[CONTRIBUTION FROM THE POLYCHEMICALS DEPARTMENT, E. I. DU PONT DE NEMOURS AND COMPANY, INC.]

The Molecular Structure of Polyethylene. VII. Melt Viscosity and the Effect of Molecular Weight and Branching[1]

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The melt viscosity of linear and branched polyethylene has been measured at very low shear rate for polymers covering a wide range of molecular weights. It is shown that the empirical law of flow found by Fox and Flory for polyisobutylene and polystyrene also holds for linear polyethylene. In this equation the melt viscosity is proportional to the weight-average molecular weight raised to the 3.4 power. Moreover, it is demonstrated that the equation may be used to describe the melt flow of branched polyethylene, provided an empirical correction is made for the amount of short chain branching.

Introduction

Several attempts have been made in the past to find a relation between the melt viscosity and molecular weight of polyethylene. One of the first of these was the work of Dienes.[3] He concluded that the melt viscosity of polyethylene followed the same relation previously found by Flory[4] for linear polyesters; that is, the logarithm of viscosity varies linearly with the square root of the weight-average molecular weight. However, Fox and Flory[5] later called attention to the fact that the apparent agreement found by Dienes was probably a result of either unreliable molecular weights (weight-average) or too narrow a range of molecular weights.

The experiments reported[6] in Paper V of this series, as well as the work by Bebbington, Hunter and Richards,[7] seemed to indicate a correlation between number-average molecular weight and polyethylene melt viscosity. Further experiments reported[8] in Paper VIII have shown this relation to be true only for a limited number of samples and not generally applicable to all types of polyethylene.

Recent experiments on polyisobutylene,[9] polystyrene[9] and polymethyl methacrylate[10] have shown that the melt viscosity is a linear function of weight-average molecular weight raised to the 3.4 power. The purpose of the present paper is to show that this form of the viscosity–molecular weight relationship also applies to linear polyethylene and the conventional Fawcett-type polyethylenes, provided a correction is made for the amount of short chain branching.

This paper is primarily concerned with the number-average number of short branches as described[11] in paper II. The weight-average number of long branches described[12,13] in Papers III and VI, which is so important in determining solution viscosity, does not appear to influence the melt viscosity to a large extent.

Experimental

Samples.—The polyethylene samples used in this paper are of three types.

1. Commercial Fawcett type[14] (branched, high-pressure free-radical) polyethylenes (samples[15] 24, 26, 49, 50, 52, 55, and 56).
2. Experimental Fawcett-type branched polyethylenes (samples 4, 6, 30, 31, 32, 51, 54, 57, and 58).
3. Linear polyethylenes of the type described by Roebuck and Zletz[16] (samples 59, 60, 61 and 62).

Apparatus.—The apparatus for the study of the viscous flow of molten polyethylene is essentially a modified Searle viscometer[17] which has been provided with an aluminum block oven and recorder for automatically recording the angular position of the rotor. In the Searle viscometer the liquid is contained between two coaxial cylinders. The inner cylinder is rotated, while the outer one is kept fixed in position. The principal difference between this type of apparatus and the one used in the present work is that the coaxial cylinders are replaced by coaxial cones. This type of construction was chosen mainly as a matter of convenience and, apart from the possible reduction of end effects, has no particular advantages over the coaxial cylinder apparatus.

Polymer Characterization.—The polymers used in this investigation were characterized with respect to molecular structure by three parameters: weight-average molecular weight, $\bar{M}_w$, long chain branching index, n_w, and short chain branching index, N_c.

The weight-average molecular weights of the branched polymers were determined by light scattering utilizing the angular dissymmetry technique described in Paper VI[13]; the molecular weights of the linear polymers were obtained from the correlation between intrinsic viscosity and weight-average molecular weight given in Paper III[12] (but see also Paper IX[18]).

The short chain branching parameter, N_c, defined as the number of methyl groups per 100 carbon atoms, either was measured directly by infrared absorption[11] or estimated from the density by means of a previously established relation between N_c and the annealed polymer density.[6]

The long chain branching index, n_w, was obtained by the procedure of papers III[12] and VI,[13] utilizing the reduction in intrinsic viscosity due to long chain branching.

Results

In view of the viscosity-molecular weight correlation previously found[9,10] for three other linear polymers, one might predict, *a priori*, that linear

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(14) E. W. Fawcett, R. O. Gibson and M. W. Perrin, U. S. Patent 2,153,553 (1939).

(15) Sample designations are the same as those in other papers of this series.

(16) A. K. Roebuck and A. Zletz, U. S. Patent 2,692,258 (1954).

(17) M. Reiner, "Deformation and Flow," H. K. Lewis and Co., Ltd., London, 1949, p. 27.

(18) J. T. Atkins, L. T. Muus, C. W. Smith and E. T. Pieski, THIS JOURNAL, **79**, 5089 (1957).

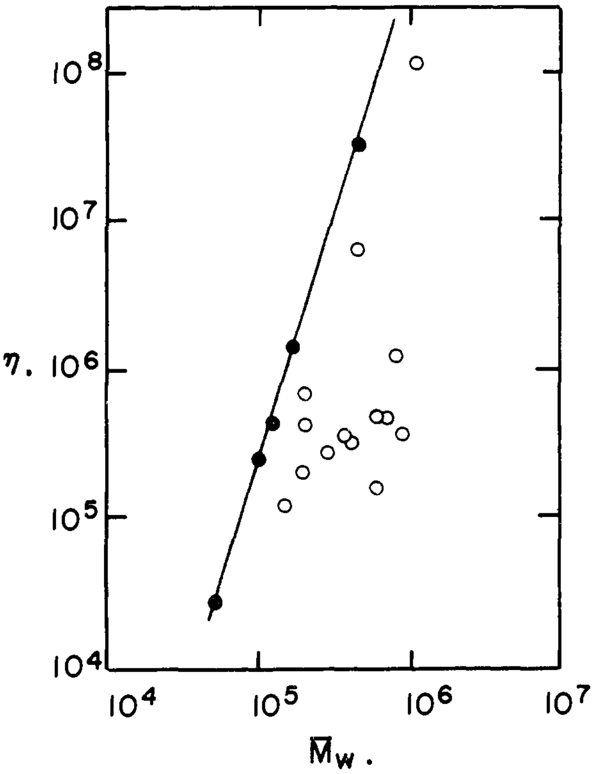

Fig. 1.—Melt viscosity and weight-average molecular weight of linear (●) and branched (○) polyethylene.

polyethylene would behave in a similar fashion. This is indeed found to be true; a plot of the logarithm of melt viscosity against the logarithm of weight-average molecular weight for linear polyethylene is a straight line with the equation

$$\log \eta_T = 3.4 \log \bar{M}_w - C(T) \qquad (1)$$

where η_T is melt viscosity in poise at the temperature T, $\bar{M}_w$ is weight-average molecular weight, and the function $C(T)$ is dependent upon temperature alone. At 150°, $C(T) = 11.6$. The form of eq. 1 is identical with that already established for other linear polymers. The only difference lies in the value of the function $C(T)$.

The correlation described by eq. 1 fails to describe the behavior of branched polyethylene of the conventional Fawcett-type. In Fig. 1 the logarithm of melt viscosity is plotted against the logarithm of weight-average molecular weight for both linear and branched polyethylene. Clearly, several of the branched polyethylenes (open circles) fall off the straight-line relation for linear polyethylene by a factor of 10^3.

Discussion

It is observed empirically for our samples that the viscosity of the polymer decreases exponentially with increasing branching for small values of N_c but at larger values tends to level off. In an attempt to explain these facts, we have employed the hypothesis advanced by Doolittle[19] and Ferry[20] that viscosity and relaxation processes depend primarily on the "free volume"

$$\eta = Ae^{B/v_f} \qquad (2)$$

where A and B are constants and v_f is the reduced "free volume," the difference between the specific volume at T°K. and that extrapolated to 0°K. divided by the extrapolated specific volume at 0°K.

The assumption is now made that the "free volume" increases proportionally to the number of branches. This hypothesis is in accord with Bueche,[10] who concluded that pendant side groups in polymethacrylates serve primarily to dilute the polymer as if they were plasticizer molecules and not attached to the chain at all.

The assumed relationship between melt viscosity and "free volume" is admittedly an oversimplification. It lacks sufficient detail to apply to the comparatively small viscosity differences among isomeric hydrocarbon liquids of low molecular weight when the "free volume" differences are derived from specific volume data.[21] We do not wish to speculate at this time on the relative merits of Bueche's observations and the evidence from low molecular weight hydrocarbons. Rather, we wish to emphasize the empirical nature of the improvement in the correlation between weight-average molecular weight and melt viscosity for branched polyethylene.

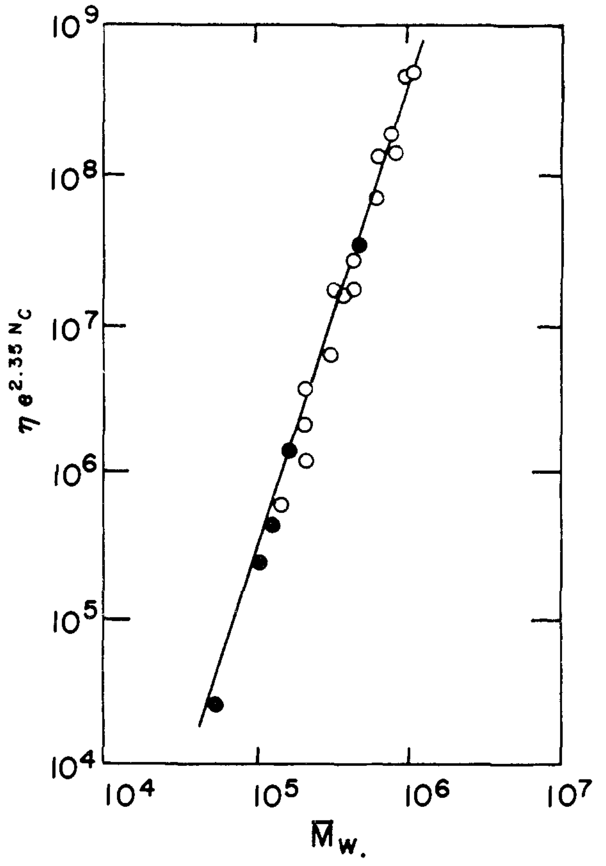

Fig. 2.—Melt viscosity corrected for short chain branching and weight-average molecular weight of linear (●) and branched (○) polyethylene.

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[19] A. K. Doolittle, *J. Appl. Phys.*, **22**, 1471 (1951).

[20] J. D. Ferry, *Rec. Chem. Progr.*, **16**, 85 (1955).

[21] See for example R. W. Schiessler, *et al.*, *Proc. Am. Petroleum Inst.*, **26**, [III] 254 (1946).

TABLE I

MOLECULAR PARAMETERS OF SOME POLYETHYLENES

Sample	$\bar{M}_w \times 10^{-5}$	η	d	N_c	$e^{2.35N_c}$	$e^{2.35N_c}$	n_w
32	10.0	1.17×10^8	0.925	0.70	5.15	6.05×10^8	23
50	9.0	3.85×10^5	.914	3.06	1310.0	5.05×10^8	
51	7.6	1.3×10^6	.920	2.03	118.0	1.53×10^8	33
24	7.0	5.0×10^5	.917	2.60	450.0	2.0×10^8	
52	6.0	5.14×10^5	.918	2.40	282.0	1.4×10^8	26
26	5.7	1.69×10^5	.917	2.60	450.0	7.65×10^7	
6	4.4	6.85×10^6	.927	0.70	5.15	3.50×10^7	16
54	4.2	1.71×10^7	.96	0.00	1.00	1.71×10^7	0
55	4.2	3.43×10^5	.921	1.87	80.6	2.77×10^7	25
49	3.5	3.72×10^5	.923	1.60	42.9	1.59×10^7	17
56	2.9	2.19×10^3	.913	3.40	2980.0	6.6×10^6	29
57	2.8	2.94×10^5	.922	1.74	59.73	1.70×10^7	17
4	2.0	4.32×10^5	.929	0.70	5.15	2.2×10^6	10
30	2.0	2.18×10^5	.930	.70	5.15	1.12×10^6	13
58	2.0	7.25×10^5	.9275	.70	5.15	3.74×10^6	8
59	1.6	1.04×10^6	.96		1.00	1.04×10^6	0
31	1.45	1.22×10^5	.93	.70	5.15	6.28×10^5	8
60	1.24	4.49×10^5	.96		1.00	4.49×10^5	0
61	1.0	2.47×10^5	.96		1.00	2.47×10^5	0
62	0.53	2.8×10^4	.96		1.00	2.8×10^4	0

From eq. 2 the ratio of the viscosities of branched and linear polymers is

$$\frac{\eta(\text{branched})}{\eta(\text{linear})} = \exp B \left\{ \frac{1}{v_f(\text{branched})} - \frac{1}{v_f(\text{linear})} \right\} \quad (3)$$

Applying the assumption of proportionality between "free volume" and the number of branches, we have

$$v_f(\text{branched}) = a + bN_c \quad (4)$$

and therefore

$$\eta(\text{branched}) = \eta(\text{linear}) \exp \frac{-\theta N_c}{qN_c + 1} \quad (5)$$

where $\theta = b\,B/a^2$ and $q = b/a$. If $qN_c \ll 1$

$$\eta(\text{branched}) = \eta(\text{linear}) \exp(-\theta N_c) \quad (6)$$

Using eq. 6 and the appropriate values of N_c, the viscosity of branched polyethylene has been corrected to that of equivalent linear polymer. It has been found experimentally that $\theta = 2.35$. In Table I are listed viscosity measured at 150°, weight-average molecular weight, polymer density measured after annealing in boiling water for 30 minutes, short chain branching parameter N_c, and long chain branching index, n_w, for typical polyethylenes. In addition, the branching correction term $e^{2.35N_c}$, and the corrected viscosity $\eta e^{2.35N_c}$ are listed. The measured viscosities cover a range from 2.8×10^4 poise to 6×10^8 poise. The molecular weights range from 5×10^4 to 10^6 and the short chain branching concentrations range from 0 to 3.5, giving values of the branching correction term between 1 and 3000. Thus it may be seen that a fairly wide range of the variables is covered.

In Fig. 2 the logarithm of corrected viscosity, including the values for linear polyethylene for which the correction term is one, is plotted against the logarithm of weight-average molecular weight. All of the points fall on a straight line of slope 3.4. The equation of the straight line may be written as

$$\log_{10} \eta e^{2.35N_c} = 11.6 + 3.4 \log_{10} \bar{M}_w \quad (1a)$$

or

$$\eta = 3.01 \times 10^{-12}\, \bar{M}_w^{3.4}\, e^{-2.35N_c} \quad (1b)$$

The long chain branching index of several of the polymers studied is given in Table I. These values show that there is considerable variation in long chain branching among the various polymers studied. The melt viscosity corrected for short chain branching does not depend greatly on this variation.

The fact that melt viscosity appears to be independent of long chain branching may be due to the relatively small amount of this type of branching. It has been estimated that the number-average number of long chain branches varies from zero to about one per molecule depending on synthesis conditions. Hence, it may be that the non-dependence of melt viscosity on long chain branching is due to its low frequency of occurrence. Charlesby,[22] for example, has shown that the viscosity of silicone polymers decreases by a factor of five when one branch per molecule is added to a linear polymer. Since the upper limit of the number-average number of long chain branches per molecule in the polyethylenes used in this study is one,[23] this type of branching should not influence melt viscosity greatly. Clearly, it would not account for the observed decrease in melt viscosity of the order of a thousand-fold.

The results of this paper may not be applicable to hydrocarbon polymers other than the Fawcett-type polyethylenes studied.

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