

Practical Use of Intrinsic Viscosity for Polyethylenes

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Synopsis

Although usually derived from measurements at several concentrations, intrinsic viscosity (IV) can be determined with good precision from a single measurement. IV tends to be a regular and distinct function of melt index (MI) for each family of high-density polyethylenes. The tendency to regularity suggests a use in routine control, uniform production being marked by a small scatter about the IV-MI line. The distinctiveness marks one family of medium high and high-density resins from another, and becomes a rapid means of identifying the production method of a resin. Further, IV at a given MI correlates roughly with properties, and can be used to characterize a resin. These attributes of the IV-MI relationship arise from the correlation of IV at a given MI with width of molecular weight distribution. Such width varies considerably among commercial high-density polyethylenes, causing a commensurate variation in IV. Among low-density polyethylenes the IV-MI relationships is less useful, being confused by long-chain branching.

INTRODUCTION

Although solution viscosity is a traditional and simple way of characterizing a polymer it has found almost no common practical use for polyethylene resins. Nor is it well understood except as a rough measure of degree of polymerization, expressing a "molecular weight" that lies between the number-average and weight-average values. The first intimation of broad practical possibilities came from a chance observation.

When intrinsic viscosity was plotted against melt index for high density polyethylene resins it was discovered that the results fell along two distinct lines (Fig. 1). The upper line described the resins made by the Phillips solution process, while the lower line applied to resins derived by the pyrolysis of a resin of less than 0.05 melt index. Such pyrolysis is commonly carried out at about 350°C. Now it is known that the pyrolysis of a polydisperse resin leads to a narrow molecular weight distribution (MWD). Sand-trap fractionation confirmed that the pyrolyzed resins of Figure 1 were narrow, with a weight-average/number-average ratio of molecular weights of 2-3. On the other hand, the solution resins were broader with a ratio varying from 6 to 12 and increasing with falling melt index. It appears, therefore, that the intrinsic viscosity at a given melt index might be an index of width of MWD. As this width in turn determines several important resin properties then IV begins to expand into the practical realm.

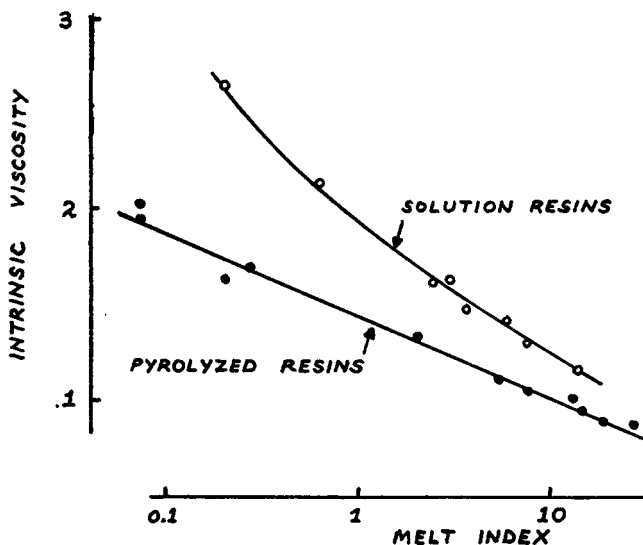


Fig. 1. Intrinsic viscosity versus melt index for high density polyethylenes.

Several demonstrations are given in this paper of the use of IV. We attempt also to explain the IV-MI relationship as a measure of width of MWD. For this purpose six high-density polyethylenes were fractionated and the results used to calculate number-average and weight-average molecular weights. These molecular weights and the width of distribution are correlated with IV and MI.

EXPERIMENTAL METHODS

Intrinsic Viscosity and Melt Index

Melt index was measured according to the standard ASTM procedure. The flow index at 440 psi was determined in a similar way.

Intrinsic viscosity is usually derived as the intercept at zero concentration of a plot of reduced viscosity vs. concentration as in Figure 2. A more rapid and economical value can be determined from a single value of reduced viscosity according to a relationship proposed by Heller¹ and found useful for polyethylene by Dagon:²

$$1/IV = 1/RV + bc \quad (1)$$

Where IV is the intrinsic viscosity, RV is the reduced viscosity (specific viscosity/ c), c is concentration in grams/100 ml, and b is a constant. From a variety of plots like that of Figure 2, we have determined the best value of b to be 0.4 for high-density polyethylene and 0.3 for low-density polyethylene. The effectiveness of eq. (1) is illustrated by the results of Figure 2.

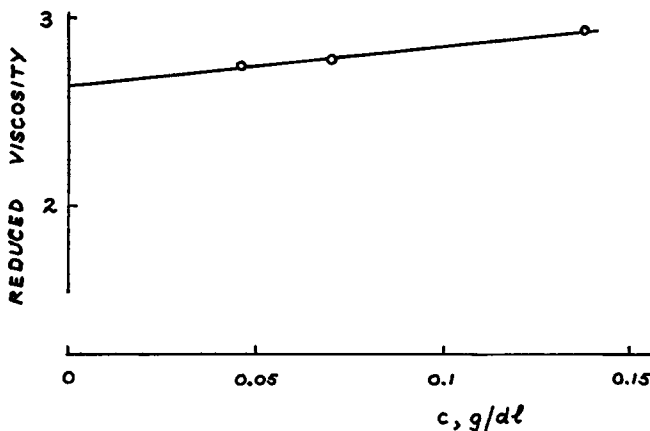


Fig. 2. Solution viscosity for a high density polyethylene in decalin at 130°C.

The actual intercept is 2.63 and the result calculated from eq. (1) from the single point giving RV as 2.95 at $c = 0.137$ on Figure 2 is 2.54. Such reliability in eq. (1) is assured if the concentration is chosen to bring RV within 5–15% of IV.

Fractionation

Several high density polyethylene resins were fractionated in order to clarify the IV–MI relationship. The orthodox sand trap method³ was practiced with the following modifications to improve the definition of the distribution curve.

(1) The resin solution to be deposited in the sand was made up at 0.5% concentration rather than 1–2%.

(2) The resin was deposited by slow cooling from its solution in xylene by a procedure devised by Dagon.⁴ Into the solution of resin at 130°C was poured preheated sand (3.0 kg for 600 ml solution). The flask was allowed to cool quickly to just above the cloud point (100°C) and was then cooled at 2°C/hr for the next 24 hr. The damp sand at about 50°C was transferred to a filter funnel, washed with cold acetone to remove xylene, and put in the fractionation column. A further wash with cold ethoxyethanol settled and wetted the sand.

(3) The time of extraction was increased for the last four to six fractions up to 45–60 min each by the use of nitrogen pressure to support the extracting composition of xylene and ethoxy ethanol in the sand bed. For the earlier fractions, on the other hand, the extractant was allowed to percolate through by gravity in about 20 min.

A result from the above procedure is shown in Figure 3 for a resin of low melt flow (less than 0.1 melt index). (This resin is the first one listed in Table III.)

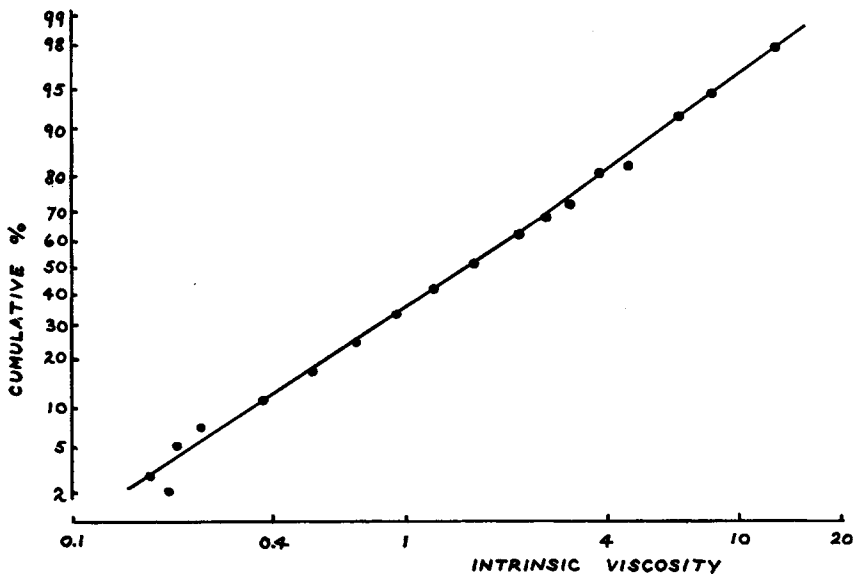


Fig. 3. Distribution curve on log-probability coordinates for high density resin (melt index 0.04, intrinsic viscosity 2.69).

Molecular Weight

Weight-average and number-average molecular weights were calculated from such distributions as that in Figure 3 by the use of the Henry relationship⁵ between intrinsic viscosity and molecular weight for narrow fractions.

$$IV = 4.6 \times 10^{-4} \bar{M}_w^{0.73} \quad (2)$$

where \bar{M}_w is the weight-average molecular weight of the fraction. Values of IV were taken from the fractionation curve at the following cumulative percentages: 2.5, 7.5, 15, 25, 35, 45, 55, 65, 75, 85, 92.5 and 97.5%. For the first point in Figure 3 $IV = 0.17$, and the corresponding MW from the Henry relationship is 3200. For this point $W_i M_i = 0.05 \times 3200$ or 160, and \bar{M}_w for the whole resin is derived as the summation of $W_i M_i$ for the 12 points chosen from the curve. Similarly $W_i/M_i = 0.05/3200 = 1.56 \times 10^{-5}$, and \bar{M}_n is derived from the sum of W_i/M_i .

DISCUSSION

Resin Characterization

The IV-MI index provides a rapid characterization of an unknown resin or group of resins.

Results for two families of experimental high-density polyethylene resins are given in Figure 4. Their IV level is considerably higher than that for present commercial types; at 0.2 melt index, for example, the experimental resins range from 3.3 to 3.7 against a level of 2.7 for the orthodox resins.

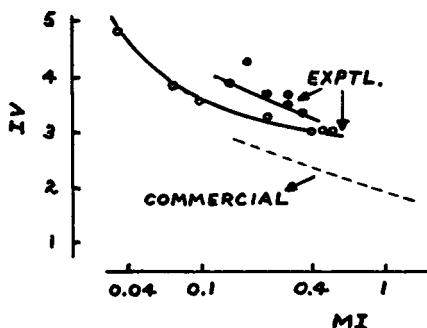


Fig. 4. Intrinsic viscosity versus melt index for experimental and commercial resins.

The broad MWD of the experimental resins suggested by these results was confirmed by sand trap fractionation and GPC results. Further, when one or two experimental resins were made in larger amounts the fabrication properties corresponded to a very broad MWD. For example, there was considerable swelling when the resin issued from an extruder die. The usefulness of IV here as a quick index that could guide bench experiments was in contrast with the failure of a popular rheological index of width MWD. The experimental resins in Figure 4 looked exactly like the commercial ones according to flow ratio, the ratio of melt index flow at 440 psi to that at 44 psi. At 0.2 melt index the flow ratios all fell in a narrow range near 120.

Production Control

A production system under good control should generate resins of closely reproducible MWD's. In present practice, a polyethylene resin is made primarily to a given melt index and density. Flow ratio or some similar rheological ratio may be applied as a secondary production control on the supposition that it is a measure of MWD. Such supposition may not always be reliable in our recent experience. If we apply IV to a series of production resins what can we conclude about their control?

From the results of Figure 5 for a number of resins made by the same process there is little scatter about the line. Nearly all points lie within a $\pm 5\%$ range. The MWD is reproducible and the family is under excellent control, actually without the use of IV which was applied as a *post facto* measure.

On the other hand, a family of high-density resins in the very early stage of production showed considerably more scatter. The boundary lines of IV fell about 12% on either side of the mean. IV was recommended for this process as a means of tightening up the control and the recommendation was persuasive in that the measurement can be made quickly and cheaply.

The combination of two simple quantities like IV and MI can reasonably be projected only as a rough measure of width of MWD. Like most practi-

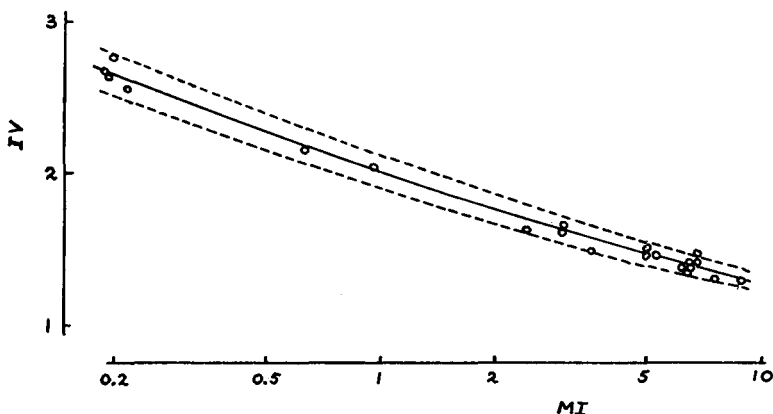


Fig. 5. IV-MI relationship for commercial high-density polyethylene. Dotted lines show $\pm 5\%$ limits of IV.

cal measures it can be expected to be more discriminating among members of one family, made by the same process, than between resins of disparate origins where the differences must be larger to be significant. In the control of a particular family of resins we have judged that a total swing of $\pm 5\%$ only is possible and desirable. A greater swing may result in undesirable variations in practical properties. On the other hand, a difference of, say, 10% , between two resins of different process origin is too small to signal a change in properties and the minimum significant difference is judged to be about 15 or 20% .

Identification of Commercial High-Density Polyethylenes

Commercial polyethylenes of density exceeding 0.945 are produced by at least five main routes: (a) Phillips solution process; (b) mixtures of resins, usually of components of low melt index and high melt index; (c) pyrolysis of resins of low melt index to a higher level of melt index; (d) Ziegler process; or (e) new processes. Often the route used for an unknown resin may be identified by IV. The expected levels of IV at 0.2 MI for the first four routes (Table I) reveal some distinct differences. The first three types are often clearly distinguishable although some resin mixtures may begin to approach the solution type in IV. The wide range of the Ziegler resins may make it difficult to distinguish them from some of the others unless the IV goes distinctly above the 2.6 level for the solution type. An IV of 3.0 at 0.2 MI is usually strong proof of a Ziegler resin. This range for the Ziegler types illustrates the well known adaptability of the process to give various widths of MWD.

The tabulated numbers illustrate a previous comment on significant differences between resins of different origins. At IV 2.6 a solution resin is 13% higher in IV than a resin mixture with a value of 2.3. Such a difference is sufficient to distinguish one origin from another but may not tell

TABLE I
Commercial High-Density Polyethylenes of 0.2
Melt Index and 0.95 Density

Process	IV
Pyrolysis	1.7
Mixture	2.2
Phillips Solution	2.6
Ziegler	2.0-3.0+

whether one resin has more desirable practical properties than the other. In fact, the two resins are interchangeable in many practical respects. Conversely a pyrolyzed resin does differ significantly from a solution resin, having poor stress cracking for example, and the change in IV from 2.3 to 1.7 or 26% is truly significant in signalling the change in properties. These comments are given against a precision of $\pm 2\%$ for IV determined with duplicate solutions.

Low-Density Polyethylenes

Little effect on either melt index or IV would be expected from moderate variations in short-chain branching from the 0.2% level or less of methyl content for high-density polyethylenes to the roughly 2% level for low-density resins. The distinct difference between the two lines (Fig. 6) for the two types of resins must be ascribed to other reasons. Long-chain branching is the most likely. As Billmeyer⁶ has pointed out, the effect of long-chain branching is to increase the molecular weight for a given end-to-end distance of a polymer chain, and so molecular weight is higher for a given IV. One aspect of this situation is that the upper end of the distribution in low-density resins is rich in long branches, and the IV in that region

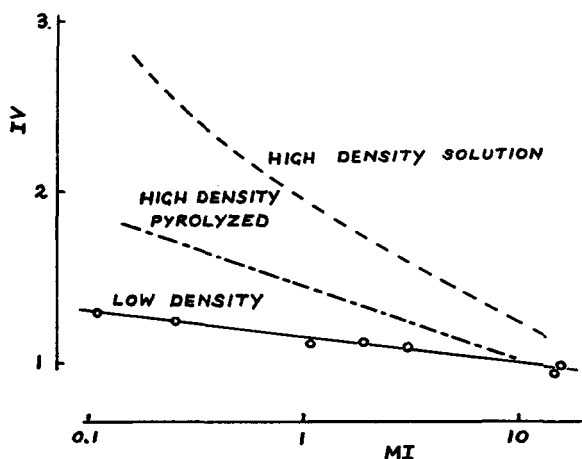


Fig. 6. Relationships for low-density and high-density polyethylenes.

is quite low for the actual level of molecular weight. In fact the upper fractions of low-density resin rarely exceed an IV of 3, whereas similar fractions of high-density resins may reach a value of 10 or more (Fig. 3). Yet the MWD is just as broad or frequently broader for the low-density resin as judged by the weight-average to number-average ratio of molecular weights, the weight-average value being determined by light scattering.

The peculiar character of the IV of low-density resins becomes valuable in identifying mixtures of low- and high-density resins. There is some compensation here for the failure of IV to indicate width of MWD of low-density resins.

Mixtures of Low-Density and High-Density Resins

Mixtures of this kind are popular when a density of 0.94 g/cc is to be achieved and direct polymerization by low-pressure processes may be difficult to control at densities of 0.945 g/cc and below.

When a commercial resin of 0.94 g/cc density was presented for identification we compared it with known single resins B, C, and D in Table II. A 50/50 mix of B and D was also listed, with predicted values of IV and flow ratio. The prediction for IV is based on the well-known principle that IV for a mix results from the addition of the weighted contributions of the components. The same principle was followed for flow ratio but with less assurance of its correctness. The listing of Table II suggests two principal possibilities. The unknown is either a mixture of high- and low-density resins (E) or possibly a pyrolyzed single resin. The former is the more probable situation, because of some difficulty of making a direct resin with a density as low as 0.940 g/cc. Had the unknown been as high in density as 0.945 g/cc, then both possibilities would have been equally likely, and more lengthy methods would have been needed to distinguish between them. Differential thermal analysis, for example, would be helpful.

TABLE II
Identification of Unknown Resin

Resin	IV	Melt index	Flow ratio	Density, g/cc
A Commercial unknown	1.8	0.2	90	0.940
B High-density, solution	2.6	0.2	120	0.96
C High-density, pyrolyzed	1.7	0.2	80	0.945
D Low-density	1.3	0.2	60	0.92
E 50% B + 50% D	1.95	0.2	90	0.94

Rationalization of the IV-MI Relationship

Molecular weights calculated from fractionation results for six high-density resins are given in Table III. The resins originate from several different processes and cover a wide range of melt index, from less than 0.1 up to 19. The fractionation results were all highly reliable as judged by

TABLE III
 High-Density Polyethylenes Fractionated

MI	FI	FR	Density, g/cc	$\bar{M}_w \times$ 10^{-3}	$\bar{M}_n \times$ 10^{-3}	\bar{M}_w/\bar{M}_n	IV
~0.04	5.8	~150	0.942	170	24	7.1	2.69
0.19	27	143	0.96	175	14.6	12.0	2.64
0.22	14	70	0.95	128	23	5.7	2.36
6.3	359	57	0.95	79	14.2	5.5	1.39
19	570	30	0.965	33.2	14.5	2.3	0.89
0.79	62	78	0.963	118	18.7	6.3	2.17

these criteria: (1) mass recovery was $99 \pm 1\%$; (2) recovery of IV was 95–100% (IV for the whole resin compared with the sum of weight fraction times intrinsic viscosity for the fractions); (3) the low and high ends of the curve were well defined, as in Figure 3; these ends strongly influence the number-average and weight-average molecular weight respectively. Even with reliable fractionations the values of the molecular weights are still approximate because they depend first on the mode of calculation: we divided the curve into 12 regions, but a finer division at the ends could yield a lower number-average molecular weight and a higher weight-average value. A second source of uncertainty is a slight loss in recovered IV, usually indicating some indefiniteness in the high end and thus some uncertainty in the weight-average molecular weight.

What is the relation between MI and IV on the one hand and molecular weights on the other? This question is examined first for intrinsic viscosity in terms of the correlations on various plots. For example, IV was plotted against weight-average molecular weight, number-average molecular weight, and combinations of the two. Two such plots appear in Figure 7. Correlation with $0.5 \bar{M}_w + 0.5 \bar{M}_n$ was the best of all tried, and it seemed to be considerably better than that between IV and \bar{M}_w . The success of the best correlation is expected in that IV is usually considered to reflect a value between the two molecular weights but nearer to the weight average value.

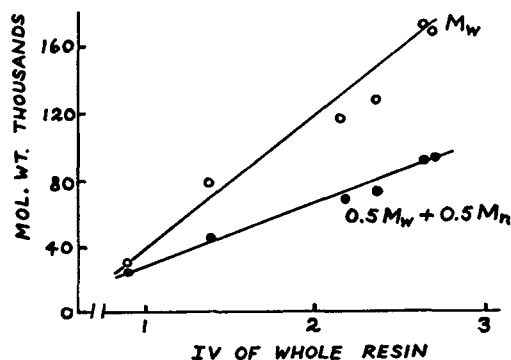


Fig. 7. Intrinsic viscosity and molecular weights.

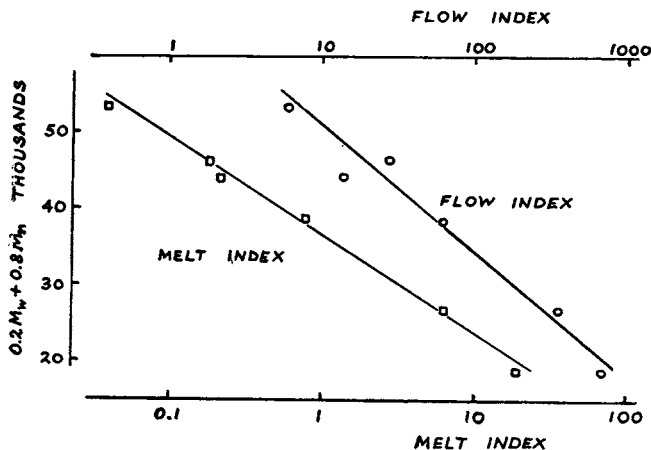


Fig. 8. A combination of molecular weights as a function of melt index and flow index.

For melt index, the most effective relationship introduces $0.8 \bar{M}_n$ and $0.2 \bar{M}_w$ as in Figure 8. The importance of \bar{M}_n in this relationship brings us into a similarity to the finding of Sperati et al.⁷ that melt index for low-density polyethylenes correlates with the number-average molecular weight. Note that there is no conflict with the well-known equation connecting melt viscosity at constant shear rate with the 3.4 or higher power of weight-average molecular weight. Melt index has little connection with melt viscosity.

These correlations lead to the explanation of IV-MI as an index of width of MWD. We may write:

$$0.2 \bar{M}_w + 0.8 \bar{M}_n = f_1(\text{MI}) \quad (3)$$

$$0.5 \bar{M}_w + 0.5 \bar{M}_n = f_2(\text{IV}) \quad (4)$$

where f_1 and f_2 are functions. Let the width of MWD be expressed as $k = \bar{M}_w / \bar{M}_n$. Then

$$0.2 \bar{M}_w + 0.8 \bar{M}_w / k = f_1(\text{MI}) \quad (5)$$

$$0.5 \bar{M}_w + 0.5 \bar{M}_w / k = f_2(\text{IV}) \quad (6)$$

These relationships can be manipulated algebraically but a specific example is more quickly revealing. Suppose resins X and Y have the same melt index but the MWD of X with $k' = 8.0$ is broader than that of Y with $k'' = 2.66$. For equal melt index we write:

$$\begin{aligned} 0.2 \bar{M}_w' + (0.8/8.0) \bar{M}_w' &= 0.2 \bar{M}_w'' + (0.8/2.66) \bar{M}_w'' \\ \text{or } \bar{M}_w' &= 1.67 \bar{M}_w'' \end{aligned}$$

On substituting into eq. (4) we find for resin X,

$$0.562 \bar{M}_w' = f_2(\text{IV})$$

and for resin Y

$$0.413\bar{M}_w' = f_2(\text{IV})$$

And so resin X with the broader MWD has the higher IV.

A similar treatment might be applied to other classes of thermoplastic resin, but IV is effective only if the members of a class cover a broad range of MWD. For example IV is ineffective for polystyrenes because they tend to show only minor variations about a narrow distribution.

While our observations are consistent and can be rationalized, there is a discrepancy with the results of Ferguson et al.⁸ for high-density resins. They found that narrow fractions tended to lie along the same IV–MI line as the parent whole resins. In our more limited experience with fractions we have established that (1) the points show much more scatter than do the pyrolyzed resins of Figure 1, (2) the average line for four fractions lies slightly above that for the pyrolyzed resins, the gap being 0.2 units of IV at 0.2 melt index (3) three mixtures of fractions, with weight/number ratios varying from 2.9 to 3.8 lie on the same line as the individual fractions of ratio 1.5 or less. In sum, all our polymers of narrow MWD are close to one line—that defined by the pyrolyzed resins—and the disagreement with Ferguson et al. remains.

References

1. W. Heller, *J. Colloid Sci.*, **9**, 547 (1954).
2. J. Dagon, personal communication.
3. P. S. Francis, R. C. Cooke, and J. H. Elliott, *J. Polym. Sci.*, **31**, 453 (1958).
4. J. Dagon, personal communication.
5. P. Henry, *J. Polym. Sci.*, **36**, 3 (1959).
6. F. W. Billmeyer, Jr., *J. Amer. Chem. Soc.*, **75**, 6118 (1953).
7. C. A. Sperati, W. A. Franta, and H. W. Starkweather, Jr., *J. Amer. Chem. Soc.*, **75**, 6127-33 (1953).
8. J. Ferguson, B. Wright, and R. N. Haward, *J. Appl. Chem.*, **14**, 53 (1964).

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