New Method for MWD Determination in Branched Polymers

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Synopsis

GPC data for long-chain branched polymers (low-density polyethylene) are interpreted
with the aid of a polynomial expression for intrinsic viscosity in terms of the molecular
weight. The resulting molecular weight distribution curves agree well with those de-
rived in an earlier work based on certain assumptions regarding the degree of long-chain
branching.

INTRODUCTION

Gel permeation chromatography (GPC) has become a popular method for
determining of the molecular weight distribution (MWD) of polymers.
Considerable difficulties are encountered, however, when the true MWD
of a branched polymer is sought, owing to the fact that separation by GPC
is based on the differences in molecular volume rather than in molecular
weight.[1-3] As long-chain branching (LCB) reduces the ultimate chain
size, conversion of the chromatogram into an MWD curve is clearly not
straightforward, and some model is needed for the degree of LCB and its
dependence on the molecular weight.

The volume of polymer chains may properly be related to the product of
intrinsic viscosity and molecular weight, $[\eta]M$, whose plot against the elu-
tion volume V_e of the GPC serves as a universal calibration curve.[1-3]
However, the intrinsic viscosity itself is reduced by LCB, and its correlation
with M is not unique either.

In an earlier work,[4] the authors analyzed three samples of carefully
characterized low-density polyethylene (LDPE). The branching model
assumed on that occasion applied beyond a threshold level of molecular
weight, and the interpreted averages of molecular weight exhibited a fair fit
(within 20%) with those measured directly.

The present work puts forward a new approach, in which the drawback of
the unknown degree of LCB is circumvented. What is needed is reformula-
tion of the Mark-Houwink equation modified so as to cover polymers with
long-chain branching. It is well known that, while linear chains have
linear correlations in logarithmic coordinates, namely,

$$[\eta]_l = K \bar{M}^a. \tag{1}$$

A branched chain obeys eq. (1) (under the same conditions) only up to a certain threshold value denoted by M_0:

$$\ln [\eta] = \ln K + a \ln M \qquad \text{for } M < M_0 \qquad (2)$$

beyond which we describe the curve by a polynomial, as follows:

$$\ln [\eta] = \ln K + a \ln M + b \ln^2 M + c \ln^3 M \qquad \text{for } M \geq M_0. \qquad (3)$$

The values of K and a are obtainable from the literature (or experimentally) for the linear polymer under predetermined conditions (solvent and temperature); the still unknown constants b and c have to be calculated. Assuming continuation of the curve at $M = M_0$,

$$\ln K + a \ln M_0 = \ln K + a \ln M_0 + b \ln^2 M_0 + c \ln^3 M_0 \qquad (4)$$

$$c = -\frac{b}{\ln M_0}. \qquad (5)$$

Obviously, the sum of the two last terms of eq. (3) is negative. As one deals with whole (unfractionated) polymers, the contribution of the intrinsic viscosity of each species is taken into account. Thus,

$$[\eta] = \Sigma w_i [\eta]_i \qquad (6)$$

where w_i represents the weight fraction of species i.

Equation (3) may be rewritten as

$$[\eta]_i = K M_i^{(a + b \ln M_i + c \ln^2 M_i)} \qquad \text{for } M \geq M_0. \qquad (7)$$

The universal calibration curve for the GPC utilizes the product $[\eta]M$. For each species, it means that

$$[\eta]_i M_i = K M_i^{(1 + a)} \qquad \text{for } M < M_0 \qquad (8)$$

$$[\eta]_i M_i = K M_i^{(1 + a + b \ln M_i + c \ln^2 M_i)} \qquad \text{for } M \geq M_0. \qquad (9)$$

The crude chromatogram (as obtained on the GPC apparatus) and the measured value of intrinsic viscosity of the whole polymer (both at the same temperature and in the same solvent) are the only data required. Equations (6), (7), (8), and (9) yield, by trial and error, the best values of the parameters b and c, and these, in turn, yield the complete MWD.

EXPERIMENTAL

A Waters Model 200 GPC apparatus was used, consisting of four columns packed with polystyrene gel with pore sizes 700–2000 Å, $1.5–5 \times 10^4$ Å, $1.5–7 \times 10^5$ Å, and $7–50 \times 10^5$ Å. The apparatus was run at 130°C, with trichlorobenzene (TCB) as solvent, and was calibrated with the aid of nine narrow-distribution polystyrene standards. The universal calibration curve was constructed from the product $[\eta]M$ versus elution volume V_e.

Intrinsic Viscosity

The intrinsic viscosity of three well-characterized LDPE samples (provided through courtesy of F. W. Billmeyer), designated PE-75, 76, and 77, was measured in TCB (at 130°C) on a Cannon-Ubbelhode viscometer. $\bar{M}_w$ and $\bar{M}_n$ data were obtained from the same source[5] and confirmed by the authors' earlier study.[4] A series of high-density polyethylene samples was also checked for intrinsic viscosity in two different solvents, with a view to determining the best values for K and a in the Mark-Houwink equation.

RESULTS AND DISCUSSION

The expression for intrinsic viscosity of linear polyethylene in TCB at 130°C was obtained as follows[4]:

$$[\eta] = 5.96 \times 10^{-4}\, \bar{M}^{0.70}. \tag{10}$$

As stated before, the same equation should also apply for low molecular weight unbranched LDPE. The threshold value M_0 was taken as 6000. (Extrapolated literature data[6] and typical curves for linear and branched fractions[7] yielded the range 5,000–12,000.) The procedure for the calculation of MWD is as follows:

The heights of the chromatogram at half-count intervals (2.5 cc) were listed, and the weight fractions were calculated for the corresponding elution volumes V_e. Equation (10) permits M to be plotted against V_e for linear polyethylenes (using the universal calibration curve), thereby yielding the first guess for a set of M_i's for each V_e. Equation (6), combined with either eq. (1) (for $M < 6000$) or eq. (7) (for $M \geqslant 6000$), and the measured value of $[\eta]$ for the whole LDPE yield the constants b and c by trial and error.
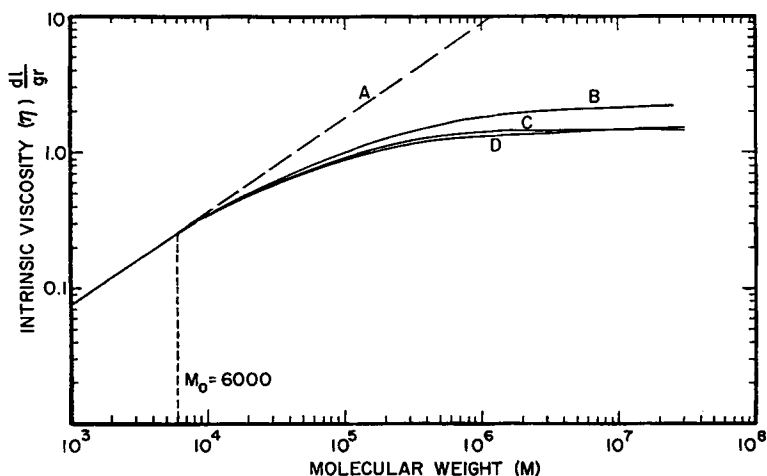

Fig. 1. Intrinsic viscosity vs. molecular weight for PE in TCB, 130°C: (A) HDPE; (B) LDPE, PE-77; (C) LDPE, PE-75; (D) LDPE, PE-76.

TABLE I
Average Molecular Weights of LDPE

| Polymer | $\bar{M}_n$ | | | $\bar{M}_w$ | | | | | |
| | Measured[a] | Calculated | | Measured[a] | Calculated | | | | |
		earlier work[b]	present work		earlier work[b]	present work	b	c
PE-75	10,700	13,300	13,000	500,000	431,000	645,000	0.01585	−0.00186
PE-76	13,300	14,400	14,000	300,000	241,000	378,000	0.01625	−0.00121
PE-77	19,100	19,000	18,600	550,000	457,000	612,000	0.01362	−0.00160

[a] From Kokle and co-workers.[5]
[b] From Miltz and Ram.[4]

Using these constants, an improved estimate of a new set of M_i's is obtained through eqs. (8) and (9), and these in turn yield corrected values for b and c. This procedure is repeated until two successive distribution curves differ by less than 1%. The molecular weight averages $\bar{M}_n$ and $\bar{M}_w$ (determined on a digital computer) are compared with Billmeyer's measured values[5] and
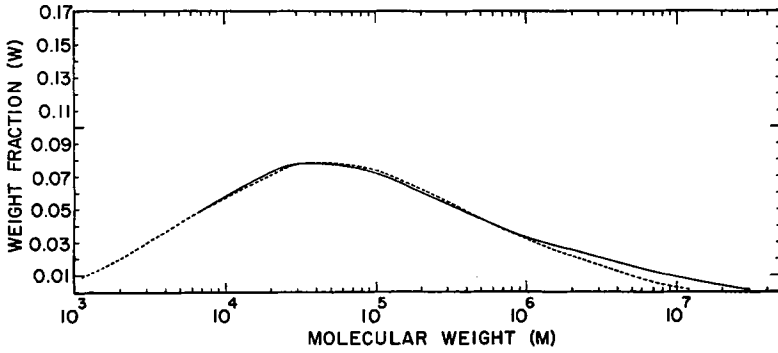

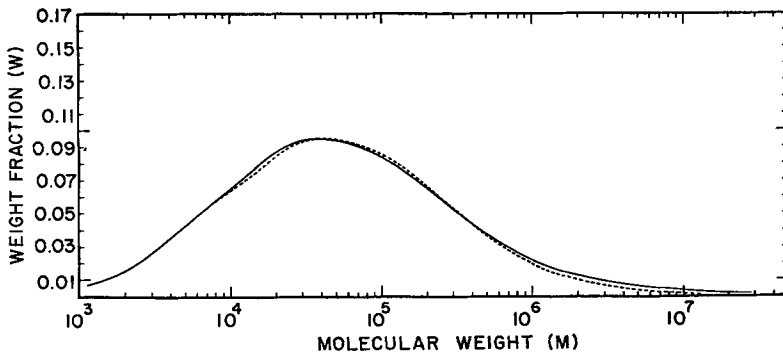Fig. 2. MWD of PE-75: (---) previous work[4]; (———) present work.

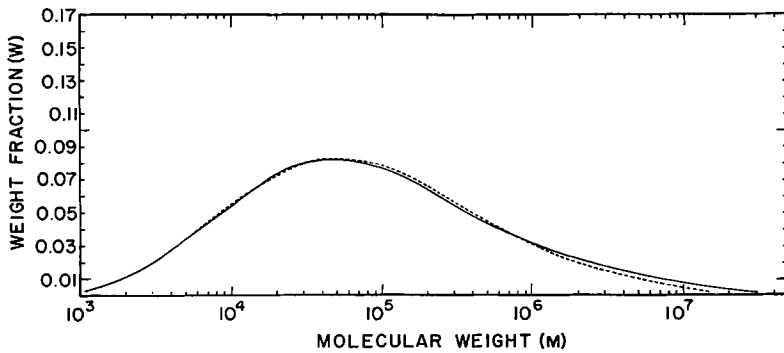Fig. 3. MWD of PE-76: (---) previous work[4]; (———) present work.

Fig. 4. MWD of PE-77: (---) previous work[4]; (———) present work.

those obtained in the authors' earlier work[4] in Table I, which also lists the b and c values.

The correlations for intrinsic viscosity of both linear and branched poly-ethylenes are shown in Figure 1. The distribution curves are shown in Figures 2, 3, and 4. Agreement between present and earlier results is almost perfect, except for a slight deviation at the extreme high molecular weight portion. This deviation affects the calculated values of $\bar{M}_w$ within $\pm 25\%$ around the measured ones, while the number averages exhibit a very close fit.

CONCLUSIONS

Substitution of a simple polynomial for the intrinsic viscosity expression of a branched polymer yields a simplified method for constructing true MWD curves, in good agreement with those derived by assuming a specific model for LCB.

Further refinement is expected through a correction for the axial dispersion of the chromatogram.

References

1. Z. Grubisic, P. Rempp, and H. Benoit, *J. Polym. Sci. B*, **5**, 753 (1967).

2. M. Le Page, R. Beau, and A. J. De Vries, *J. Polym. Sci. C*, **21**, 119 (1968).

3. T. Williams and J. M. Ward, *Polymer Letters*, **6**, 621 (1968).

4. J. Miltz and A. Ram, *Polymer* (London), in press.

5. V. Kokle, F. W. Billmeyer, L. T. Muss, and E. J. Newitt, *J. Polym. Sci.*, **62**, 251 (1962).

6. E. E. Drott, and R. A. Mendelson, *J. Polym. Sci. A-2*, **8**, 1373 (1970).

7. J. E. Guillet, *J. Polym. Sci. A*, **1**, 2869 (1963).