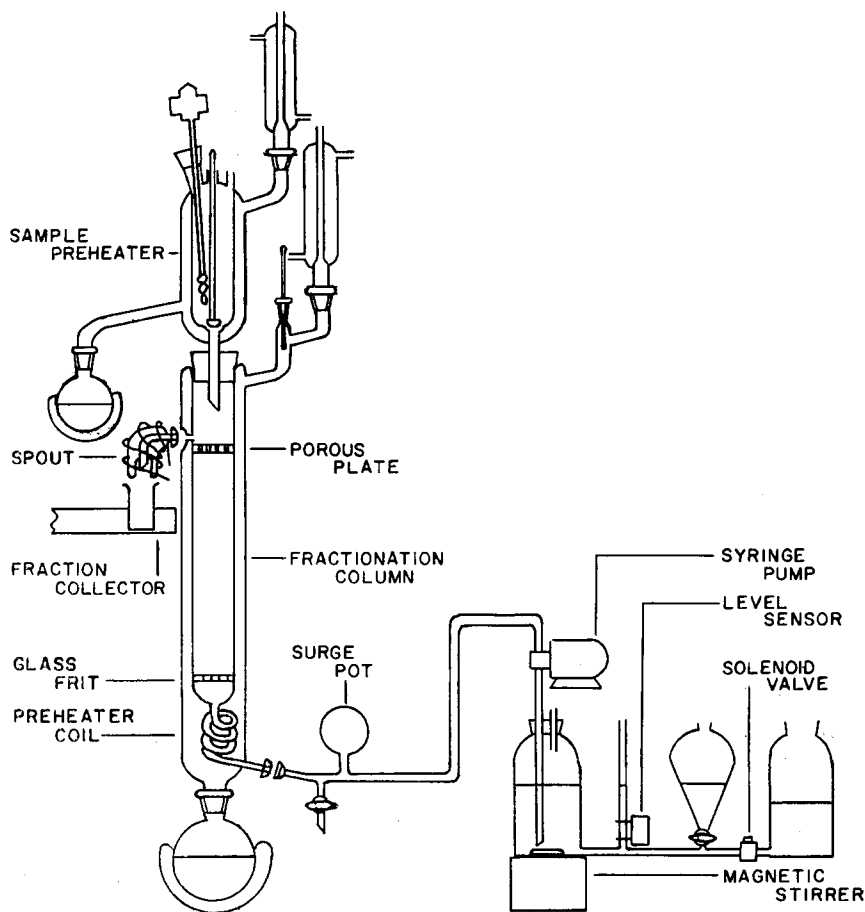


Fig. 1. Fractionation apparatus.

frit and held down with a porous plate just below the outlet. The outlet itself proved to be the most troublesome part of the apparatus because of precipitation of polymer at the tip, which eventually plugged the outlet, leading to flooding of the column. The final design consisted of a vacuum-jacketed, electrically heated spout with a recessed drip tip. Below the sand column but inside the heating jacket were several coils of glass tubing, which acted as a preheater for the incoming solvent-nonsolvent mixture. The whole column was insulated in order to allow slow cooling during polymer deposition on the sand.

The solvent-nonsolvent mixture was pumped into the column by means of a syringe type of metering pump. A surge pot teed into the line helped to reduce the pulsation in the flow to the column. The arrangement of solvent and nonsolvent reservoirs was arrived at by trial and error. From batch fractionation, it had been realized that a slow change in solvent con-

centration in the medium molecular weight range and a rapid change at either end was desirable. In the high molecular weight region the rapid change occurred only during the elution of the last fraction. Hence, the mixing vessel was connected to a pear-shaped separatory funnel and, through a solenoid valve, to a second cylindrical vessel. The solenoid valve was activated by a Thermo-O-Watch controller when the liquid in the mixing vessel fell below a certain level. Thus, as the initial solvent-nonsolvent mixture was pumped out of the mixing vessel, a relatively large amount of solvent was added from the large-diameter upper portion of the separatory funnel but, as the level dropped, so did the relative amount of solvent being added. At the appropriate time the solenoid valve opened, and a large amount of solvent was added from the third vessel. In this manner, slightly less than 3 liters of total solvent-nonsolvent mixture pumped at a rate of 6.5 ml/min was adequate to remove essentially all the polymer from the column in less than 8 hr.

The fractions were collected in 120 ml portions in beakers mounted on a rotating turntable type of fraction collector operated on a time cycle.

After dissolving the polymer in the preheater it was precipitated on the sand, as previously described.¹ The starting solvent-nonsolvent mixture, 1770 ml of 22.5 vol-% *p*-xylene in Dowanol EB (Dow's *n*-butyl ether of ethylene glycol), was placed in the mixing vessel, and 500 ml of pure *p*-xylene was added to each of the other two vessels.

When the column was at operating temperature after the precipitation step, the liquid flow was started, and the fractions were collected in the beakers, each of which contained 15 ml of methanol and about 50 g of solid carbon dioxide, which provided a quick quench for the sample. After the fractionation was complete, consecutive beakers were combined in such a way as to provide ten to fifteen fractions of approximately equal size.

Experiments were carried out that compared the present method with the earlier batch method and which investigated the possible advantage of characterizing more than the usual ten fractions.

Melt flow determinations were carried out according to ASTM D-1238-65T, as previously described.⁶ The I_{10} indicates melt flow with a 10 kg weight on the piston; I_2 is the normal melt index with a 2.16 kg weight. Inherent viscosities were determined as described by Cottam,¹ except that it was found necessary to work at concentrations of less than 0.05 g/100 ml of tetralin, as opposed to the normal 0.1 g per 100 ml, when measuring the viscosity of fractions above about 200 000 molecular weight.

All polymers fractionated belonged to either the D series or K series referred to in previous reports from this laboratory.^{4,6}

Swell Determinations

The swell of the polymer samples was taken as the weight of a 64 fl-oz Javex bleach bottle as blown on a 2 $\frac{1}{2}$ -in. Hartig ram accumulator blow

TABLE I
Reproducibility of Continuous Method and Comparison with Batch Method

	Continuous method		Batch method	
	1	2	1	2
Sample K-1:				
\bar{M}_n	14100	15200	14700	14200
\bar{M}_w	91600	100700	104800	90600
\bar{M}_z	291500	362300	354000	350000
\bar{M}_w/\bar{M}_n	6.49	6.60	7.13	6.43
Recovery, %	99.7	98.7	99.2	101.8
Sample D-4:				
\bar{M}_n	15000	14400		
\bar{M}_w	98300	96300		
\bar{M}_z	314000	304500		
\bar{M}_w/\bar{M}_n	6.54	6.67		
Recovery, %	98.4	101.5		

moulding unit. Day-to-day consistency was provided by running a standard sample each day, providing a correction factor for all samples run that day. This test does not provide a measure of swell alone, since other resin properties, particularly melt strength, also contribute to the weight of a blown bottle. It does, however, provide a practical test that correlates with field experience.

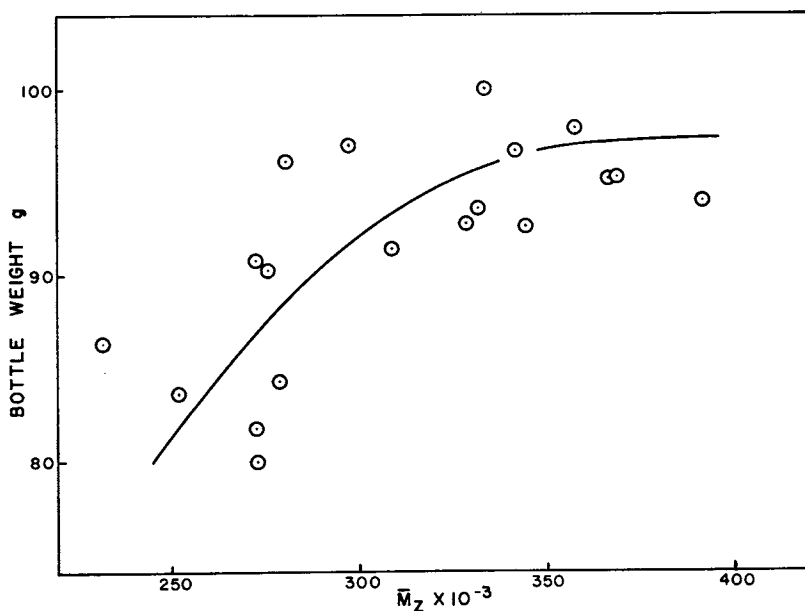


Fig. 2. Relationship between bottle weight and M_z .

RESULTS AND DISCUSSION

The agreement between the batch and the continuous fractionation and the repeatability of the procedure can be ascertained from the data in Table I and the curves in Figure 1. The examples chosen indicate the maximum spread observed in replicate determinations. Increasing the number of fractions from ten to fifteen was found to increase \bar{M}_z marginally but did not improve reproducibility to any noticeable extent. Some of the fractionations exhibited a slight inversion in the high molecular weight end, but this was found to have no discernible effect on the various molecular weight parameters.

A correlation was sought between the various average molecular weights and molecular weight ratios, such as \bar{M}_w/\bar{M}_n , but the only one that showed a definite relationship is displayed graphically in Figure 2. Despite the scatter in the data, the bottle weight obviously increases with increasing Z-average molecular weight. It should be noted that the samples fractionated showed a narrow range of melt index and of \bar{M}_w .

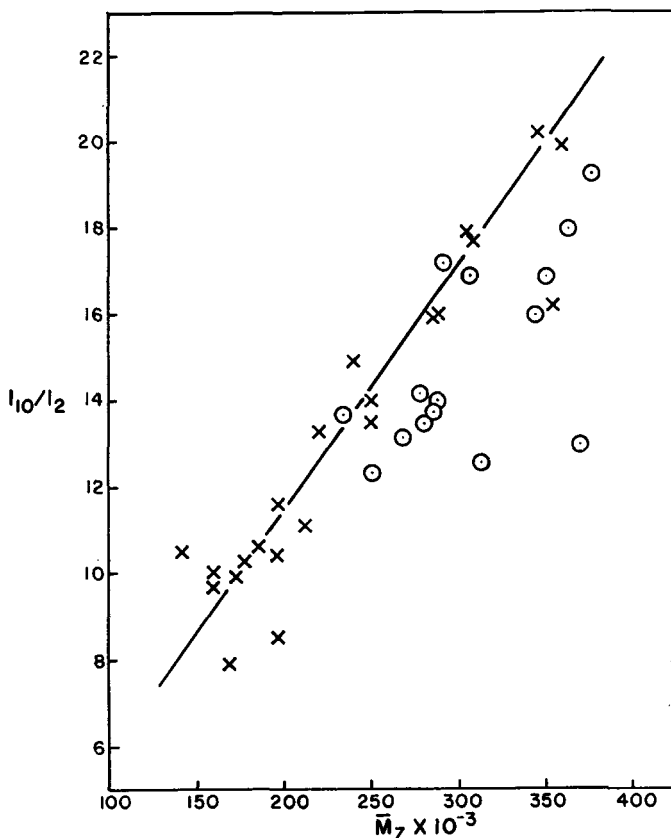


Fig. 3. Relationship between flow ratio and M_z : (\odot) present results; (\times) data from Cottam.¹

The present results were also compared with the \bar{M}_z -flow ratio correlation proposed by Cottam.¹ As can be seen from Figure 3, the data points scatter about the line reported by Cottam, with perhaps a slight shift to a higher \bar{M}_z for a given flow ratio.

To summarize, a method of sand column fractionation has been devised that reduces the number of man-hours required for a determination. Results are comparable to those obtained by earlier, more tedious methods. The swell of a polyethylene bottle blowing resin is shown to be dependent on the Z-average molecular weight.

The authors wish to thank personnel in Dow Canada's Technical Service and Development Department who carried out the bottle weight determinations and those in the production unit who supplied the samples. Some of the fractionations were carried out by J. M. B. Johnston. Many helpful suggestions were made by D. M. Young.

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Received March 25, 1968

Revised April 30, 1968