Melt Viscosity of Polyethylenes

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The viscosity of molten polyethylenes at different temperatures and over a broad range of shear rates is of interest, not only because of the practical importance in extrusion and molding, but also because of the important relations that may exist between the molecular and flow properties of the polymer. The viscosity of polyethylenes has been studied by a number of techniques,[1-7] but, except for the recent studies of Philippoff and Gaskins,[7] most of the measurements have been carried out over an insufficient range of shear rates. Especially notable is a lack of melt viscosity data at low rates of shear and on well characterized polyethylene fractions.

In the characterization and evaluation of commercial polyethylenes, the criterion of melt index,[8] a measure of the flow properties of molten polyethylene, is commonly used. Whether the melt index values have any correlation with the melt viscosity of various polyethylenes at low shear rates has not been established.

This paper describes studies on the melt viscosities of polyethylene by the use of capillary viscometers of simple design. The melt viscosities measured by these viscometers may be considered as having been obtained under Newtonian flow conditions, since very low shear rates were used. Results are given for unfractionated polyethylenes and for several carefully fractionated samples. The melt viscosities of unfractionated polyethylenes have been compared with the corresponding values of the melt index, and the melt index appears to be not an adequate measure of the melt viscosity determined under Newtonian flow conditions. The relationship between melt viscosity and the intrinsic viscosity of the fractions in toluene at 80°C. is discussed. Finally, from the determinations of melt viscosity at a number of temperatures, values of the activation energy of viscous flow were obtained.

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EXPERIMENTAL

Determinations of Melt Viscosity by Capillary Viscometers

The method used for measurements of melt viscosity of polyethylenes was adapted from the procedure described by Flory.[9] This method is based on the measurement of the rate of flow of the molten polymer up a capillary tube of calibrated bore under a known steady pressure. Figure 1 shows schematically the apparatus used in our studies.

The experimental technique for making the measurements was simple. Approximately 0.5%, by weight, of an antioxidant was mixed with 4-5 grams of the polymer. (Phenyl-β-naphthylamine was found to be a suitable antioxidant for these studies.) The polymer sample with antioxidant was placed in the tube C, and the viscometer A was introduced through a tightly fitting rubber stopper. The lower end of the viscometer was held a few inches above the solid polymer sample. The system was alternately evacuated and flushed with nitrogen at least three times before heating, since otherwise the viscosity of the molten polymer was considerably affected by oxidative degradation and crosslinking. The change in melt viscosity of a typical sample with time of heating at 202°C. is shown in Figure 2. When air had been carefully removed by flushing the system with nitrogen, and antioxidant (0.5% by weight) had been added to the polymer, the viscosity increased by about 20% in an hour, a period of time much greater than that used in the measurements reported here. On admission of air to the system, a rapid increase in viscosity ensued, similar to that obtained in air in the absence of inhibitor. If air was removed but no antioxidant added, the increase of viscosity was about 40% in an hour. When the precaution of flushing the system with nitrogen was taken and the antioxidant was mixed with the polymer before melting, measurements of melt viscosity were
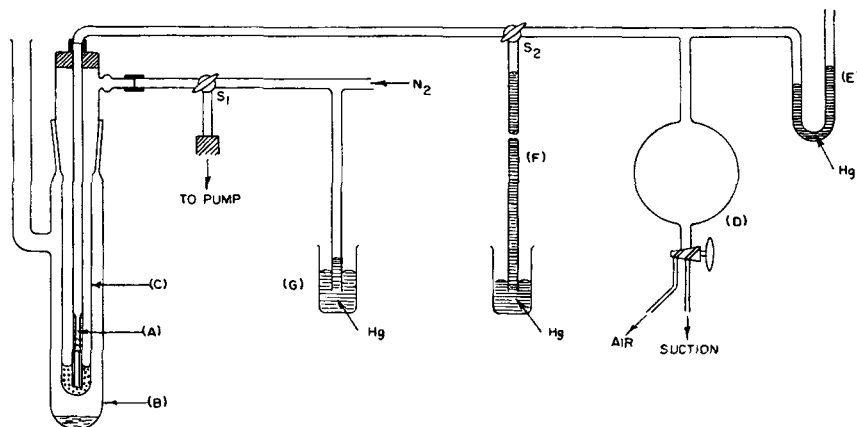
Fig. 1. Apparatus for measuring melt viscosity of polyethylene: (A) calibrated bore capillary; (B) vapor bath; (C) tube containing polymer; (D) air reservoir; (E) manometer; (F) straight-tube mercury manometer; (G) bottle containing mercury.

usually reproducible within 10%. In the few experiments in which results were found to be not reproducible within 10% (despite the precautions mentioned) this behavior was attributed to some structural feature or to excessive amounts of oxygen not usually present in polyethylenes, and the samples were discarded.

After the system had been flushed with nitrogen, melt viscosity measurements were made as follows. The polymer was melted by the boiling liquid in the vapor bath. As the polymer began to melt, the semimolten polymer sample was pushed down

Fig. 2. Variation of viscosity of DYNH at 202°C. with time of heating: (⊙) viscosity after system flushed with nitrogen and antioxidant added (discontinuity marks the time of opening the system to air); (⊕) viscosity after system flushed with nitrogen but without antioxidant; (⊗) viscosity in the presence of air without antioxidant.

gradually by forcing down the viscometer. This helped to dispel trapped bubbles from the melt, and a clear melt was obtained. The viscometer was dipped into the clear melt up to approximately the midpoint between the lower end and the first mark. The upper end of the viscometer was connected through S_2 to the air reservoir, and the pressure difference between the atmosphere and the system was read from the millimeter scale of the manometer E. The time required for the flow of the melt between successive marks etched on the viscometer was measured to the nearest tenth of a second.

This method was found to be particularly suitable for the measurements of melt viscosity at different temperatures. Vapor baths containing liquids of boiling points in the desired temperature range were made. The vapor baths used, and the corresponding boiling points measured with calibrated thermometers, included dimethyl phthalate, 282.6°C.; diethylene glycol, 242.3°; naphthalene (sublimed), 217.7°; m-cresol, 202.2°; propylene glycol, 187.5°; p-cymene, 177.7°; cyclohexanol, 161.5°; and p-xylene, 138.7°. After a clear melt had been obtained, at a suitable temperature, the tube containing the sample was transferred from one vapor bath to another. The measurements of melt viscosity at different temperatures could thus be made on the same sample of the melt. This convenience was especially important for studying the viscosities of the polyethylene fractions, because the quantity of each fraction was small.

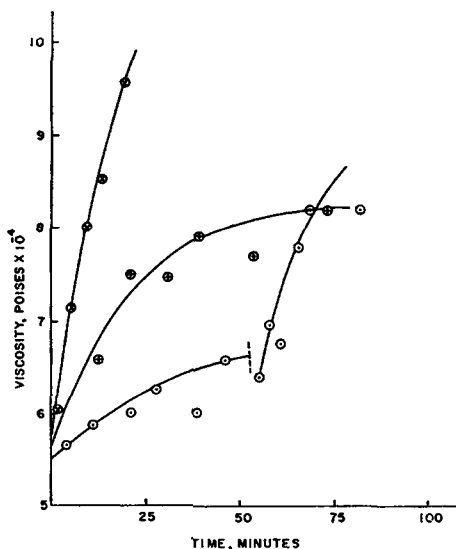Melt viscosity was calculated from the time of flow of the melt between two successive marks on

the viscometer by the application of Poiseuille's Law for flow through a capillary. For flow between two marks at distances h_0 and h_1 centimeters from the lower end of the capillary the viscosity η in poises is given by: $\eta = 1056\sigma t\Delta P/(h_1{}^2 - h_0{}^2)$, where ΔP is the pressure difference in centimeters of mercury, σ is the cross-sectional area of the capillary, and t is the time of flow in seconds. It should be noted that, as the melt rises through the capillary, its weight acts in the opposite direction and tends to reduce the effective pressure difference. It is therefore necessary to apply a correction to the pressure difference as read from the open-end manometer E in Figure 1. This correction in ΔP, because of the height of the polymer column in the capillary, equals $(2\gamma/3)[h_1 + h_0 - h_1h_0/(h_1 + h_0)]$, where γ is the ratio between the densities of molten polyethylene and mercury, and h_0 and h_1 are the heights of the marks from the lower end of the capillary. Similar relations hold for flow between other successive marks.

Fractionation

Two polyethylene samples, Du Pont Alathon-14 and Bakelite DYNH-3, were fractionated. In both cases fractionation was carried out by cooling a 2% solution of the polyethylene in amyl acetate. The first major fraction in both cases separated as a gel phase at 133°C., and was separated by careful suction of the sol phase through a heated transfer tube. The separated gel phase was redissolved in amyl acetate (solution concentration approxi-

mately 1.0%), and the temperature was lowered to 100°C. The fraction which then separated was taken as the first fraction, and the sol was combined with the original sol. Further fractionation was carried out by successively lowering the temperature of the combined sol and by separating the gel or the solid phase that separated at each temperature. Table I gives the temperatures at which the fractions were removed, the amount of each fraction as weight percent of the unfractionated polyethylene sample, and the intrinsic viscosity of the fractions at 80°C. in toluene.

RESULTS AND DISCUSSION

Melt Viscosity by Capillary Viscometers. Comparison with Melt Index

In Figure 3, the melt viscosity at 202.2°C., as determined by the capillary viscometers, is plotted as a function of the reciprocal of melt index at 190°C. for a number of unfractionated polyethylenes. Table II gives the values of melt viscosity at 202.2°C. and the melt index at 190°C. for some of the polyethylenes that were studied.

TABLE I
Fractionation of Polyethylene from Amyl Acetate

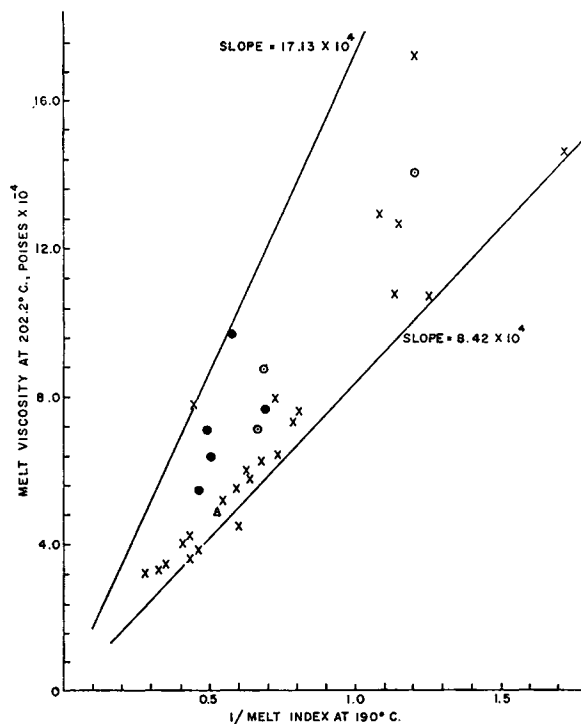| Fraction number	Tempera- ture of precipita- tion, °C.	Amount of fraction, wt.-% of sample	$[\eta]$ in toluene at 80°C., (g./100 ml.)$^{-1}$
Alathon-14; $[\eta]$ in Toluene at 80°C. = 1.078 (g./100 ml.)$^{-1}$			
FC 3011	133	15.0	
FC 302	125	25.0	1.40
FC 303	111	18.9	0.97
FC 304	87.5	18.4	0.58
FC 305	80	15.1	0.29
FC 306	30	7.6	0.29
DYNH-3; $[\eta]$ in Toluene at 80°C. = 0.950 (g./100 ml.)$^{-1}$			
FC 401	133	26.3	1.79
FC 402	109	29.0	0.96
FC 403	89	22.7	0.57
FC 404	73	13.0	0.31
FC 405	30	9.0	0.16

Fig. 3. Plot of melt viscosity of polyethylene at 202.2°C. vs. the reciprocal of melt index at 190°C.: (●) Alathon polyethylenes (Du Pont); (⊙) DYNH and DYNJ polyethylenes (Bakelite); (×) experimental samples; (△) alkathene polyethylene (I.C.I.).

TABLE II
Melt Viscosities at 202.2°C. by Capillary Viscometers and Melt Index at 190°C.

Sample number	Polyethylene designation and source[a]	Methyl groups/ 100 C atoms	$[\eta]$, (g./100 ml.)$^{-1}$	Density at 25°C.	Melt viscosity, poises × 10^{-4}		Melt index[b]	
					Mean	σ	Mean	Average deviation from mean
1	DYNH-3, Bakelite	2.5	0.950	0.9090	8.76 ±	0.77	1.48 ±	0.02
2	DYNH-3, Bakelite	2.5	0.970	0.9135	7.15 ±	0.70	1.51 ±	0.01
3	Alathon-10, Du Pont	2.5	0.950	0.9123	6.35 ±	0.45	1.96 ±	0.01
4	Alathon-14, Du Pont	3.0	1.078	0.9066	9.69 ±	0.74	1.73 ±	0.04
5	Alathon-10, Du Pont				5.46 ±	0.17	2.16 ±	0.02
6	Alathon-10, Du Pont		3.32		7.11 ±	0.20	2.03 ±	0.11
7	Alathon-10, Du Pont				7.69 ±	0.39	1.90 ±	0.04
8	Alkathene-2, I.C.I.		1.111		4.91 ±	0.39	1.90 ±	0.04
9	Experimental sample	2.6	1.125	0.9179	3.57 ±	0.31	2.37 ±	0.02
10	Experimental sample	2.6	1.125	0.9184	16.37 ±	0.36	0.58 ±	0.01
11	Experimental sample	2.7	1.052	0.9184	10.75 ±	0.55	0.88 ±	0.03
12	DYNJ, Bakelite		1.120		14.13 ±	0.22	0.83 ±	0.22
13	Experimental sample	2.8	1.095	0.9175	7.36 ±	0.23	1.27 ±	0.04
14	Experimental sample	2.3	1.052	0.9122	3.78 ±	0.14	2.02 ±	0.02
15	Experimental sample	2.3	0.975	0.9118	5.53 ±	0.29	1.68 ±	0.04
16	Experimental sample	2.3	1.000	0.9111	4.22 ±	0.13	2.35 ±	0.02
17	Experimental sample	2.2	1.140	0.9193	14.63 ±	0.41	0.58 ±	0.02
18	Experimental sample	2.2			12.96 ±	0.32	0.92 ±	0.02
19	Experimental sample	2.3	0.98		3.51		2.90 ±	0.02
20	Experimental sample	2.3	0.96		3.32 ±	0.13	3.08 ±	0.04

[a] Experimental samples were from high pressure polymerization with a peroxide catalyst. I.C.I.: Imperial Chemical Industries Limited; Bakelite: Bakelite Company, a division of Union Carbide Corporation; Du Pont: E. I. du Pont de Nemours and Company.

[b] The melt index is the weight in grams of polyethylene extruded in 10 min. at constant temperature through an orifice of specified diameter when a given weight is placed on the driving piston.[8]

Table II also includes the values of the number of methyl groups per 100 carbon atoms as a measure of short-chain branching,[10] intrinsic viscosity in toluene at 80°C., and density of the samples at 25°C.

The correspondence between reciprocal of melt index and melt viscosity, it may be noted from Figure 3, is quite poor. Polyethylenes with approximately the same melt-index value have, in many cases, appreciably different melt viscosities. The main reason for this observed lack of correspondence is that melt index is a compound measure of the Newtonian viscosity and the dependence of viscosity on shear rate. In another paper,[11] we report results which show that the shear dependence of melt viscosity of different polyethylenes varies appreciably.

Temperature Dependence of Melt Viscosity

Melt viscosities of a number of polyethylenes were measured at different temperatures in the range of 138–242°C. to determine the activation energy for viscous flow of different polyethylenes. Plots of the logarithm of melt viscosity as a function of the reciprocal of absolute temperature in most cases were not linear, but showed a slight curvature. In the case of some polyethylene resins, the curvature was quite pronounced and was beyond experimental error. The plots of the logarithm of melt viscosity versus $1/T$ were therefore fitted to the equation of a parabola. Data were treated by the method of least squares applied to the equation:

$$\log \eta = a(1/T)^2 + b(1/T) + c \qquad (1)$$

where η is the melt viscosity at absolute temperature T. Slopes were calculated from this equation at two temperatures, 150 and 235°C. Apparent activation energy values at these two temperatures calculated from the slopes are given in Table III for the polyethylenes whose melt viscosities were measured at different temperatures.

The values of E_v at 150°C. are 12–18 kcal./mole except for sample 21, which had an E_v value of

TABLE III

Apparent Energy of Activation for Viscous Flow
of Polyethylenes at 150 and 235°C.

Sample number[a]	Polyethylene designation and source	Apparent energy of activation for viscous flow E_v, kcal./mole	
		150°C.	235°C.
1	DYNH-3, Bakelite	17.6	8.9
2	DYNH-3, Bakelite	13.8	10.7
3	Alathon-10, Du Pont	12.9	11.3
4	Alathon-14, Du Pont	11.8	10.9
5	Alathon-10, Du Pont	14.5	10.6
8	Alkathene-2, I.C.I.	13.4	10.6
12	DYNJ, Bakelite	13.2	13.0
21[b]	Semet-Solvay[b]	5.85	5.85

[a] Refer to Table II for molecular properties and melt viscosities at 202.2°C.

[b] Polyethylene of low viscosity (melt viscosity at 202.2°C. = 23.5 poises) obtained from Semet-Solvay Division, Allied Chemical and Dye Corporation.

about 6. The melt viscosity of this sample was also considerably lower than that of other polyethylenes. The melt viscosity at 202.2°C. for sample 21 was only 23.5 poises, as compared to melt viscosity values of $6 \times 10^4 - 14 \times 10^4$ poises for the others studied. Since melt viscosity is a function of weight-average molecular weight, the low value of E_v for sample 21 indicates that polyethylenes with low weight-average molecular weights have low activation energies for viscous flow.

We also measured the melt viscosities at different temperatures of a few polyethylene fractions. In Table IV are given the melt viscosity of these fractions at different temperatures and the values of E_v calculated from the slopes of plots of the logarithm of melt viscosity as a function of $1/T$. These results also show that, as molecular weight increases, the apparent activation energy for viscous flow increases. The E_v values increase from 8 to 13 kcal. as the intrinsic viscosity of the fractions (in toluene at 80°C.) increases from 0.16 to 0.96 (g./100 ml.)$^{-1}$.

The E_v values at 150 and 235°C. given in Table III for unfractionated polyethylenes are equal within experimental error for some samples, while for others they are appreciably different. The different polyethylene samples having the same designation and source in Tables II and III came from different lots of the same commercial resin, however, and there are measurable differences in the molecular and structural properties from lot to lot as a result of unavoidable variations in the manufacturing process. It is possible that difference in the amount of crosslinking at temperatures above 200°C. results in some cases, in a different flow mechanism at the two temperatures. A similar variation in activation energy of viscous flow did not occur with carefully fractionated samples.

Melt Viscosity of Fractionated Samples and Dependence of Melt Viscosity on Molecular Weight

To study the dependence of melt viscosity on molecular weight, the melt viscosities of a number of polyethylene fractions described in Table I were determined at 202.2°C. by the capillary viscometer method. The melt viscosity of polyethylene fractions is a function, not only of the molecular weight, but also of the number of short-chain branches in the molecule.[12] In the fractions of polyethylenes studied, the number of methyl groups per 100 carbon atoms (N_c) was nearly

TABLE IV

Temperature Dependence of Melt Viscosity of Polyethylene Fractions and Dependence of
Activation Energy for Viscous Flow on Intrinsic Viscosity $[\eta]$ in Toluene at 80°C.

Temperature, °C.	Melt viscosity, poises, for various polyethylene fractions				
	FC 405 $[\eta] = 0.16$	FC 403 $[\eta] = 0.57$	FC 304 $[\eta] = 0.58$	FC 303 $[\eta] = 0.97$	FC 402 $[\eta] = 0.96$
242.3	1.0	1.6×10^2	5.5×10^2	2.4×10^4	4.5×10^4
217.7	1.4	3.0	6.3	4.2	6.7
202.2	2.0	4.1	8.9	6.4	11.1
187.5	2.6	5.9	15.5	10.6	17.2
177.7	2.8	7.1	19.4	11.9	20.0
161.5	5.3	10.7	30.4	19.0	48.0
138.7	6.4	17.4	51.1	58.1	
E_v, kcal./mole	8.2	8.9	10.7	12.6	13.2

constant. The effect of short-chain branching on melt viscosity of the polyethylene fractions was therefore nearly constant.

In Table V are the melt viscosities at 202.2°C. and the intrinsic viscosities in toluene at 80°C. of the polyethylene fractions studied. The results show how sensitive the melt viscosity is to a change in intrinsic viscosity, i.e., to molecular weight. Figure 4 is a log-log plot of the melt viscosity of the polethylene fractions versus intrinsic viscosity in toluene at 80°C.

TABLE V
Melt Viscosity of Polyethylene Fractions at 202.2°C.

Fraction number	$[\eta]$ in toluene at 80°C., (g./100 ml.)$^{-1}$	Melt viscosity, poises
FC 303	0.97	6.43 × 10⁴
FC 304	0.58	9.5 × 10²
FC 305	0.29	21.0 × 10⁰
FC 402	0.96	11.1 × 10⁴
FC 403	0.57	4.1 × 10²
FC 404	0.31	25.0 × 10⁰
FC 405	0.16	2.0 × 10⁰
JM 402[a]	1.033	18.3 × 10⁴

[a] Fraction from DYNH-3 polyethylene from another fractionation run.

The intrinsic viscosity of polyethylene fractions varies as approximately the 0.8 power of the weight-average molecular weight.[13,14] Also, it has been proposed that for polymers in general the melt viscosity varies as the 3.4 power of the weight-average molecular weight,[15] provided that the molecular weight is above a critical value. The dependence of isothermal melt viscosity of the polymers as approximately the 3.4 power of the weight-average molecular weight is also in accord with flow theory of polymers.[16] On this basis it would be expected that a log-log plot of melt viscosity versus intrinsic viscosity would be linear with a slope of approximately 4.2. The initial portion of the plot in Figure 4 has a slope of 3.95, in fair agreement with that expected from theory. Beyond an intrinsic viscosity of about 0.5 (g./100 ml.)$^{-1}$, however, the melt viscosity increases much more sharply than 4.25-power dependence on intrinsic viscosity requires. This observed sharp increase in the melt viscosity of the high molecular weight fractions is probably a result of the low values of the intrinsic viscosity caused by the presence of long-chain branching[17] in the molecules of the high molecular weight fractions. It has
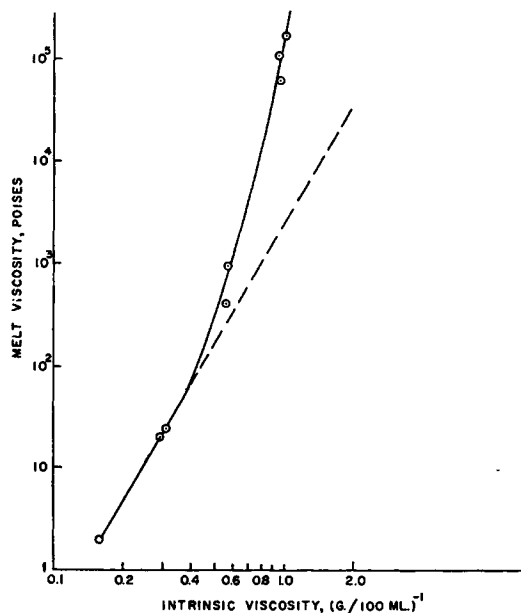

Fig. 4. Plot of log melt viscosity of polyethylene fractions at 202.2°C. vs. log intrinsic viscosity in toluene at 80°C.

been shown that the intrinsic viscosity of branched molecules is lower than that of linear molecules of the same average molecular weight[18-20] and the probability of long-chain branches increases with increasing molecular weight.[17,18] If an exact relation between melt viscosity and intrinsic viscosity of linear polyethylenes is established, it should be possible to calculate the weight-average number of branch points from measurements of intrinsic viscosity and melt viscosity of polyethylenes containing long-chain branching, by use of the equations developed by Zimm and Stockmayer[18] and Stockmayer and Fixman.[19] It should therefore be possible to estimate the long-chain branching in polyethylenes without the need of light-scattering measurements of weight-average molecular weights, which are experimentally difficult and are subject to many uncertainties. Measurements of melt viscosity of fractions of strictly linear polyethylenes will serve an important need in the molecular characterization of polyethylenes.

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Synopsis

The melt viscosity of fractionated and unfractionated polyethylenes at low shear rates have been measured in the temperature range 140–280°C. The melt index is not an adequate measure of melt viscosity determined at low shear rate. From melt viscosity and intrinsic viscosity determinations on fractions an estimate of the degree of long-chain branching can be made. From viscosity measurements at several temperatures between 140 and 280°C. values of the apparent activation energy for fractionated and unfractionated polyethylenes were obtained. The activation energy increases from 8 to 13 kcal. as the weight-average molecular weight increases about 20,000 to about 200,000.

Résumé

On a mesuré, dans le domaine de température de 140 à 280°C, la viscosité à l'état fondu de polyéthylènes fractionnés et non-fractionnés aux faibles tensions de cisaillement. L'indice de t° de fusion n'est pas une mesure adéquate de la viscosité déterminée sous faible tension de cisaillement. On peut estimer le degré de ramification à longue chaîne à partir de déterminations de viscosités à l'état fondu et de viscosités intrinsèques sur des fractions. A partir de mesures de viscosités à différentes températures entre 140° et 280°C, on a obtenu des valeurs de l'énergie d'activation apparente pour des polyéthylènes fractionnés et non-fractionnés. L'énergie d'activation croît de 8 à 13 Kcal lorsque le poids moléculaire moyen en poids croît de 20.000 à 200.000.

Zusammenfassung

Die Schmelzviskosität von fraktionierten und unfraktionierten Polyäthylenen wurde bei niedriger Schergeschwindigkeit im Temperaturbereich 140–280°C gemessen. Aus der Bestimmung der Schmelzviskosität und der Viskositätszahl kann das Ausmass der Langketten-Verzweigung abgeschätzt werden. Durch Viskositätsmessungen bei mehreren Temperaturen zwischen 140 und 280°C wurden Werte für die scheinbare Aktivierungsenergie für fraktionierte und unfraktionierte Polyäthylene erhalten. Mit Zunahme des Gewichtsmittels des Molekulargewichts von 20000 auf etwa 200000 steigt die Aktivierungsenergie von 8 auf 13 kcal an.