

Viscosity of Polyethylenes: Dependence on Molecular Weight at High Shear*

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INTRODUCTION

Reversible and irreversible changes in viscosity with shear are established phenomena for polymer systems. The behavior of pure liquids of molecular weight below 10,000 at high shear is less well understood.

Results on a structurally simple system are desirable to aid in understanding the mechanism of flow. The simplest system of compounds is that of the normal alkanes. The lower members of the series are available as pure substances. Polyethylenes simulate high molecular weight members of this series as their structures are approximately equivalent. Tests have been made on this series at high shear in evaluating the theories of flow.

EXPERIMENTAL

A concentric cylinder viscometer similar to that described by Barber et al.¹ was used in this work. The test fluid was held between the cylinders. The inner cylinder was rotated, and the torque transmitted through the test fluid was measured on the outer cylinder. The speeds of rotation were proportional to shear rate, and the resultant torques were a function of viscosity. Torque measurements were made using strain gages so that measurements could be recorded automatically, as were the speeds of rotation.

Several inner cylinders were used to provide varying clearances and, hence, to cover different rates of shear. All clearances were relatively small. The outer cylinder had a diameter, measured by a micrometer, of 1.00004 in. The clearance between an inner cylinder A and the outer cylinder was 3.05×10^{-4} in.; for cylinder F it was 1.09×10^{-4} in., for Z 1.51×10^{-3} , and for cylinder Y, 8.74×10^{-4} . These clearances were determined by instrument calibration with Newtonian oils of known viscosity behavior at low shear rates. The small

change in shear rate across the test film was within the experimental error of the method. Viscosities and shear rates were measured within $\pm 2\%$ of the true values. Both the inner and outer cylinders were thermostatted. Test temperatures were controlled and measured with an uncertainty of less than 1°C .¹ The test liquid was retained between the cylinders by surface tension; hence, there was no axial flow. Calculated Reynolds numbers were below 5 for all measurements. At Reynolds numbers below about 2000, laminar flow commonly exists.^{2,3}

RESULTS

Figure 1 shows the viscosity of several normal alkanes as a function of shear rate. There was no observable decrease in viscosity up to the maximum observed shear rate. Table I gives the maximum experimental shear rate and shear stress. In no case was there any observable change in viscosity due to shear. Capillary viscosities, at low shears, agreed with the results obtained in the concentric cylinder viscometer.

In order to obtain a measurable decrease in viscosity with increase in shear, higher molecular weights and shear stresses were necessary. Therefore, the viscosity—shear relationships for six polyethylenes were determined. Porter and Johnson⁴ describe these low density polymers and the

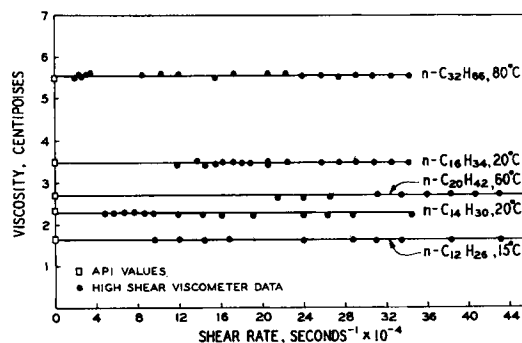


Fig. 1. Viscosities of normal alkanes.

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TABLE I
Viscosities of Normal Alkanes

Com- pound	Temp., °C.	Inner cyl- inder	Vis- cosity, poise	Maximum experimental value	
				Shear rate, sec. ⁻¹ × 10 ⁻⁵	Shear stress, dynes/ cm. ²
<i>n</i> -C ₁₂ H ₂₆	15	F	0.0166	3.85	6.39 × 10 ³
	20	F	0.0150	3.85	5.68 × 10 ³
<i>n</i> -C ₁₆ H ₃₄	20	A	0.0345	3.44	1.19 × 10 ⁴
	20	F	0.0345	9.65	3.33 × 10 ⁴
	40	A	0.0235	3.44	8.08 × 10 ³
	40	F	0.0235	3.36	7.90 × 10 ³
<i>n</i> -C ₂₀ H ₄₂	80	F	0.0173	5.69	9.34 × 10 ³
	40	F	0.0444	4.06	1.80 × 10 ⁴
	60	F	0.0278	5.75	1.60 × 10 ⁴
<i>n</i> -C ₃₂ H ₆₆	80	A	0.0556	3.44	1.91 × 10 ⁴
	80	F	0.0556	9.65	5.37 × 10 ⁴

method for determination of their molecular weights. The three polymers from Allied Chemical Corp. gave viscosity-average molecular weights (determined in Decalin at 70°C.) of 2800, 3300, and 8300; those from Eastman, 3900 and 5000; Bake-lite Corporation, 18,000.

Viscosities of polyethylenes are shown in Figures 2 and 3. For the two samples of lower molecular weight in Figure 2, little if any decrease in viscosity was observed with shear. The polyethylene sample with a molecular weight of 8300, however, showed a pronounced decrease in viscosity, falling from 108 poises to less than 7 poises over a short shear rate range. This was an entirely reversible effect. Measurements were made at three temperatures on this sample. Even at the lowest temperature, 110°C., the sample was in the true liquid state, as

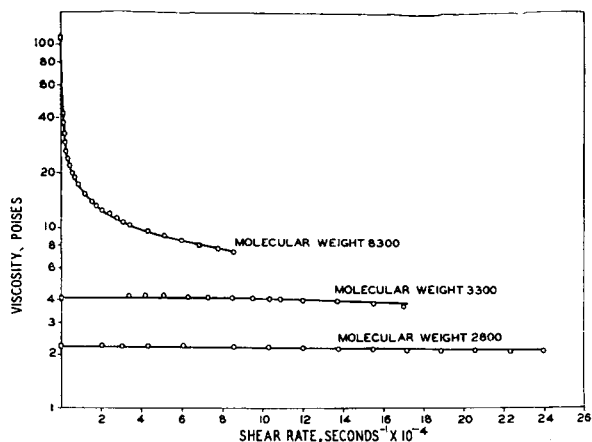


Fig. 2. Viscosities of polyethylenes at 110°C.

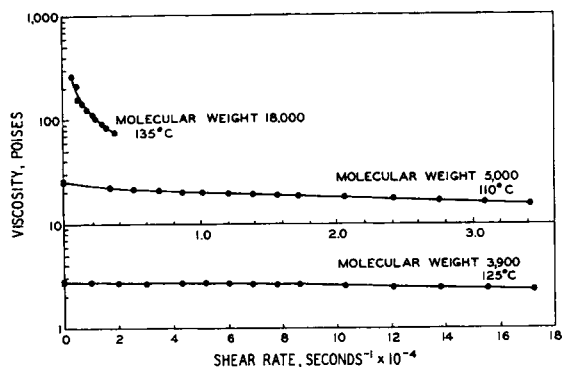


Fig. 3. Viscosities of polyethylenes.

characterized by a constant coefficient of thermal expansion.⁵ The higher temperature measurements at 120 and 125°C. insured that there was no possibility that a two-phase system existed. The results at the various temperatures are consistent and eliminate any chance that a suspended solid phase was present. The second series of polymers showed similar results. The polymer with molecular weight 3900 showed a small but real decrease in viscosity with shear; those with molecular weights of 5000 and 18,000 exhibited large effects. Low shear capillary viscometer results are shown on the ordinate in Figures 2 and 3.

COMPARISON OF THEORY WITH EXPERIMENT

There are a number of theories that explain the decrease in the apparent viscosity of bulk polymers with increase in rate of shear. The comparisons that follow were made on only one series of polymers from the same source to minimize differences due to the chemical composition of the polymers.

The comparisons with the various theories are not intended to check the validity of the theories over the broad combination of molecular weights and shear conditions that are possible. This study is concerned only with the lower molecular weight region and shears where a change from Newtonian to non-Newtonian flow is observed for polyethylene.

In all cases the observed data for the polymer with molecular weight of 8300 have been fitted to the various theories at one shear where a considerable decrease in apparent viscosity is observed. By doing this, uncertainties in the values of some of the parameters have been bypassed. As the comparisons are intended to test the effect of the molecular weight term in the equations in going from a region of no effect of shear to one where shear produces a large effect, this procedure should be valid.

TABLE II
Calculated^a vs. Observed Viscosities for Polyethylene at 110°C.

Molecular weight = 8300			Molecular weight = 3300			Molecular weight = 2800		
Shear rate, sec. ⁻¹ × 10 ⁻⁴	η (calc.)	η (obs.)	Shear rate, sec. ⁻¹ × 10 ⁻⁴	η (calc.)	η (obs.)	Shear rate, sec. ⁻¹ × 10 ⁻⁴	η (calc.)	η (obs.)
0.5	29.5	20.6	0.1	3.84	3.97	0.1	2.13	2.17
1	19.7	16.3	1	3.34	3.97	1	1.96	2.17
2	12.65 ^b	12.65 ^b	10	1.93	3.97	10	1.72	2.17
3	9.63	11.0	18	1.50	3.97	24	1.02	2.17
4	7.90	9.90						
5	6.76	9.10						
6	5.94	8.48						
7	5.33	7.95						
8	4.84	7.52						

^a See ref. 8.

^b Used to fit curve.

Bueche⁶⁻⁸ has explained the decrease in the viscosity of polymers with increasing shear stress as a consequence of rotation of the molecules by the shearing action: the sinusoidal forces which result from the rotation stretch and compress the molecules alternately. The theory predicts that a single universal curve will result if η/η_0 is plotted versus $\log(S\tau)$. Here we denote by η_S the measured viscosity at shear rate S and by η_0 the viscosity at essentially zero shear rate; τ at a given temperature for a series of molecular weights with approximately the same density is equal to a constant, C , times the product of molecular weight, M , and η_0 . The curves found for bulk polymers and concentrated solutions were well represented by the equation:⁶⁻⁸

$$\eta_0/\eta_S = 1.00 + 0.60(S\tau)^{3/4} \quad (1)$$

Expressing $(S\tau)^{3/4}$ as $(SCM\eta_0)^{3/4}$ and evaluating C at $S = 2 \times 10^4$, $\eta_0 = 108$, $\eta = 12.65$, $M = 8300$, we calculated from the observed values at 110°C., values for η for other molecular weights and shears as shown in Table II. It can be seen from Table II that predicted values for the viscosity of the lower molecular weight polymers change much more than the observed values. There may be considerable uncertainty in the value of η_0 , but even so the theory will not account for the behavior in the transition region. The equation developed by Pao^{9,10} which is similar to that of Bueche also does not predict the abrupt transition from Newtonian to non-Newtonian flow.

The well-known development by Eyring and co-workers¹¹ treats the flow of liquids as a rate process and applies the theory of absolute reaction rates. The resulting equation does not contain shear rate

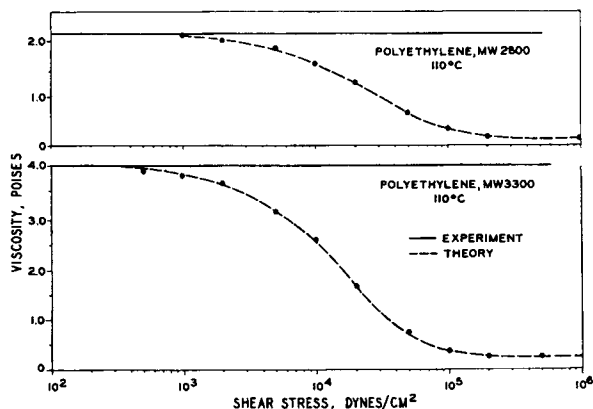


Fig. 4. Comparison with theory of Bondi.

or shear stress explicitly and must be modified to account for the effect of shear. Bondi¹² has proposed such a modification based on a relationship giving the change in entropy accompanying molecular orientation under the influence of a stress field.

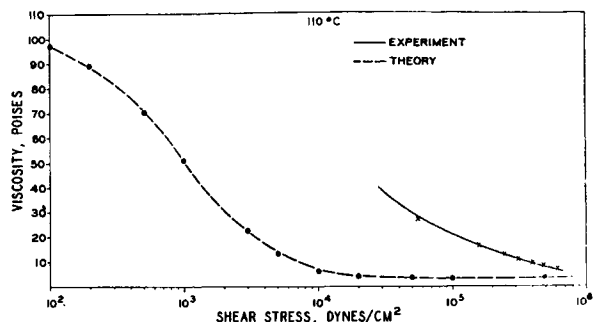


Fig. 5. Comparison with theory of Bondi; polyethylene, molecular weight 8300.

This results in

$$\eta_0/\eta_Z = 1 + [Z/(Z + 6kT/h_2^2h) \exp \{ -Zh_2^2h/kT \}] [(h_2/V^{1/3}) - 1] \quad (2)$$

where η_Z is the viscosity at a shear stress Z , h_2 is the intermolecular length assumed to be 1.21×10^{-8} ($M/14$), h is the length of equilibrium jump (assumed to be 1.22×10^{-7}), k is Boltzmann's constant, T is absolute temperature, and V is molar volume. With the assumed values as stated, eq. (2) can be compared with the present experimental results. This comparison is shown in Figures 4 and 5. For the lower molecular weight materials the predicted viscosity decreases are too large.

Another modification of the Eyring theory to account for the effect of shear is due to Grunberg and Nissan.¹³ Their equation may be written as

$$\eta_s = A/f \exp \{ fE/RT \}$$

where

$$f = X/(X + S) \\ X = B/M\eta_0 \quad (3)$$

and where E is the activation energy per mole for viscous flow, A and B are terms containing molecular parameters, and R is the gas constant. Other symbols have been defined previously. Values for E are available.⁴ Near zero shear $f = 1$, so A can be calculated from capillary viscosity data. At a known shear rate S where the measured change in viscosity is appreciable, f can be found by trial and error and X can then be calculated. Here B is a constant for a homologous series and is found from the value for X . These calculations are summarized in Table III.

TABLE III

Values Used to Calculate Viscosities for Grunberg-Nissan Theory

Poly-ethylene mol. wt.	E , kcal./mole	Viscosity poises, 110°C.	$\ln A$	X
2800	8.02	2.17	-9.7641	1.486×10^6
3300	8.32	3.97	-9.5517	6.893×10^6
8300	10.03	108	-8.5519	1.007×10^{10}

^a Based on an adjusted fit of equation at 2×10^4 sec.⁻¹ for which a viscosity of 12.65 poises was measured at 110°C.

Comparisons of experimental and theoretical results are shown in Figures 6 and 7. Predicted decreases in viscosity are much larger than those ob-

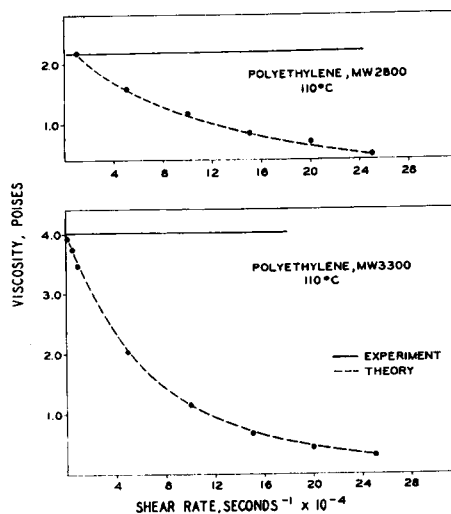


Fig. 6. Comparison with theory of Grunberg and Nissan.

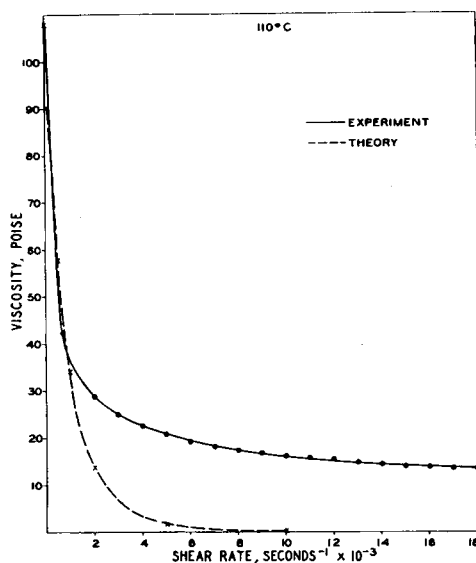


Fig. 7. Comparison with theory of Grunberg and Nissan; polyethylene, molecular weight 8300.

served. An arbitrary adjustment of parameters has been used to provide the best possible fit.

Ree and Eyring¹⁴⁻¹⁶ explain non-Newtonian viscosity behavior by assuming a flow system made up of three groups of flow units. Each of the groups is assumed to have an average relaxation time appreciably different from the others. The several parameters in the equation describing viscosity as a function of shear are determined from the experimental results.¹⁴ The equation can be made to fit a wide variety of systems, probably including the data reported here. However, there is no derivation of the parameters from properties of the poly-

mers, such as molecular weight, and in fact the parameters vary with molecular weight for solutions of polymers in an unpredictable fashion.¹⁰ Therefore no determination of the parameters for this type of equation was made. Similarly no comparison has been attempted with the empirical relationships proposed by Spencer.¹⁷

DISCUSSION

The lack of agreement between experimental results and molecular orientation theories for relatively low molecular weight polymers indicates that the major portion of the viscosity change due to shear may arise from some mechanism other than shear deformation and orientation. At a shear stress of 5×10^5 dynes/cm.², the polyethylene sample, with a molecular weight of 8300, shows a very large decrease in viscosity; under the same stress the change is less than 5% for a molecular weight of 3300. It would be expected that any theory involving the length of a molecule would express the viscosity as some function of the molecular weight. The ratio of these two molecular weights is 2.5. To account for the 400-fold difference observed, such a function would involve a sixth or higher power of the molecular weight. This seems improbable.

From experimental data on polyethylenes, it appears that non-Newtonian flow occurs abruptly above a critical molecular weight. For polymers, there is a critical molecular weight above which molecular entanglement becomes important.^{4,18} This critical molecular weight, M_c , can be determined from low shear viscosity measurements. At 110°C., for the systems studied in this work, M_c is about 2100.⁴ There is thus a reasonable correspondence between M_c and the onset of non-Newtonian flow. Polyethylenes with molecular weights of 2800 and 3300, respectively, are Newtonian, but have molecular weights above M_c . The reason for finding Newtonian flow above M_c may possibly be due to branching or molecular weight determination or definition. At the least, the concept of a critical molecular weight can account for the abrupt onset and large magnitude of non-Newtonian flow with increasing molecular weight. Bagley and West¹⁹ have independently concluded that poly(dimethylsiloxane) fluids exhibit non-Newtonian flow only above the critical molecular weight, in this case 29,000.

If indeed the non-Newtonian process is associated with chain disentanglement, then the low shear viscosity versus molecular weight slope below

M_c should predict the minimum values of viscosity at high shear. For polyethylenes, these values may be calculated from:

$$\log \eta = D (\log M) - G \quad (4)$$

where η is viscosity, poises $\times 10^3$ and D and G are constants, see reference 4, Table 2. For polyethylene with a molecular weight of 8300, such results are shown in Table IV. The agreement of

TABLE IV
Comparison of Calculated and Measured High Shear Viscosities

Temp., °C.	Values for eq. (4)		Infinite high shear viscosity	
	D	G	Calc. from eq. (4)	Extrapolated from data
110	1.94	3.64	9.2	6.0
120	1.92	3.64	7.6	5.0
125	1.91	3.65	6.9	4.5

calculated and experimental viscosities at high shear is considered reasonable. The calculated values are considerably better than derived from previously discussed theory (see Fig. 4-7). It may also be recalled that the low shear viscosity of this polyethylene, molecular weight 8300, is over 100 poises, while the calculated and measured high shear values at the same temperature are in the range 4-10 poises.

If molecular entanglement is the explanation for the relatively abrupt onset of non-Newtonian flow at low polymer molecular weights, it would suggest that the molecular weight term should be of the form $M-M_c$. This correction term would not perceptibly change existing theories at higher molecular weights. On the limited data presented here, no firm conclusions can be drawn; it would be of interest to see if other systems show a similar effect in the region of the critical molecular weight.

References

1. Barber, E. M., J. R. Muenger, and F. J. Villforth, Jr., *Anal. Chem.*, **27**, 425 (1955).
2. Gazley, C., Jr., *Trans. Am. Soc. Mech. Engrs.*, **80**, 79 (1958).
3. Barr, G., *A Monograph of Viscosity*, Oxford Univ. Press, London, 1931, p. 39.
4. Porter, R. S., and J. F. Johnson, *J. Appl. Polymer Sci.*, **3**, 192 (1960).
5. Ueberreiter, K., and H. J. Orthmann, *Kolloid-Z.*, **128**, 125 (1952).
6. Bueche, F., *J. Chem. Phys.*, **22**, 1570 (1954).
7. Bueche, F., *J. Chem. Phys.*, **22**, 603 (1954).

8. Bueche, F., and S. W. Harding, *J. Polymer Sci.*, **32**, 177 (1958).
9. Pao, Yoh-Han, *J. Appl. Phys.*, **28**, 591 (1957).
10. Pao, Yoh-Han, *J. Chem. Phys.*, **25**, 1294 (1956).
11. Glasstone, S., K. J. Laidler, and H. Eyring, *The Theory of Rate Processes*, McGraw-Hill, New York, 1941.
12. Bondi, A., *J. Appl. Phys.*, **16**, 539 (1945).
13. Grunberg, L., and A. H. Nissan, *Nature*, **156**, 241 (1945).
14. Ree, T., and H. Eyring, *J. Appl. Phys.*, **26**, 793 (1955).
15. Ree, T., and H. Eyring, *J. Appl. Phys.*, **26**, 800 (1955).
16. Ree, F. H., T. Ree and H. Eyring, *Ind. Eng. Chem.*, **50**, 1036 (1958).
17. Spencer, R. S., *J. Polymer Sci.*, **5**, 591 (1950).
18. Bueche, F., *J. Chem. Phys.*, **20**, 1959 (1952).
19. Bagley, E. B., and D. C. West, *J. Appl. Phys.*, **29**, 1511 (1958).

Synopsis

A high shear, concentric cylinder viscometer was used to study polyethylene samples which differed in molecular weight. Viscosities were measured at several temperatures in laminar flow at shear rates up to $2.5 \times 10^6 \text{ sec}^{-1}$. Five high molecular weight normal alkanes were also studied in evaluating shear dependent flow. Viscosities of the normal alkanes and polyethylenes with molecular weights up to about 3300 were Newtonian over the shear range studied. Polyethylenes with higher molecular weights showed large and reversible decreases in viscosity with increasing shear. Viscosity results at high shear were compared with available theory. Previous concepts based on molecular orientation apparently cannot account for the abrupt onset of non-Newtonian flow with increasing molecular weight. An alternate explanation of non-Newtonian flow is offered in terms of molecular disentanglements. This concept permits a qualitative prediction of the magnitude of non-Newtonian flow, as well as the molecular weights for which it will become important.

Résumé

Des échantillons de polyéthylènes de différents poids moléculaires ont été étudiés dans un viscosimètre à cylindre concentrique à tension de cisaillement élevée. Des viscosités ont été mesurées à plusieurs températures en écoulement laminaire à des vitesses de cisaillement allant jusque $2.5 \times 10^6 \text{ seconds}^{-1}$. Cinq alcanes à chaîne normale de poids

moléculaire élevé ont également été étudiés pour évaluer la dépendance de l'écoulement sur le cisaillement. Les viscosités des alcanes à chaîne normale et des polyéthylènes ayant des poids moléculaires allant jusque environ 3300 étaient Newtoniennes dans le domaine de cisaillement étudié. Des polyéthylènes ayant des poids moléculaires plus élevés présentent des diminutions de viscosité importantes et réversibles avec une augmentation de cisaillement. Les résultats viscosimétriques à cisaillement élevé ont été comparés avec une théorie valable. Les concepts antérieurs basés sur une orientation moléculaire ne peuvent pas apparemment expliquer le brusque changement de l'écoulement non-Newtonien avec l'accroissement du poids moléculaire. Une explication de l'écoulement non-Newtonien peut-être donnée en faisant appel aux déroulements moléculaires. Ce concept permet de prévoir d'une façon qualitative l'importance de l'écoulement non-Newtonien et des poids moléculaires pour lesquels cela deviendra important.

Zusammenfassung

Ein Viskosimeter mit konzentrischen Zylindern, das für Messungen bei hohem Schub geeignet war, wurde zur Untersuchung von Polyäthylenproben mit verschiedenem Molekulargewicht verwendet. Die Viskosität wurde bei mehreren Temperaturen unter laminarem Fließen bei Schergeschwindigkeiten bis zu $2,5 \times 10^6 \text{ sek}^{-1}$ gemessen. Auch fünf normale Alkane mit hohem Molekulargewicht wurden zur Ermittlung ihres Fließverhaltens in Abhängigkeit vom Schub untersucht. Die Viskosität der normalen Alkane und der Polyäthylene mit Molekulargewichten bis zu etwa 3300 entsprach über den ganzen verwendeten Schubbereich dem Newtonschen Gesetz. Polyäthylene mit höheren Molekulargewichten zeigten mit zunehmendem Schub eine grosse und reversible Viskositätsabnahme. Die Viskositätsergebnisse bei hohem Schub wurden mit der bestehenden Theorie verglichen. Die früheren Erklärungsversuche, die auf der Molekülorientierung basieren, können offenbar den plötzlichen Eintritt eines nicht-Newtonischen Fließens mit steigendem Molekulargewicht nicht richtig wiedergeben. Eine andersartige Erklärung für das nicht-Newtonische Fließen auf Grundlage einer Auflösung der Molekülverschlingungen wird vorgeschlagen. Ein solches Konzept erlaubt eine qualitative Voraussage sowohl der Grösse des nicht-Newtonischen Fließens, als auch des Molekulargewichts, bei welchem es praktische Bedeutung gewinnt.

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