

Structural Turbulence in Polymer Solutions

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Synopsis

The appearance of structural turbulence in polyisobutylene solutions at low Reynolds numbers has been detected and analyzed. This type of turbulence is characterized by a critical shear stress rather than a critical Reynolds number. The critical shear stress decreases with increasing molecular weights or dilution. The role of deformability of the polymer chains under shear flow is found to be significant.

Introduction

In a previous study,¹ published in part elsewhere,² some anomalous behavior of polymer solutions under shear was detected. These solutions were subjected to high shear conditions in a specially designed Merrill-Brookfield viscometer of the coaxial cylinder type.³ In a couette flow developing between an inner rotor and an outer stator, vortices may arise known as Taylor vortices.⁴ The onset of these vortices generally depends solely on the geometry of the rotating cylinders. The critical Reynolds number associated with this type of turbulence is usually lower than the one characterizing onset of turbulence in pipes. In the polymer solutions exhibiting an anomalous behavior "early turbulence" appeared at Reynolds numbers that were lower than those predicted by Taylor.

A typical flow curve of shear stress versus shear rate of a pseudoplastic liquid is given in Figure 1. The apparent viscosity, η_{ap} , of such a liquid is defined by the ratio of shear stress to shear rate at a given stress in the laminar region. The onset of turbulence is indicated by a sharp and steady rise of the apparent viscosity with increasing rates of shear. The rise is due to the contribution of eddy viscosity E to the apparent viscosity. Consequently for the shear stress τ

$$\tau = (\eta + E)du/dy \quad (1)$$

In calculating the critical Reynolds number of early turbulence use is made of the local value of apparent viscosity in the laminar region at the onset of turbulence.

In the present study the behavior of polymer solutions under high shear was investigated by use of a capillary viscometer. The results of this work present new information concerning early turbulence that may provide a better understanding of this phenomenon.

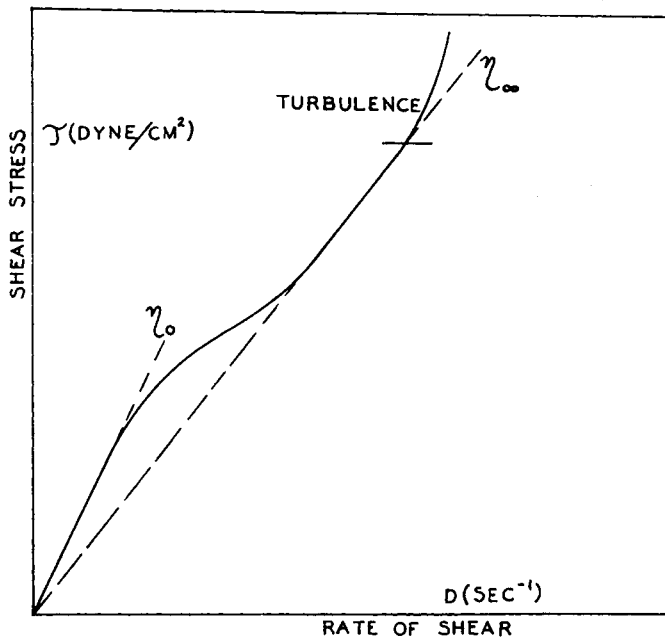


Fig. 1. A complete flow curve of a pseudoplastic liquid.

Experimental

Experiments were carried out with the use of a stainless capillary viscometer designed for high shear rates of about 10^5 – 10^6 sec^{-1} . Details of this viscometer and its use are published elsewhere.⁵

The polymer tested was polyisobutylene of four different grades supplied by Enjay Co. The viscosity-average molecular weights \bar{M}_v were as follows: LMMS, $\bar{M}_v = 50,000$; L - 120, $\bar{M}_v = 1.75 \times 10^6$; L - 140, $\bar{M}_v = 2.17 \times 10^6$; L - 250, $\bar{M}_v = 6.22 \times 10^6$.

The solvents used were: kerosene, mineral oil A (viscosity 8.04 centipoise at 100°F .); and mineral oil B (viscosity 26.3 centipoise at 100°F .). Solutions of various concentrations were carefully prepared. Viscometric data at a wide range of shear rates and temperatures were determined by the capillary viscometer. Flexibility of working conditions was achieved by using an external source of nitrogen pressure and variety of capillaries of different radii and lengths.

The readings of pressure heads and volumetric flow rates were translated into shear stress and shear rates, respectively, by using a rigorous mathematical treatment, developed by Rabinowitsch.⁶ The latter calculates conditions at the wall for any rheological system regardless of its flow character. By using the shear values at the wall, the uncertainty entailed in an unknown average shear rate is avoided.

Shear rate at the wall is given by Rabinowitsch as:

$$(du/dr)_w = (4\bar{U}/R)[(3n' + 1)/4n'] = [(3n' + 1)/4n']D^*_w \quad (2)$$

where \bar{U} is the average velocity, R is the capillary radius,

$$n' = d \log \tau_w / d \log D_w^* \quad (3)$$

and where D_w^* is the shear rate at the wall for a Newtonian liquid. The shear stress at the wall is represented by:

$$\tau_w = \Delta P R / 2L \quad (4)$$

where ΔP is the pressure drop and L is the length of the capillary. Equation (4) should be corrected for kinetic energy effect, capillary end effects, and elastic dissipation of pressure. The correction for the part of pressure energy transformed into kinetic energy is given in terms of pressure head by:

$$\Delta F = \Delta P^* - m\rho\bar{U}^2 \quad (5)$$

where ΔP^* is the measured pressure head and ρ is the density. The coefficient m , named after Hagenbach, takes care of contraction effects at the entrance. Most investigators take m to be 1.12.

Capillary end corrections for establishing the flow profile are taken into consideration by using an equivalent length L' ;

$$L' = L + NR \quad (6)$$

where N is the Couette coefficient.

In the present study the capillaries used were sufficiently long, the range of L/R being 100–1500, to eliminate these end corrections. Details of these capillaries are given in Table I.

TABLE I
Details about Capillaries Used

Symbol*	Radius R , cm.	Length L , cm.	L/R
•	0.0104	3.51	338
∇	0.015	2.22	148
○	0.0204	11.76	576.5
■	0.0204	30.11	1475
+	0.0261	6.74	258
●	0.0261	5.68	218
^	0.0297	6.0	202
□	0.0297	40.46	1360
▲	0.0306	5.99	196
△	0.0425	15.25	359
▽	0.0425	4.93	116

* Symbols used in Figs. 2–7.

Lastly the role of the elastic deformation generated by pressure dissipation was checked following Philippoff,⁷ by modifying eq. (5) to:

$$\Delta P = \Delta P^* - m\rho\bar{U}^2 - P_{11w} \quad (7)$$

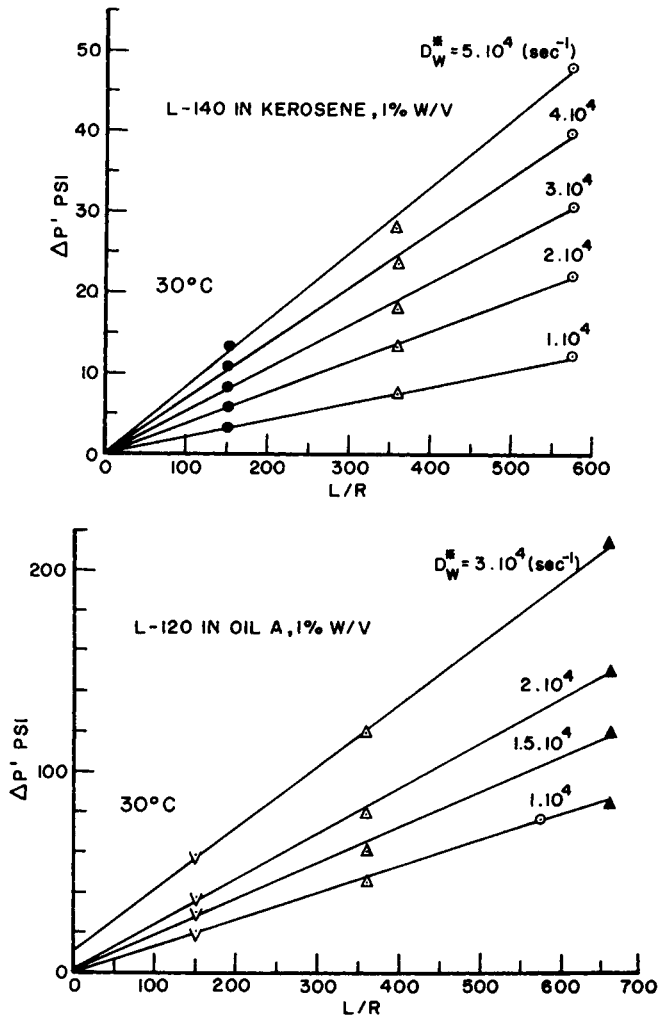


Fig. 2. Dependence of corrected pressure head $\Delta P'$ on capillary geometry L/R (ratio of length to radius of capillary). The purpose of this plot is to detect the elastic component for various shear rates.

The axial normal stress, P_{11} , is given by:

$$P_{11} = \tau S \quad (8)$$

where S is the recoverable shear.

Rearranging eq. (7) gives:

$$\Delta P' = \Delta P^* - m\rho\bar{U}^2 = \Delta P + P_{11w} = \tau_w[(2L/R) + S_w] \quad (9)$$

Equation (9) predicts a linear relationship between $\Delta P'$, the corrected pressure head for kinetic energy effects, and L/R . From this equation the value of $\tau_w S_w$ equals $\Delta P'$ at $L/R = 0$.

A plot of $\Delta P'$ versus L/R , based on experimental results of this study, is represented in Figure 2. It is readily seen that the elastic term was in most cases negligible. In contrast, the kinetic energy correction amounted to about 40% of the pressure head in extreme cases. The effect of temperature variations and dissipation of energy into heat on the measured viscosity was generally found to be small.

Results

The calculated values of the shear stresses and shear rates are shown as flow curves in Figures 3-5. The onset of turbulence is clearly detected in the flow curve. Mathematically, turbulence is represented either by a value of n' exceeding 1, or by an increase of apparent viscosity. The use of the latter criterion for various molecular weights of the polymer is shown in Figure 6. Typical results of turbulence are summarized in Table II.

The flow curves, in addition to the onset of turbulence, indicate the effects of polymer degradation under conditions of high shear. It is indicated by a non-reversible viscosity drop due to chain scission. In reviewing the results, it is interesting to note that LMMS, having the lowest molecular weight, showed neither turbulence nor degradation. As the polymer chain, i.e., its molecular weight increased, both phenomena became more and more significant. A more detailed analysis of chain degradation in polymer solutions may be found elsewhere.⁸ In this work degradation appeared in the turbulent as well as in the laminar regions.

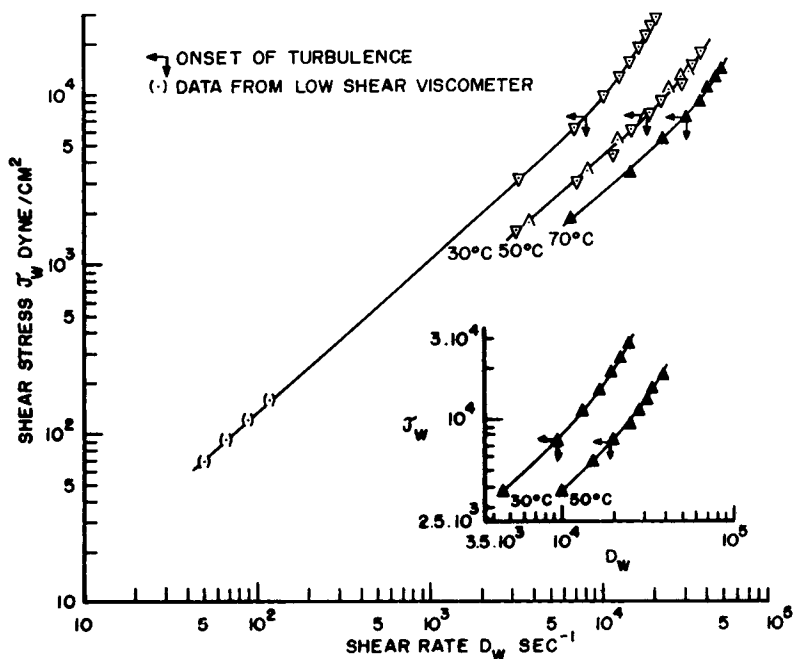


Fig. 3. Flow curves for solutions of polyisobutylene L-120 in oil B ($c = 0.52\%$ w/v).

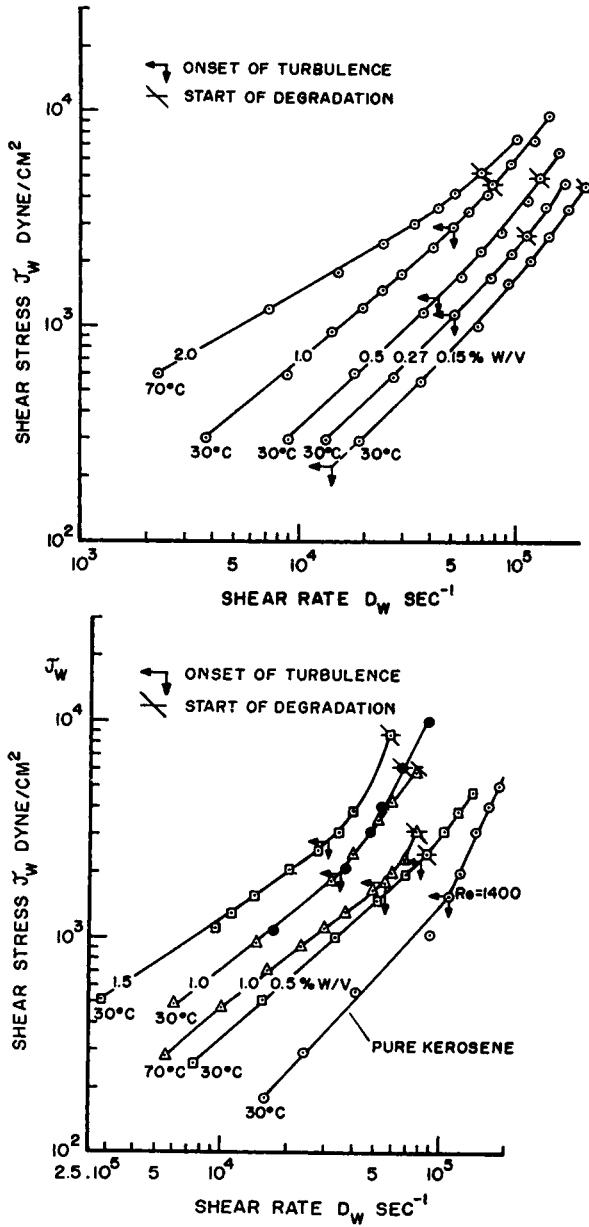


Fig. 4. Flow curves for solutions of polyisobutylene L-140 in kerosene.

The results may be summarized as follows.

- (1) Dilute solutions of polyisobutylene (molecular weight above 1.7×10^6) show early turbulence at critical Reynolds numbers in the range of 1-1000.

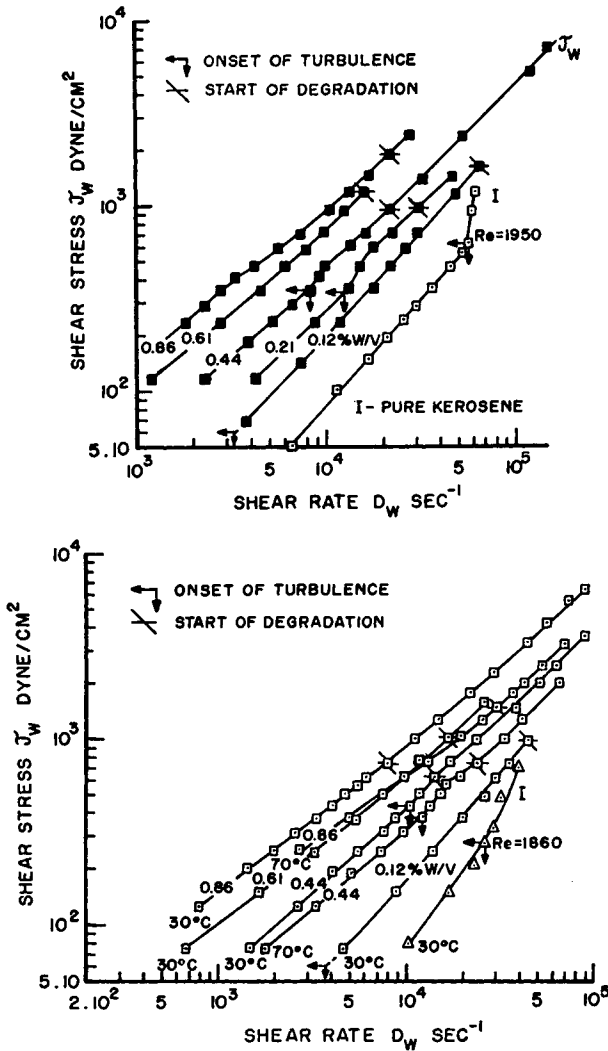


Fig. 5. Flow curves for solutions of polyisobutylene L-250 in kerosene.

(2) The critical Reynolds numbers decrease upon increasing molecular weight or concentration of the polymer in the solution.

(3) The critical Reynolds numbers decrease on decreasing capillary diameters.

(4) The critical velocity at the onset of turbulence, \bar{U}_c , increases linearly with capillary radius.

(5) The critical shear stress, at the onset of turbulence, τ_{wc} , decreases upon dilution or increase of the molecular weight of the polymer solute.

(6) The type of solvent or the test temperature does not alter the rheological behavior of the polymer solution.

TABLE II
Onset of Structural Turbulence in Polyisobutylene Solutions at 30°C.

Polymer	Solvent	Concentration, g./100 cc.	R, mm.	τ_{w0} , dyne/cm. ²	Re _c	\bar{U}_c , cm./sec.
L-120	Kerosene	0.17	0.20	$<5.7 \times 10^2$	<384	<188
"	"	0.30	0.20	$<8 \times 10^2$	<290	<194
"	"	1.0	0.20	7×10^3	209	314
"	"	2.0	0.20	^a	^a	^a
"	Mineral oil A	1.0	0.10	6.6×10^3	1.3	36
"	"	1.0	0.15	7.7×10^3	4.7	62
"	"	1.0	0.20	7×10^3	6.5	82
"	"	1.0	0.30	6×10^3	10	95
"	"	1.0	0.40	7.8×10^3	43	220
"	Mineral oil B	0.28	0.26	5.7×10^3	4.5	62
"	"	0.28	0.31	5.7×10^3	5.3	66
"	"	0.28	0.42	5.6×10^3	12	98
"	"	0.52	0.31	7.6×10^3	3.7	64
"	"	0.52	0.42	7.1×10^3	7.4	88
L-140	Kerosene	0.15	0.20	2.9×10^2	<200	<98
"	"	0.27	0.20	1.1×10^3	397	270
"	"	0.5	0.20	1.4×10^3	245	235
"	"	0.5	0.30	2.3×10^3	1090	630
"	"	1	0.10	2.1×10^3	21	85
"	"	1	0.2	3×10^3	148	265
"	"	1	0.26	2×10^3	162	228
"	"	1	0.42	1.9×10^3	378	340
"	"	1.5	0.30	2.8×10^3	137	230
"	"	1.5	0.42	2.9×10^3	280	362
L-250	"	0.12	0.20	$<7 \times 10$	<35	<20
"	"	0.12	0.30	$<7.6 \times 10$	<100	<35
"	"	0.44	0.20	3.5×10^2	30	40
"	"	0.44	0.30	4.5×10^2	85	78
"	"	0.61	0.20	^a	^a	^a
"	"	0.61	0.30	^a	^a	^a

^a Not detected under test conditions.

Discussion

The appearance of early turbulence in colloidal and polymer solutions was reported for the first time by Ostwald,⁹ Hatschek and Jane,¹⁰ and Andrade and Lewis.¹¹ Ostwald named his phenomenon "structural turbulence" since it appears only in systems which exhibit a special structure. The subject was discussed later by Schnurmann,¹² Davies,¹³ Bestul and Bryant,¹⁴ and recently by Brodnyan and Kelley.¹⁵ Porter and Johnson¹⁶ found early turbulence to be confined to jet viscometers but not to rotational ones. In most studies the criterion for the onset of turbulence was a sharp increase of apparent viscosity. In one case,¹¹ vortices were actually observed by optical means. Critical Reynolds numbers were found in extreme cases to be as low as 1.

The best criterion for distinguishing between "Reynolds turbulence" and

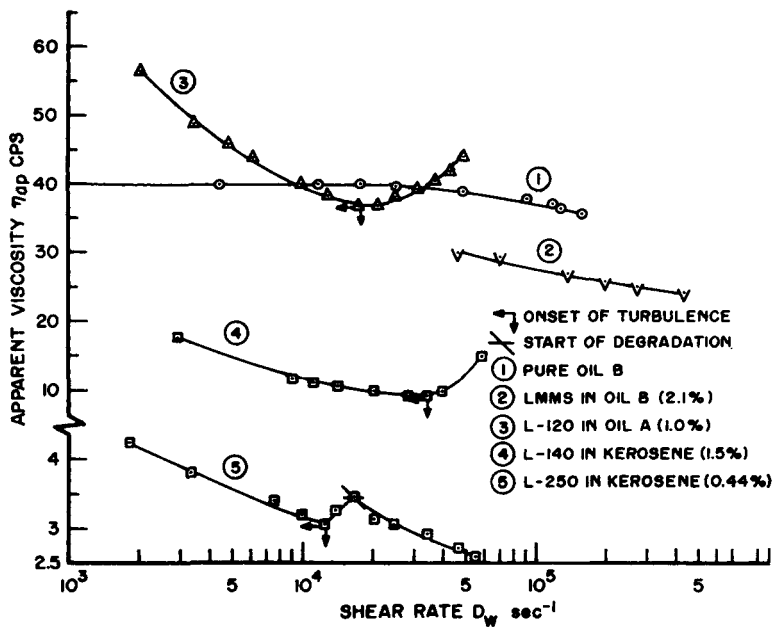


Fig. 6. Summary of viscosity changes under shear. Dependence of apparent viscosity of polymer solutions on shear rate.

“structural turbulence” was suggested by Reiner.^{17,18} According to Reiner, Reynolds turbulence is characterized by a critical Reynolds number, Re_c , defined as:

$$Re_c = \bar{U}_c 2R\rho/\eta \quad (10)$$

The critical Reynolds number was found to be a constant and independent of the material properties.

It may be seen from eq. (10) that:

$$\bar{U}_c \propto 1/R$$

$$\bar{U}_c \propto \eta$$

Structural turbulence, however, is characterized by a critical shear stress, τ_c , which has a typical value for every substance. This critical shear stress indicates a collapse of the structure of the fluid. Its value at the wall of the capillary is given by:

$$\tau_{wc} = \Delta PR/2L = 4\bar{U}_c\eta/R = (4\bar{U}_c/R)\eta_{sp}[(3n' + 1)/4n'] \quad (11)$$

Here

$$\bar{U}_c \propto R$$

$$\bar{U}_c \propto 1/\eta$$

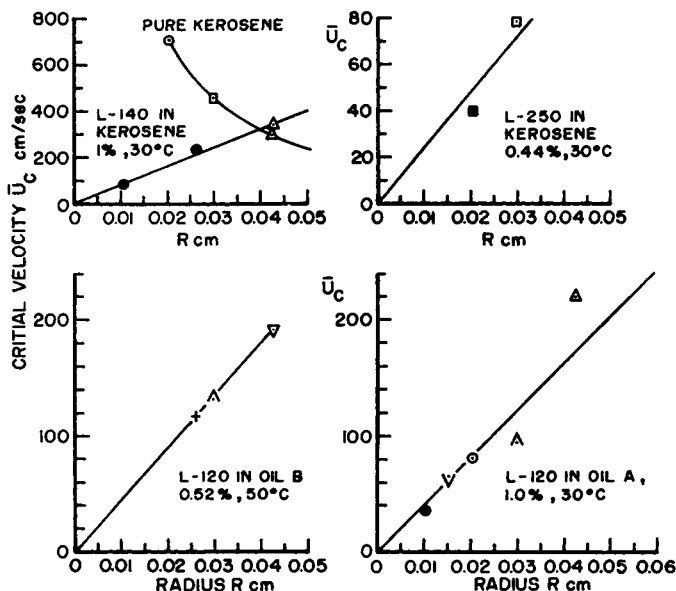


Fig. 7. Critical velocity \bar{U}_0 vs. radius of capillary R . Criterion for structural or Reynolds turbulence.

As the product $\bar{U}_c R$ appears in Reynolds number, it is obvious that Re_c , in the case of structural turbulence, varies as R^2 .

The difference between Reynolds and structural turbulence is clearly visualized. On plotting the critical velocity, \bar{U}_c , versus the capillary radius R , structural turbulence is described by a straight line extrapolated to the origin. The Reynolds turbulence, on the other hand, is characterized by a hyperbolic curve.

The data for the various polymer solutions were plotted as \bar{U}_c versus R in Figure 7. Structural turbulence is clearly indicated, whereas Reynolds turbulence is exhibited by the pure solvent only. From the above analysis it may be concluded that the numerical value of Re_c loses its significance as a criterion for structural turbulence.

The anomalous behavior of polymer melts in extrusion termed "melt fracture" bears much resemblance to the structural turbulence. Melt fracture is characterized by rigidity, waviness, and fracture of polymer melts which appear respectively upon increasing shear rates.¹⁹ In such melts, the values of Re_c are exceedingly low. However, a critical shear stress is found which is inversely proportional to the molecular weight of the polymer species.

Independent of the theory of structural turbulence, Peterlin^{20,21} predicts a rise in the intrinsic viscosity of completely flexible polymer chains sheared in extremely dilute solutions. According to his theory individual polymer chains, after being oriented in the direction of flow, will uncoil and elongate under shear. Experiments carried out by Peterlin and Turner²²

showed "rheopexic" behavior, while Selby²³ noticed "pseudo-dilatancy" in polymer solutions. However, the idea of materials changing their rheological character under shear from pseudoplasticity to pseudodilatancy does not seem convincing. Structural turbulence might as well be the cause for the viscosity rise in such experiments.

In contrast to early turbulence, regular turbulence at Reynolds numbers exceeding 2000 was noticed by Dodge and Metzner in some polymer solutions.²⁴ It should be emphasized, however, that the materials tested by the latter, like carboxymethyl cellulose and Carbopol, are definitely nonflexible in shear flow. Moreover, the shear stresses were not high enough to cause any structural effect. Consequently, structural turbulence could not be detected.

Data of this study indicate the existence of a critical shear stress at the onset of turbulence. Its value decreases with increasing of either molecular weight or dilution. Dilution provides better chances for the elongation of the individual chains. Therefore it promotes the idea of turbulence being initiated by expansion of polymer chains under shear. By increasing the molecular weight the flexibility or deformability of the chains increase. Therefore, structural turbulence may be the result of chain deformation. Thus it appears that the conditions for the onset of turbulence are closely related to the deformability of the polymer chains under shear. Any previous structure such as association or entanglement must be broken before the effects of elongation show up. On increasing concentration, this structure is obviously much less liable to break, and higher shear stresses are needed. It is here postulated that uncoiling of long polymer chains, rotating at high speed under severe shear conditions, generates nuclei of turbulence vortices.

Work on the theoretical aspects of structural turbulence is in progress. In addition, experimental techniques for visualization of vortices are being developed. Results will be reported in due time.

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Résumé

On a détecté et analysé l'apparition pour des nombres de Reynolds peu élevés d'une "turbulence structurelle" dans des solutions de polyisobutylène. Ce type de turbulence est caractérisé par une force de cisaillement critique plutôt que par un nombre de Reynolds critique. La force de cisaillement décroît avec l'augmentation des poids moléculaires ou la dilution. On a trouvé que le rôle de la déformabilité des chaînes de polymère sous l'écoulement de cisaillement avait une certaine importance.

Zusammenfassung

Das Auftreten von "Strukturtrubulenz" in Polyisobutylenlösungen bei niedrigen Reynolds-Zahlen wurde festgestellt und untersucht. Diese Art von Turbulenz wird besser durch eine kritische Schubspannung als durch eine kritische Reynolds-Zahl charakterisiert. Die kritische Schubspannung nimmt mit steigendem Molekulargewicht oder steigender Verdünnung ab. Die Rolle der Deformierbarkeit der Polymerketten bei Schubfließen scheint bedeutend zu sein.

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