Normal Stress Effects in Polymer Solutions. I. Measurements in a Parallel Plate Instrument

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It is well noted that a visco-elastic fluid under steady shear flow usually generates not only shearing stress but also normal stresses. Thus, the essential requirement for obtaining the complete information for flow behavior of such a fluid is the development of the *goniometry of flow*, or in other words, the development of experimental procedures for the determination of all stress components, i.e., shearing stress and normal stresses[1,2].

In this report, as the first step of the stress-goniometry of flow, we will describe some findings on the normal stress measurements in a parallel plate instrument. Correlations between observed normal pressure and dimension of the instrument, and influences of secondary effects which inevitably arise in the course of measurements will be discussed at some length[3]. Detailed descriptions of the data and their physical interpretations will be published in a subsequent paper[4].

Padden and DeWitt[5], and recently Markovitz and Williamson[6] have suggested that the concentration and temperature dependencies of normal stress should be expressible in terms of "*reduced variables*". These suggestions are tested with the data obtained in our measurements.

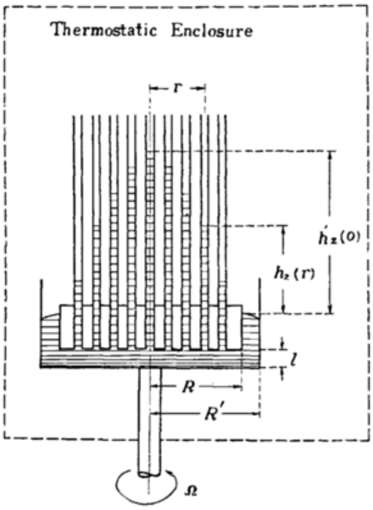

Fig. 1. Schematic diagram of the parallel plate instrument.

TABLE I. DIMENSIONS OF BOBS AND CUPS FOR NORMAL STRESS MEASUREMENTS

	Radius cm.	Manometer tubes		
		Number	Diameter cm.	Spacing cm.
Bob A	5.0	9	0.5	1.0
Bob B	6.5	13	0.2	0.8
Bob C	7.0	15	0.2	0.8
Cup 1	6.0			
Cup 2	8.0			

Experimental

Instrument and Principles.—A parallel plate instrument used in this study is shown in Fig. 1. The figure itself is self-explanatory. An outer cup containing a test fluid is rotated at a steady speed within the range of 5 to 170 rpm by driving through a pulley and belt system by a 1/2 H. P. induction motor. The rotating bob is held at a distance of one centimeter or less above the cup. The dimensions of two outer cups and three inner bobs used in this study are listed in Table I. When the cup is rotated, the fluid, if it shows the normal stress effect, rises in the manometer tubes mounted on the stationary bob and reaches equilibrium levels. Equilibrium heights of the fluid were read by a travelling microscope. The non-parallelism and the non-concentricity of two plates, especially the former, largely affect the pressure distribution and disturb the quantitative measurements. A con-

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[1] The general review on this subject is obtained in the following article: M. Kurata, "The Weissenberg Effect", in Kobunshi-Jikkengaku-Koza, Vol. V, ed. S. Kambara, Kyoritsu Publishing Co., Tokyo (1958), Chap. 15.

[2] See also, A. Jobling and J. E. Roberts, "The Goniometry of Flow and Rupture", in Rheology Vol. II, ed. F. Eirich, Academic Press, New York (1958), Chap. 14.

[3] Works of similar nature were developed by Greensmith and Rivlin, but they are different from ours in the standpoint and the approach to the problem. H. W. Greensmith and R. S. Rivlin, *Phil. Trans. Roy. Soc.* (*London*), **245**, 399 (1953).

[4] T. Kotaka, M. Kurata and M. Tamura, in preparation.

[5] F. J. Padden and T. W. DeWitt, *J. Appl. Phys.*, **25**, 1086 (1954).

[6] H. Markovitz and R. B. Williamson, *Trans. Soc. Rheology*, **1**, 25 (1957).

dition free from such disturbances is easily attained by making sure that the symmetry in pressure distribution is established and that the pressure values are kept unchanged by clockwise and counterclockwise rotations at the same speed. The temperature at which the measurements were run was roughly controlled within ±1.0°C by a simple thermostatic enclosure.

The normal pressure is correlated to the normal stresses by the relation of force equilibrium in torsional shear flow as follows:

$$-\frac{\partial P_z(r)}{\partial \ln r}=\sigma_{11}-\sigma_{33}+\frac{\partial(\sigma_{22}-\sigma_{33})}{\sigma \ln r} \tag{1}$$

or in the integral form

$$\begin{aligned}\Delta P_z(r)&=P_z(0)-P_z(r)\\&=\int_0^r(\sigma_{11}-\sigma_{33})\frac{\mathrm{d}r}{r}+\sigma_{22}-\sigma_{33}\end{aligned} \tag{2}$$

and

$$P_z(0)-P'=\int_0^R(\sigma_{11}-\sigma_{33})\frac{\mathrm{d}r}{r} \tag{3}$$

where $P_z(r)$ denotes the pressure exerted on the stationary bob of radius R at the distance r from the rotating axis, P' denotes the pressure exerted on the fluid in the gap from the outside, σ_{ii} ($i=1,2,3$) denotes the normal stress component parallel to the direction of flow ($i=1$), and perpendicular to the shearing surface ($i=2$), and perpendicular to both ($i=3$), respectively. It should be noted here that in the derivation of the above equations the influences of the centrifugal force, and of disturbances of flow arising from edge effects were all neglected. It is readily seen that, if the state of flow were ideally torsional shear and undesirable disturbances were depressed within the experimental error, the left hand sides of the equations from 1 to 3 should be dependent on the rate of shear, $D=r\Omega/l$, alone. Here r is the distance from the axis, Ω is the angular velocity of rotation and l is the gap between two plates.

Materials.—Solutions of a commercial sodium carboxymethylcellulose (Na-CMC; Harcules, Cellulose Gum Type 70 sp-High) obtained through the courtesy of Dr. H. Inagaki of this University were mainly used in this study. Its molecular weight was about 10^5, and the range of degree of carboxymethylation was from 0.65 to 0.95. The data obtained on the solutions of commercial methylcellulose* (Interchemical, Methocell 4000 cp: $\bar{M}_V \sim 10^5$, *D.S.*$\sim$0.92) in water and polystyrene* (Lustrex Hi-Flow 77, $\bar{M}_V \sim 10^5$) in decalin are also described for the sake of comparison.

Results and Discussion

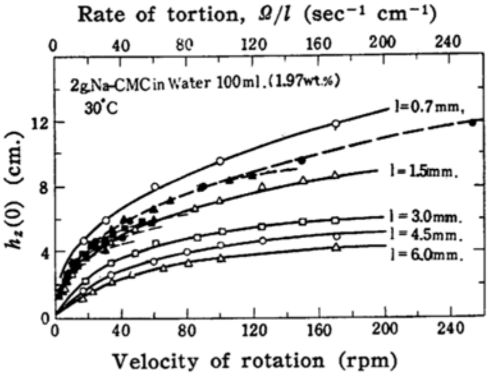

Fig. 2. $h_z(0)$ vs. velocity of rotation (solid lines) and $h_z(0)$ vs. rate of torsion, Ω/l (broken lines); Na-carboxymethylcellulose in water 1.97% at 20°C.

Some Geometrical Studies in a Parallel Plate Instrument.—*$h_z(0)$ vs. Ω Relations: the Centrifugal Force Effect:*—With the combination of bob A and cup 1, we first read $h_z(0)$ against the rotational velocity, Ω, with various gaps, l, on solution of 2g. Na-CMC in 100 ml. water (1.97 wt.%). The results are shown by solid lines in Fig. 2. If the curves of $h_z(0)$ vs. Ω with different l are replotted against the rate of torsion, Ω/l, they fall on a single reduced curve as shown by a broken line in Fig. 2. Close inspection, however, reveals that $h_z(0)$ value begins to deviate below the reduced curve when the rotational speed exceeds about 70~80 rpm irrespective of the gap, l. This tendency should be attributed mainly to the influence of the centrifugal force which repels the fluid outward in a radial direction and also acts as a rotational couple in r-z plane. The exact mathematical treatment of this effect is quite difficult, but in any case, the action of the centrifugal force may lower the $h_z(0)$ values, especially may lower them remarkably at a high velocity. Thus we may conclude that, to eliminate the effect of the centrifugal force, it is preferable to keep the rotational speed below about 70~80 rpm with a cup of this dimension ($R'=6.0$ cm.).

Pressure Distribution on a Stationary Bob: the Edge Effect:—In the derivation of Eqs. from 1 to 3, the influence arising from the side gap was simply replaced by an isotropic term P'. To check the validity of this assumption, measurements were performed with two different combinations of bob A ($R=5.0$ cm.) with cup 1 ($R'=6.0$ cm.), and bob A with cup 2 ($R'=8.0$ cm.) on solutions of Na-CMC-water, and the pressure distributions on the bob were compared. Fig. 3 indicates the pressure distributions, $h_z(r)$, with various velocities.

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* Samples of methylcellulose and polystyrene were obtained through the courtesy of Toyo Ink Mfg. Co., Ltd., and Nagase and Co., respectively.

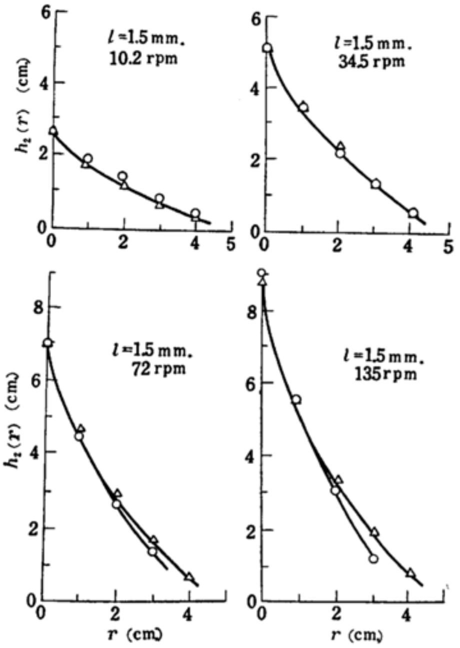

Fig. 3. Pressure distributions on a stationary plate (R=5.0 cm.) with cup 1 (R'=6.0 cm.)…Δ, and cup 2 (R'=8.0 cm.)…0. 1.97wt.%-CMC-water.

It is seen that when the rotational velocity is not so high the pressure distribution, $h_z(r)$, is practically unaffected by the difference in the side gap, but, the higher the velocity becomes (above 70 rpm), the more significant the deviation becomes. The pressure falls more rapidly in the larger cup. The plots of $h_z(0)$ vs. Ω/l, though the data are not shown here, are reduced on a single curve except at high speed and show no indication of edge effect.

Effect Arising from the Finite Size of Accesses of Manometer Tubes.—It might be expected that the presence of holes of manometer tubes on the base of a bob would disturb the flow pattern in their neighbor. Also for the finite size of accesses of manometers, the observed pressure does not represent a value at its center but the average over the area. That the quantitative estimation of this average with a parallel plate instrument is impracticable without the dependence of $h_z(r)$ on r (namely on the rate of shear) has been known. It can be said, however, that when the diameter of holes is larger, their influence is also greater. Actually, in our measurements, for the bob A (diameter of holes is 5 mm.) a slight but appreciable deviation was observed, while for the bob with smaller holes (diameter 2 mm.) no appreciable disturbance was observed. This had also been observed by Greensmith and Rivlin[3]. It is desirable to keep the size of holes as small as possible, but if too small, it becomes time-consuming for the fluid to attain equilibrium positions in each manometer.

The Normal Pressure Gradient $-\partial P_z(r)/\partial \ln r$ vs. Rate of Shear D.—Eqs. 1 and 2 indicate that the normal pressure difference, $\Delta P_z(r)$, or the normal pressure

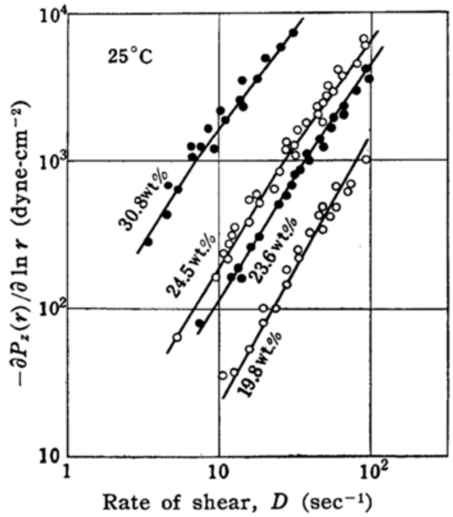

Fig. 4 (a). Normal pressure gradient, $-\partial P_z(r)/\partial \ln r$, as a function of rate of shear, D. Solutions of polystyrene in decalin.

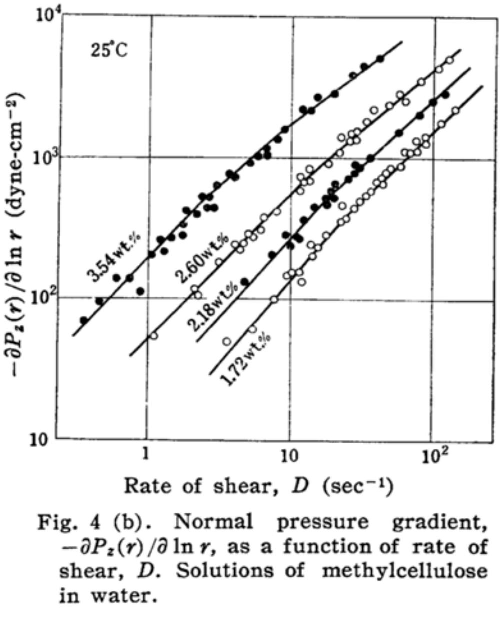

Fig. 4 (b). Normal pressure gradient, $-\partial P_z(r)/\partial \ln r$, as a function of rate of shear, D. Solutions of methylcellulose in water.

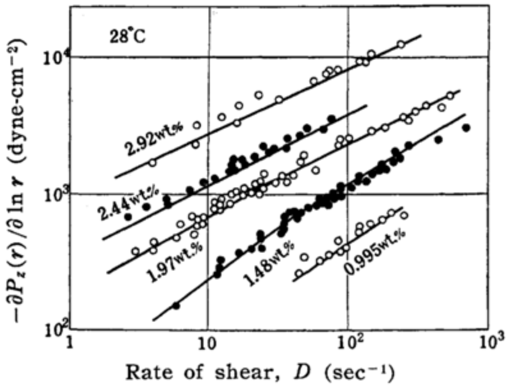

Fig. 4 (c). Normal pressure gradient, $-\partial P_z(r)/\partial \ln r$, as a function of rate of shear, D. Solutions of Na-carboxymethylcellulose in water.

gradient, $-(\partial P_z(r)/\partial \ln r)$**, should be a function of the rate of shear, $D=r\Omega/l$. Fig. 4 indicates the curves of $-\partial P_z(r)/\partial \ln r$ vs. D for three different polymer species, all of which show that the expected relations safely hold. Of course, the data which were beyond the limitations mentioned in the previous subsections were eliminated in the plots.

It should be noticed that the dependences of normal stresses on the rate of shear differ remarkably in each polymer species, which reflect the essential difference in characteristic rheological properties of those polymers. The detailed discussions will be given in our subsequent paper[4].

The Applicability of the Superposition Principle.—It has been suggested that from the normal stress data obtained on solutions of various concentrations and temperatures, a single reduced curve should be obtained by applying the superposition procedure which is currently used for the dynamic data[5,6]. In this case, reduced quantities are defined such as

$$[-\partial P_z(r)/\partial \ln r]_r = [-\partial P_z(r)/\partial \ln r]\cdot[T_0/Tf(c)]$$

and $$D_r = D\eta\, T_0/Tf(c)$$

where T is the absolute temperature, T_0 is a reference temperature, and η is the *zero shear* viscosity of the solution. $f(c)$ is a function of concentration, and was chosen by Padden and DeWitt[5] as $f(c)=c$ and by Markovitz and Williamson[6] as $f(c)=c/c_0$ for $c<c_0$ and $f(c)=c^2/c_0^2$ for $c\geqq c_0$. The reduced plot of the data with solutions of methylcellulose in water is shown in Fig. 5, in which $T_0=298$°K and $f(c)=c$. It is seen that the reduction is not so satisfactory, but rather a systematic deviation is observed. Although results are not shown here, another choice of $f(c)$ improves the situation slightly. For another two polymer species, polystyrene in decalin and Na-CMC in water, the reductions are a little better than for methylcellulose in water, but again not so satisfactory.

On the basis of the cross-elasticity theory[4], the normal stresses and the apparent viscosity (=shearing stress/rate of shear) are given as follows:

$$-\frac{\partial P_z(r)}{\partial \ln r}=\sigma_{11}-\sigma_{33}=G\tau^2D^2 \tag{4}$$

$$\eta=\sigma_{12}/D=G\tau \tag{5}$$

where G and τ are the shear modulus and the relaxation time of the solution, respectively. The superposition procedures are based on the following assumptions: the shear modulus and the relaxation time of the solution are dependent on such concentration and temperature that $G=G_0[Tf(c)/T_0f(c_0)]$ and $\tau=a_Ta_c\tau_0$. Here G_0 and τ_0 are the values of G and τ, respectively, at the reference temperature T_0 and concentration c_0. Introducing these assumptions into Eqs. 4 and 5, we obtain

$$-\frac{\partial P_z(r)}{\partial \ln r}=\frac{Tf(c)}{T_0f(c_0)}G_0\tau_0^2(a_Ta_cD)^2 \tag{6}$$

$$D\eta=\frac{Tf(c)}{T_0f(c_0)}G_0\tau_0(a_Ta_cD) \tag{7}$$

and

$$a_Ta_c=\frac{T_0f(c_0)}{Tf(c)}\,\frac{\eta}{\eta_0} \tag{8}$$

With the choice of such a reference state that η_0 and $f(c_0)$ are unity and a *zero shear* value for η, the reduced variables indicated before are determined.

It should be mentioned, however, that the above-mentioned definitions of reduced variables implicitly include such a further assumption namely that the reducing factors, $f(c)/f(c_0)$ and a_Ta_c, are independent of the rate of shear. This assumption may be valid in the case of a dynamic measurement if the amplitudes of vibrational motion are sufficiently small. On the other hand, in the steady flow measurements over wide range of rates of shear, this assumption may be improper, or valid only within a limited range of rates of shear, or of concentrations. Actually, the flow curves of polymer solutions

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** Many experimental evidences show that the difference of σ_{22} and σ_{33} is nearly zero, so it may be considered taht $[-\partial P_z(r)/\partial \ln r]=\sigma_{11}-\sigma_{33}$. See references 1), 2) and 4).

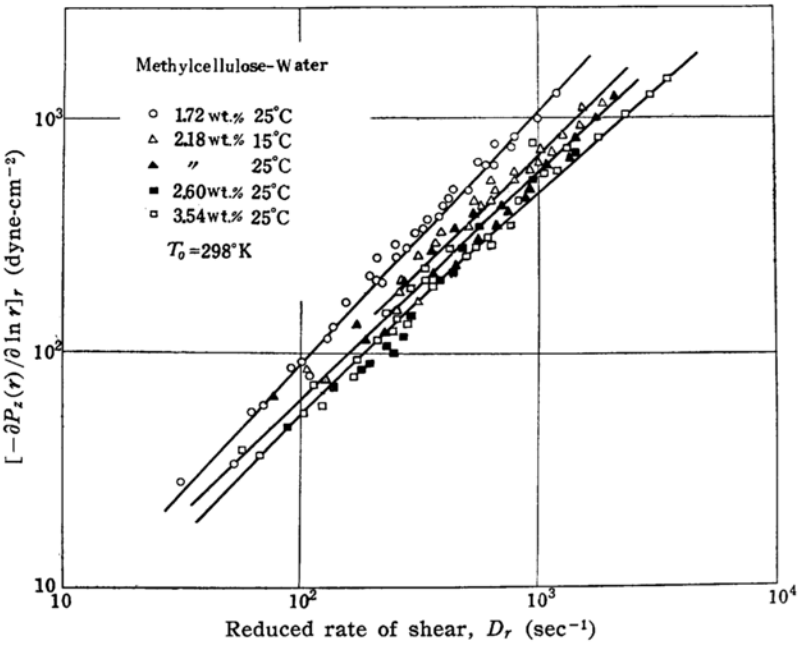

Fig. 5. Reduced normal pressure gradient, $[-\partial P_z(r)/\partial \ln r]_r = -[\partial P_z(r)/\partial \ln r][T_0/Tf(c)]$ vs. reduced rate of shear, $D_r = \eta T_0/Tf(c)$, where $f(c)=c$, $T_0=298°\text{K}$, solutions of methylcellulose in water.

have a distinct S shape⁷⁾, which indicates the presence of two different Newtonian regions at low rate of shear and at high rate of shear. In concentrated solutions the initial viscosity, $\eta_{D=0}$, at a low rate of shear increases more rapidly than the fifth or tenth power of the concentration⁸⁾, and the final viscosity, $\eta_{D=\infty}$, at a high rate of shear is proportional to the concentration itself⁷⁾. These facts suggest that the whole feature of the flow curve can not be determined by their initial branch. This situation probably reflects also on the normal stresses, therefore, the above-mentioned superposition procedures should be valid only for the data obtained within the limited range of rates of shear and concentrations.

One more remark should be added to the factor T/T_0 of the shear modulus. This factor was derived from the conception of the entropy elasticity of the flexible chain polymer system. But in the case of concentrated solutions, in which the presence of transient junctions due to entanglements or interactions between polymer chains plays an important role and their number itself varies with temperature, the temperature dependence of the modulus of the solution is perhaps more complicated. A correct choice of this factor is a problem for further investigation.

Summary

Results of some geometrical studies of normal stress effects in a parallel plate instrument have been discussed. The parallelism and the concentricity of two plates are necessary conditions for the quantitative measurement. The rotational velocity of a cup should be kept below about 70 rpm for the apparatus with the cup radii about 6～8 cm. to avoid the influence of the centrifugal force. Accesses of manometer tubes with the diameter about 2 mm. cause no appreciable disturbances. The influence of side gap may also be neglected. With these experimental remarks, the normal stresses are obtained as a function of the rate of shear.

The applicability of the concentration-temperature superposition procedures has been tested with the data obtained here. They are partly valid in some limited range of variables.

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7) J. G. Brodnyan, F. H. Gaskins and W. Philippoff, *Trans. Soc. Rheology*, 1, 109 (1957).

8) T. G. Fox, S. Gratch and S. Loshaek, "Viscosity Relationships for Polymer in Bulk and in Concentrated Solutions", in Rheology, Vol. I ed. F. Eirich, Academic Press, New York (1956), Chap. 12.

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