Viscosity of Polyethylenes: Dependence on Molecular Weight and Temperature*

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INTRODUCTION

In this study, viscosity-molecular weight relationships for polyethylenes and for normal alkanes were developed over a broad temperature and molecular weight range. The results were used to test the empirical correlation of Fox and Loshaek and Bueche's theory of viscosity.[1-5] Flow activation energies were also evaluated as a function of molecular weight. The data were primarily from previously reported work.[6-13] As an aid in testing theory, new viscosity measurements were made on six polyethylene samples.

Experimental

Tests were made on six unfractioned samples of low density polyethylenes. They were contributed by Allied Chemical Corp., Eastman Chemical Products, Inc., and by the Bakelite Company. Data on the three low density samples most extensively studied are given in Table I.

TABLE I
Properties of Polyethylenes

$\bar{M}_v$	$[\eta]$ in Decalin, 70°C. dl./g.	Approx. melting temp., °C.	Density, g./ml. 110°C.	Density, g./ml. 135°C.
2800	0.137	102	0.802	0.787
3300	0.154	104	0.802	0.787
8300	0.301	107	0.802	0.788

Bulk polymer and solution viscosities were measured in a conventional manner in capillary viscometers.[14] Data were reproducible to ±0.2%. Corrections were not made for shear rate or kinetic energy. Density measurements by hydrometers were accurate to ±0.2%. Tests were made with a minimum exposure to air.[15] Temperatures and molecular weights of liquid polyethylenes were

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such that their coefficients of thermal expansion were linear.[13,16]

Intrinsic viscosities were obtained in Decalin at 70°C. by extrapolation of data at four concentrations in the range 0.16–1.2 g./100 ml. Polyethylenes were dissolved at 100°C. with no measurable solvent loss. The Decalin used showed no viscosity change with time.[17] A viscosity-average molecular weight, $\bar{M}_v$, was calculated from intrinsic viscosity, $[\eta]$, by using eq. (1), which was derived from cryoscopic and osmotic pressure data for molecular weights of 2600–35,000.[17] The precision in $\bar{M}_v$ is no better than ±5%. Comparisons indicate that eq. (1), as developed by Ueberreiter, gives relatively high molecular weights.[17] In every case, eq. (1) gave a higher molecular weight than the commercial specifications for the samples tested.

$$[\eta] = 3.873 \times 10^{-4} \bar{M}_n^{0.738} \qquad (1)$$

A small percentage of side chains are known to occur in polyethylenes.[18,19] For low molecular weights, the ratio of CH_3 to CH_2 groups is less than 21. The presence of side chains is considered in the interpretation of data. Infrared studies on the polymers tested confirmed the presence of OH and unsaturated groups in Allied Chemical and Eastman polyethylenes, respectively.

THE CHANGE OF VISCOSITY WITH MOLECULAR WEIGHT

Low Molecular Weights

It appears that the viscosity of low molecular weight compounds depend upon simple frictional forces between molecules.[2] Bueche, considering the "free-draining" model of Debye, concludes that viscosity of such compounds should, thus, increase as the first power of molecular weight for short chain homologs. The predicted exponent is greater than one for viscosities at constant pressure
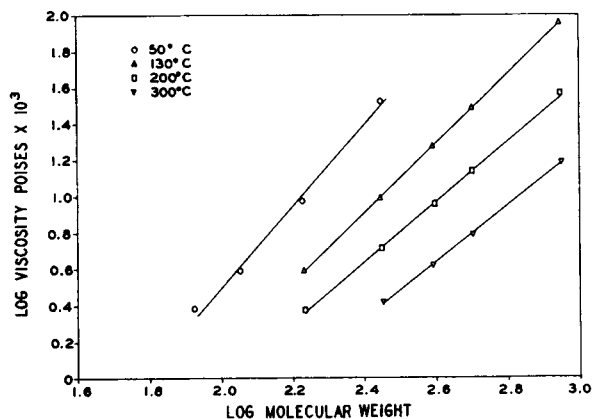
Fig. 1. Viscosities of normal alkanes of low molecular weight.

because chain ends tend to "open up" liquid structure and reduce viscosity.[4] It is postulated that this effect will decrease and that viscosity will approach a linear relationship with molecular weight at elevated temperatures. This idea is tested in Figure 1 in a plot of log viscosity vs. log molecular weight for normal alkanes up to $C_{64}H_{130}$. Data from two sources,[6,8] with some interpolated values, were treated by least-squares analyses. Deviations in log η were minimized and gave regression correlation coefficients averaging over 0.999 at constant temperatures from 50 to 300°C. The data may be represented by

$$\log \eta = A \log (M) - B \qquad (2)$$

where η is the viscosity in poises $\times 10^3$, and A and B are isothermal constants. Table II gives values obtained for A and B. The term A, which is the slope in Figure 1, is found to decrease and approach one with increasing temperature as predicted by Bueche.[4] The value of A is also remarkably independent of chain length over a tenfold range of molecular weights (see Fig. 1). The results are also consistent with viscosity data on other high molecular weight normal alkanes which are being developed by API Project 42.

Intermediate Molecular Weights

The empirical viscosity-molecular weight equation of Fox and Loshaek[1] applies remarkably well to a variety of polymer systems. Their equation has been theoretically derived by Bueche.[2,5] This relationship, which has the form of eq. (2), applies above a critical molecular weight, M_c, where intermolecular entanglements determine the flow process.[2-4]
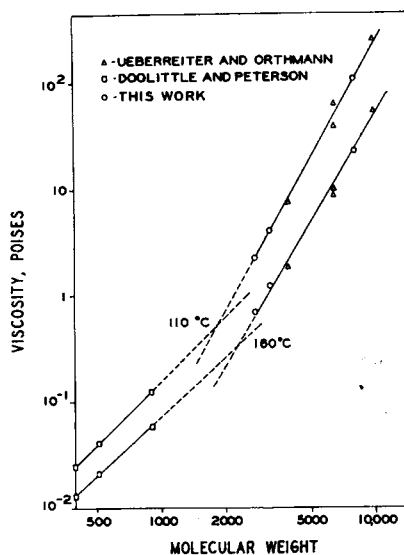

Fig. 2. Viscosities of polyethylenes and normal alkanes of intermediate molecular weight.

The variables in the Fox and Loshaek equation are plotted in Figure 2. The data shown are from several sources. The lowest molecular weights, up to 900, represent an interpolation of Doolittle's data on normal alkanes.[8] The higher molecular weights in Figure 2 are for polyethylenes. The data of Ueberreiter are for unfractionated, free radical polymers.[12,16,17] All polymer molecular weights are defined by the same expression, eq. (1), for an intrinsic viscosity in Decalin at 70°C.[17] Some of the polyethylene data from this work are given in Table III.

A second set of values for A in eq. (2) were

TABLE II
Constants for Equation (2), Molecular Weights 86–900

Temp., °C.	A	B
50	2.22	3.95
110	1.94	3.64
130	1.90	3.65
160	1.79	3.53
200	1.67	3.38
300	1.53	3.35

TABLE III
Absolute Viscosities of Polyethylenes

Polyethylene, mol. wt.	Viscosity, poises		
	110°C.	130°C.	160°C.
2800	2.17	1.27	0.70
3300	3.97	2.30	1.23
8300	108.0	52.8	22.0

determined in the molecular weight range of 2800–10,200, which is above M_c. They were 3.3, 3.5, and 3.6 at 110, 130, and 160°C., respectively. These agree with 3.4 ± 0.1, the universal value for A reported to cover weight-average molecular weights above M_c at constant temperature and density.[1] No correction to constant density was necessary, as specific volumes of liquid polyethylene are nearly independent of molecular weight.

Polyethylene data in Figure 2 indicate that both the number-average molecular weights $\bar{M}_n$ reported by Ueberreiter and the viscosity-average molecular weights $\bar{M}_v$ from this work give essentially independent and identical slopes of 3.4. It may be significant that what Ueberreiter reports as $\bar{M}_n$ may actually be $\bar{M}_v$. A third set of data on polyethylenes also yields a value for A of 3.4. These data, in weight-average molecular weight, $\bar{M}_w$, do not extend down to molecular weights shown in Figure 2.[10] They indicate, however, a compliance of linear polyethylenes to the conditions of the Fox and Loshaek equation. It is thus concluded that the 3.4 value of A in eq. (2) holds in certain conditions for each of $\bar{M}_n$, $\bar{M}_v$, and $\bar{M}_w$. This may follow from an approximately constant molecular weight distribution and degree of chain branching for a specific molecular weight series.[10,20,21]

The effective coincidence in Figure 2 of viscosity data for polymers from different sources is not unreasonable,[18] and may be due to the fact that intrinsic and bulk viscosities are changed in the same way by changes in chain branching and in molecular weight distribution. This is corroborated by data obtained here on low density, low molecular weight Eastman polyethylenes. Although differing greatly in method of synthesis, they give $\bar{M}_v$–viscosity data qualitatively consistent with those in Figure 2.

Data in Figure 2 do not indicate the sharpness of the transition in slope at M_c. For other systems the transition is sharp,[1] and for convenience it is shown here as the intersection of lines. At 110°C., M_c occurs at a molecular weight near 2000 or at a chain length of about 150. This is the shortest chain length reported for M_c. For other polymers M_c occurs at chain lengths between 200 and 1000.[1] Any chain branching in the polyethylenes shown in Figure 2 will give a high rather than low value for M_c.[10,22]

In Figure 2, M_c is determined by viscosity-average molecular weights. Because of molecular weight distribution, it may be argued that the intersection of lines using weight averages should be displaced toward a higher value of M_c. In a test of this, the weight-average molecular weight data of Peticolas and Watkins for linear polyethylenes have been extrapolated down to M_c.[10] At 150°C., a low value of about 1700 is obtained for M_c from these values. This corroborates the view that eq. (1) gives relatively high molecular weights. A firmer and more important conclusion is that data based on each of $\bar{M}_n$, $\bar{M}_v$, and $\bar{M}_w$ give consistently low values for M_c for polyethylenes. The absolute value of M_c is difficult to ascertain because of problems in molecular weight definition, distribution, and determination. However, a short chain length for M_c is reasonable for polyethylenes. That is, molecular entanglements should be most easily formed and M_c extend to the shortest chain lengths for flexible polymers with a minimum of side chains.

From data in Figure 2 it is found that the chain length for M_c changes by about 30 carbon atoms from 110 to 160°C. An increase in M_c with temperature, although reasonable, has not been previously reported. Correspondingly, the entanglement point occurs at higher molecular weights in polymer solutions as the polymer concentration is decreased.[1] The conditions for an infinite network of entangled chains is that $KM \geq 1$, where K is the coupling constant.[2,4] The coupling constant for these data changes from 5.4×10^{-4} at 110°C. to 4.4×10^{-4} at 160°C.

High Molecular Weights

The 3.4 slope, as typified in Figure 2, is reported to apply at high molecular weights for bulk and solution viscosities of many polymers. The correlation has been extended to chain lengths above 10^4 and viscosities in excess of 10^6 poises.[1] In accord, Peticolas and Watkins report that linear polyethylenes for $\bar{M}_w$ from 0.53 to 4.2×10^5 also give a 3.4 slope. They find, as expected, that branched polyethylenes give relatively low viscosities.

At least three polymer systems have been reported for which slopes, or values of A, markedly exceed 3.4.[3,7,12,13,23] Certain polyethylene data, which fit this class, are plotted in Figure 3. Molecular weights of Ueberreiter are higher members of the same series which produce the 3.4 slope in Figure 2.[13] The high molecular weight slope is 6.4. This high value may be caused by a change in chain branching with increasing mo-
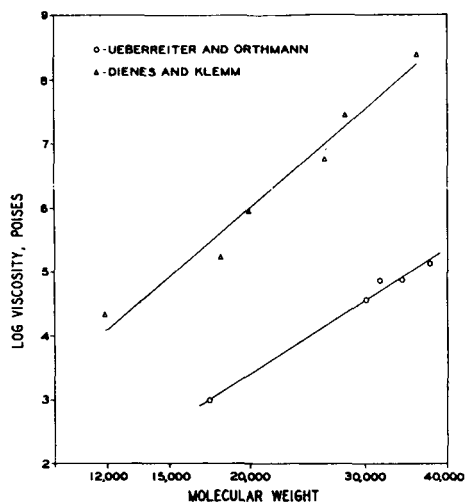
Fig. 3. Viscosities of polyethylenes of high molecular weight at 130°C.

lecular weight. The $\bar{M}_w$–viscosity data of Dienes in Figure 3,[7] as well as certain other $\bar{M}_n$ and $\bar{M}_v$–viscosity data on polyethylenes,[12,24] also give abnormally high slopes, sometimes with values above 8. The Fox and Loshaek equation is, therefore, not universal. It does apply, however, to weight-average molecular weights for linear polyethylenes.[10]

THE CHANGE OF FLOW ACTIVATION ENERGY WITH MOLECULAR WEIGHT

The activation energy for viscous flow, ΔE^*, may be calculated from eq. (3) where T is the absolute temperature, R the gas constant, and D a constant.[25,26]

$$\eta = De^{\Delta E^*/RT} \tag{3}$$

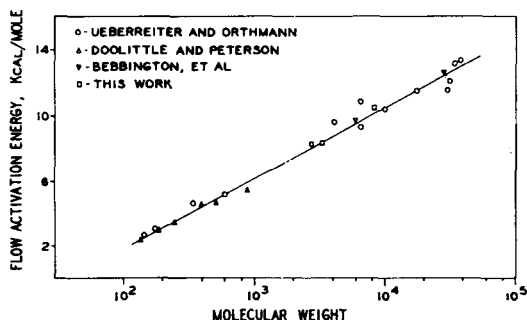The change in ΔE^* with polyethylene molecular weight at 130°C. is shown in Figure 4. This

relation holds for molecular weights determined from eq. (1). A least-squares analysis of these data showed that eq. (4) fits data for both polyethylenes and normal alkanes for molecular weights of 128–37,600 with a regression correlation coefficient of 0.994. Since the development of this correlation, other data have come to light.[21] These additional values for ΔE^*, as plotted in Figure 4, agree with the existing correlation within experimental error.

$$\Delta E^*_{130} = -6.70 + 4.27 \log M \tag{4}$$

Equation (4) and one proposed by Ueberreiter are the only ones showing a change in ΔE^* with polyethylene molecular weights.[13] Equation (4) covers a tenfold larger molecular weight range and fits the data better at lower molecular weights. No tendency is observed for ΔE^* to approach a limiting value at molecular weights, up to 37,600 (chain length 2600).[26] For polystyrene and polyisobutene,[27] ΔE^* is constant at chain lengths above 1000 which approximates M_c.

Figure 4 indicates consistent values of ΔE^* for polymers from different syntheses; this despite the fact that ΔE^* is reported to change with degree of chain branching.[28] An explanation for the coincidence of data may be made on the basis that viscosity-average molecular weights decrease with chain branching but that branching also induces the same directional change in the ΔE^* for polyethylenes.[28]

In Figure 5, ΔE^* is plotted against the square root of chain length, in the manner of Ueberreiter.[13] In this correlation, ΔE^* changes linearly at the higher molecular weights but breaks off toward 0 for short chains. The maximum curvature occurs near M_c. Polyisobutene and polystyrene show markedly different behavior.[27]

Fig. 4. Flow activation energies for polyethylenes and normal alkanes: dependence on log molecular weight at 130°C.
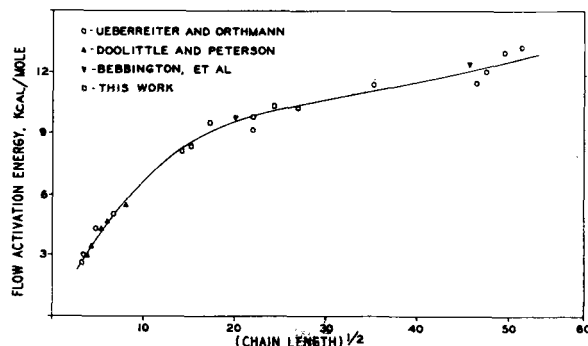

Fig. 5. Flow activation energies for polyethylenes and normal alkanes: dependence on square root of chain length at 130°C.

Bulk viscosities of polyethylenes may be calculated from molecular weight by using eq. (3) and an established relationship for D. Values for D, in eq. (5), apply to ΔE^* in kilocalories and for molecular weights of 1400–37,600.[13]

$$D = \Delta E^* - 14 \qquad (5)$$

FLOW PROCESS

The increase of ΔE^* per carbon atom for polyethylenes decreases with increasing chain length (see Fig. 4). Based on normal hydrocarbon data up to $C_{32}H_{66}$, it has been postulated that the maximum ΔE^* for long hydrocarbon chains corresponds to 6–7 kcal.[26] This energy, by analogy with vaporization, is equivalent to a ΔE^* for a molecular segment of 25–30 carbon atoms. It is evident from branched polyethylene data that ΔE^* and, consequently, the required size of the flow segment continue to increase with molecular weight up to the highest values in Figure 4. For polyethylenes with molecular weights of 10,000 and 37,600, ΔE^* increases to energies equivalent to activation of flow segments of 40 and 50 carbon atoms, respectively.[13]

The theory of flow by molecular segments may be tested by calculation. The value for D in eqs. (3) and (5) is proportional to the displacement volume in the flow process.[13,26] A calculation has previously been made for the size of the flow segment based on a mean value of -4 for D.[13] The resultant volume, 6.5×10^{-23} cm.^{3}, is reported to be about twice that obtained for a CH_2 group by x-ray analysis.[29] This suggests that the flow process is the movement of small volumes which are a tenth or less of that originally predicted from the theory of segmental jump. Based on other reasoning, Fox et al. have postulated displacement volumes in the flow of alkanes.[30] They conclude that flow segments are not more than chains of five carbon atoms.

Ueberreiter has mathematically treated polyethylene as a vibrating string with periodic nodes.[13] The distance between nodes increased with increasing molecular weight. The spacing between nodes approximates the flow units predicted from vaporization.[26] Actual flow, however, is postulated to take place through the displacement of volumes of the order of a CH_2 group. Flow by the movement of small segments, thus, appears to explain the behavior of all members of the n-alkane-polyethylene series.

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Synopsis

Existing viscosity data on polyethylenes were studied as a function of temperature and molecular weight. New measurements were made on low density polyethylenes which had molecular weights useful for the test of theory. Viscosities of normal alkanes, considered as a lower extension of polyethylenes, were also correlated. The equation, $\log \eta = A \log$

$(M) - B$ (where η is absolute viscosity, M is molecular weight, and A and B are constants), is applicable over a wide range of Newtonian viscosities. Bueche's theory postulates that A approaches unity for chain lengths up to a critical molecular weight, M_c, where molecular entanglement abruptly becomes important. Above M_c, the theory requires A to be 3.4. Values of A for normal alkanes are shown to approach unity below M_c. The entanglement point, M_c, is temperature dependent and occurs at relatively low molecular weights. Above M_c, A for linear polyethylenes is near 3.4. However, certain polyethylene data give higher values for A. Activation energies for viscous flow, ΔE^*, were obtained for polyethylenes and normal alkanes. They were found to be internally consistent and to vary as a linear function of the log of molecular weight. The change of ΔE^* with less general functions of moleculare weights shows a maximum curvature near M_c. Results are considered in terms of flow theory.

Résumé

Les résultats viscosimétriques existants sur des poly-éthylènes ont été étudiés en fonction de la température et du poids moléculaire. De nouvelles mesures ont été effectuées sur plusieurs polyéthylènes de poids moléculaires convenables pour le contrôle de la théorie. Des viscosités d'alcanes à chaîne normale, considéré commee les homologues inférieurs des polyéthylènes, ont aussi été rapportées. L'équation, log $\eta = A$ log $(M) - B$ où η est la viscosité absolue, M le poids moléculaire et A et B des constantes, est applicable dans un vaste domaine de viscosités Newtoniennes. La théorie de Bueche postule que A tend vers l'unité pour des longueurs de chaîne allant jusqu'à un poids moléculaire critique, M_c, où l'enroulement moléculaire devient brusquement important. Au dessus de M_c, la théorie exige que A soit égal à 3,4. Pour les alcanes à chaîne normale les valeurs de A tendent vers l'unité au dessous de M_c. Le point d'enroulement, M_c, dépend de la température et a lieu pour des poids moléculaires relativement bas. Au dessus de M_c, A est pour des polyéthylènes linéaires voisin de 3,4. Cependant, certains résultats obtenus avec le polyéthylène donnent des valeurs plus élevées pour A. On a obtenu les énergies d'activation pour l'écoulement visqueux, ΔE^*

dans le cas des polyéthylènes et des alcanes à chaîne normale. On a trouvé qu'elles étaient valables et variaient comme une fonction linéaire du log du poids moléculaire. La variation de ΔE^* avec des fonctions moins générales des poids moléculaires présente un maximum de curvature au voisinage de M_c. Les résultats sont considérés en fonction de la théorie de l'écoulement.

Zusammenfassung

Vorhandene Angaben über die Viskosität von Polyäthylenen wurden in bezug auf die Abhängigkeit von Temperatur und Molekulargewicht untersucht. Neue Messungen wurden an einigen Polyäthylenen ausgeführt, deren Molekulargewichte eine für die Überprüfung der Theorie brauchbare Grösse hatten. Auch die Viskosität von normalen Alkanen, die man als niedrigere Glieder der Polyäthylenreihe betrachten kann, wurde in die Untersuchung einbezogen. Die Gleichung log $\eta = A$ log $(M) - B$, wo η die absolute Viskosität, M das Molekulargewicht und A und B Konstante sind, kann über einen weiten Bereich Newtonscher Viskositäten angewendet werden. Die Theorie von Bueche fordert, dass sich A für Kettenlängen bis zu einem kritischen Molekulargewicht, M_c, bei welchem Molekülverschlingungen plötzlich Bedeutung gewinnen, dem Wert eins nähert. Oberhalb M_c verlangt die Theorie für A den Wert 3,4. Es wird gezeigt, dass sich für normale Alkane die Werte für A unterhalb M_c eins nähern. Der Verschlingungspunkt, M_c, hängt von der Temperatur ab und liegt bei verhältnismässig niedrigen Molekulargewichten. Oberhalb M_c liegt A für lineare Polyäthylene in der Nähe von 3,4. Bestimmte Ergebnisse an Polyäthylen liefern jedoch höhere Werte für A. Aktivierungsenergien für das viskose Fliessen, ΔE^*, wurden für Polyäthylene und für normale Alkane erhalten. Sie bildeten eine in sich übereinstimmende Reihe und zeigten eine lineare Abhängigkeit vom Logarithmus des Molekulargewichts. Die Abhängigkeit von ΔE^* von weniger allgemeinen Funktionen des Molekulargewichts zeigt eine grösste Krümmung in der Nähe von M_c. Die Ergebnisse werden im Rahmen der Theorie des Fliessens diskutiert.