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The Non-Newtonian Flow of Poly(Dimethyl Siloxane)

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The non-Newtonian flow of poly(dimethyl siloxanes) with a wide variety of degrees of polymerization (Z), 31.6 to 6.02×10^3, was studied by using short capillary viscosimeters. Measurements were performed in the range of rate of shear from 10^{-1} to 3×10^6 sec^{-1}. It was found that the flow behavior was markedly affected by the value Z of the test materials. That is, the flow was practically Newtonian over the entire range of shear rates when Z was less than 1.55×10^2. For higher values of Z, however, typical non-Newtonian behavior was observed in the range of moderate shear rates. At extremely high shear rates, the materials with $Z=3.23\times10^2$ to 2.63×10^3 exhibit the upper (or second) Newtonian flow, but the materials with still higher values of Z exhibit the spiral flow. It was also found that the Shishido equation (*J. Chem. Soc. Japan, Pure Chem. Sect. (Nippon Kagaku Zasshi)*, **84**, 889 (1963)) was applicable to this polymer in describing the observed viscosity vs. shear rate dependence. Finally, an empirical method was proposed for estimating the upper Newtonian viscosity value from the viscosities at zero shear stress and at the inflection point of the flow curve.

Recently, the flow behavior of molten polymers or polymer solutions in short capillaries has attracted the attention of many investigators. This is because: (a) the flow data at a very high shear stress or shear rate are obtainable by this means if an adequate end correction is made to the capillary length, and (b) the data obtained can be used to evaluate the various rheological properties of polymer systems.

Shishido¹⁻⁴⁾ proposed a semi-empirical theory for the non-Newtonian flow on the assumption that the viscosity of the fluid is closely related to the deformation of the polymer molecules caused by shear stress; he applied this theory to dilute and concentrated solutions of high polymers.

This paper will present the results of the application of his theory to poly(dimethyl siloxanes) of various molecular weights in the molten state. The measurements cover a wide range of shear stress, from the lower (or first) Newtonian region up to the upper (or second) Newtonian region.

Experimental

The poly(dimethyl siloxanes) used in this study were obtained from the Shin-Etsu Chemical Industry Co., Ltd. The degree of polymerization (Z) were calculated from the zero shear viscosities (η_0) by using the relationship given in Refs. 5 and 6. These values of η_0 and Z are given in Table I.

The viscosity measurements were performed with extrusion capillary viscosimeters1) driven by nitrogen pressure. The lengths (l) and radii (r) and the ratios between them (l/r) of the capillaries used are listed in Table II. The temperature was kept at 35°C throughout the measurements. The extruding pressure was adjustable up to 150 kg./cm².

Results and Discussion

The End Correction of Capillary.—For the flow of a Newtonian fluid in a long capillary, the maximum shear rate (D_N) and shear stress (τ') (at the wall of the capillary) are given by:

$$D_N = 4Q/\pi r^3 \tag{1}$$

$$\tau' = Pr/2l \tag{2}$$

where r and l are the radius and the length of the capillary respectively, Q is the output rate of the fluid, and P is the applied pressure corrected by the kinetic energy effect.

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1) S. Shishido and Y. Ito, *J. Chem. Soc. Japan, Pure Chem. Sect.* (*Nippon Kagaku Zasshi*), **84**, 889 (1963).
2) S. Shishido and Y. Ito, ibid., **85**, 13 (1964).
3) S. Shishido and Y. Ito, ibid., **85**, 191 (1964).
4) S. Shishido and Y. Ito, ibid., **85**, 195 (1964).
5) M. J. Hunter, E. L. Warrick, J. F. Hyde and C. C. Currie, *J. Am. Chem. Soc.*, **68**, 2284 (1946).
6) T. G. Fox, S. Gratch and S. Loshaek, "Rheology, Theory and Application," Vol. 1, Academic Press Iac., New York (1956), p. 431.

TABLE I. VISCOSITIES AT ZERO SHEAR STRESS AND DEGREES OF POLYMERIZATION FOR POLY(DIMETHYL SILOXANES)

Name of sample		Viscosity η_0 (poise)	Degree of polymerization Z *4	
KF96	(10)	9.4×10^{-2}	3.16×10	*1
	(30)	2.9×10^{-1}	7.07×10	
	(50)	4.35×10^{-1}	9.55×10	
	(100)	8.7×10^{-1}	1.55×10^2	
	(300)	2.45	3.23×10^2	*2
	(500)	4.4	5.00×10^2	
	(1000)	9.7	8.70×10^2	
	(3000)	2.45×10	1.15×10^3	
KF96H	(6000)	4.9×10	1.41×10^3	
	(10000)	8.0×10	1.66×10^3	
	(50000)	4.2×10^2	2.63×10^3	
	(100000)	8.5×10^2	3.31×10^3	*3
	(500000)	4.3×10^3	5.25×10^3	
	(1000000)	7.2×10^3	6.02×10^3	

Footnotes, *1—3, show the flow behaviors.

*1: Newtonian flow throughout the whole range of shear stress measured.

*2: Non-Newtonian flow at moderate shear stress and upper Newtonian flow at high shear streess.

*3: Non-Newtonian flow at moderate shear stress and spiral flow at high shear stress.

*4: The degree of polymerization (Z) was calculated by the equations in Refs. 5 and 6 from the viscosities at zero shear stress.

TABLE II. DIMENSIONS OF CAPILLARIES

Capillary No.	Radius r, cm.	Length l, cm.	l/r
I	0.0526_9	0.994_0	18.9
II	0.0527_5	0.636_5	12.0
III	0.0680_0	0.275_0	4.05
IV	0.0682_5	0.114_5	1.68
E	0.202_6	4.48_0	22.1
H	0.0134_9	1.95_5	145
K	0.0135_0	0.687_0	50.9
W	0.0135_0	0.149_5	11.0
X	0.0112_5	0.0785	6.98
Y	0.0135_0	0.0762	5.64
Z	0.0265_0	0.0818	3.09

Considering the entrance effect (Couette correction) ($c=0.65$)[1-3] and the elastic effect (e), we may obtain, instead of Eq. 2, the following relationship for a non-Newtonian fluid passing through a comparatively short capillary:

$$\tau = P/2(l/r+c+e) \tag{3}$$

where $(c+e)$ is the total end correction and τ is the corrected shear stress. The total end correction can be determined by extrapolating the plot of P versus l/r to the zero value of P at a constant shear rate (D_N). This is the usual method for determining the end correction. Figure 1 shows such plots obtained for Shin-Etsu Silicone KF96H-(10000).

An approximate method for obtaining the end correction, e, has been proposed by Shishido on the basis of his empirical theory of the non-Newtonian flow of polymer solutions.[1-4] This method has been applied to our molten polymers. The results are shown in Fig. 2, where the approximate estimates of e obtained by the Shishido method (open circles) are compared with the ordinary estimates obtained by the above extrapolation method (solid curve). The agreement between the

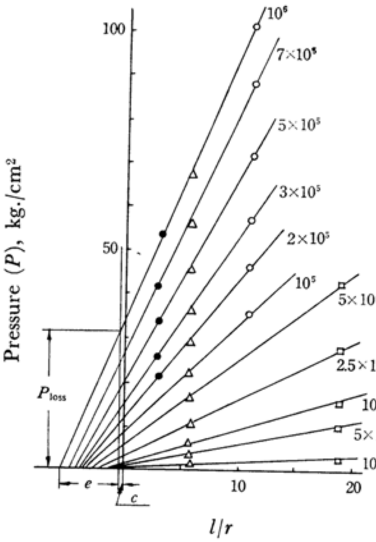

Fig. 1. Relations between pressure and capillary dimension (l/r) at a constant shear rate (D_N) for Shin-Etsu Silicone KF96H (10000).
The numerals in the figure represent the shear rates in sec^{-1}.
Symbols of capillaries in Table II.
●: Z, △: Y, ○: W, □: I

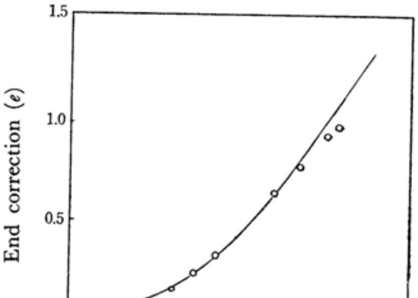

Fig. 2. Comparison between a usual end-correcting method (solid curve) and results (open symbols) calculated by Shishido's method[1] for Shin-Etsu Silicone KF96 (1000).

two estimates was satisfactory over a wide range of shear rate, D.

Flow Curve.—After the end correction is established, it is possible to calculate the corrected flow curve, i. e., the τ vs. D relationship, which should be independent of the l/r values of the capillaries used. The results obtained for the present samples are shown in Fig. 3, where the non-Newtonian shear rate (D) was calculated by:

$$D=(D_{\mathrm{N}}/4)(3+\mathrm{d}\log D_{\mathrm{N}}/\mathrm{d}\log\tau) \qquad (4)$$ 7)

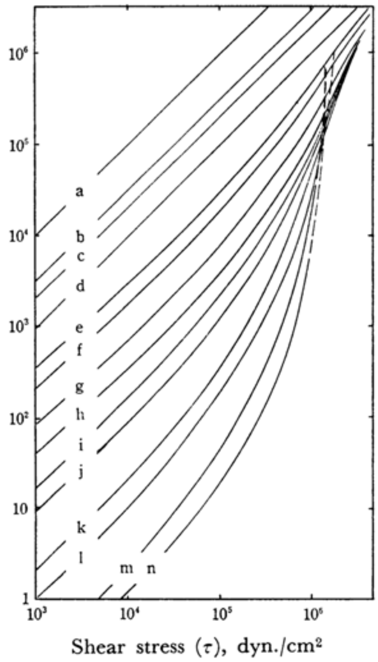

Fig. 3. Flow curves for poly(dimethyl siloxanes) of different molecular weights.
The dotted part in the curve indicates the region of spiral flow.
Degree of polymerization

a : 3.16×10	b : 7.07×10	c : 9.55×10
d : 1.55×10^2	e : 3.23×10^2	f : 5.00×10^2
g : 8.70×10^2	h : 1.15×10^3	i : 1.41×10^3
j : 1.66×10^3	k : 2.63×10^3	l : 3.31×10^3
m: 5.25×10^3	n : 6.02×10^3	

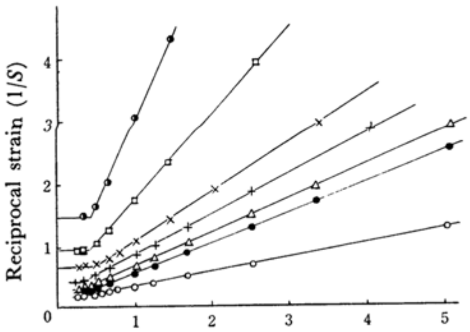

Fig. 4. Relations between $1/S$ and $1/\tau$ for different poly(dimethyl siloxanes).
Degree of polymerization

◑: 3.23×10^2	□: 5.00×10^2	×: 8.70×10^2
+: 1.15×10^3	△: 1.41×10^3	●: 1.66×10^3
○: 2.63×10^3		

From Fig. 3, it may be seen that the siloxanes with degrees of polymerization less than 1.55×10^2 exhibit Newtonian behavior. For the materials with a higher degree of polymerization, i. e., from 3.23×10^2 to 8.7×10^2, typical non-Newtonian behavior is observed at moderate shear rates. These materials exhibit the upper (or second) Newtonian flow at extremely high shear rates. The materials of still higher degrees of polymerization, i. e., 1.15×10^3 to 2.63×10^3, do not exhibit the upper Newtonian flow, probably because of the disturbance by the spiral flow. The dotted parts of the flow curves for the materials with $Z=3.31\times10^3$, 5.25×10^3, and 6.02×10^3 indicate this range of spiral flow. When the spiral flow occurs instead of the upper Newtonian flow, the apparent viscosity becomes smaller for the materials with higher degrees of polymerization than for those with lower degrees of polymerization, as is shown in Fig. 3. Such inversion must be physically nonsensical; accordingly, we shall omit these parts of the flow curves from the following discussions.

Flow Equation.—Shishido's proposed equations for the non-Newtonian flow of a polymer solution are:1)

$$(\eta_{\mathrm{app}}-\eta^*)/(\eta_0-\eta^*) = \exp(-S) \qquad (5)$$

$$1/S = 1/S_\infty + (1/\tau-1/\tau_{\mathrm{c}})/S_\infty\beta \qquad (6)$$

where τ is the shear stress; η_{app}, the apparent viscosity; η^*, the viscosity of the solvent, and η_0, the viscosity at zero shear stress. The symbol S represents the strain exerted on each polymer molecule; S_∞, the value of S in the flow of the upper Newtonian range; β, the flexibility parameter of the polymer molecule, and τ_{c}, the critical shear stress above which S attains its saturated value (S_∞). These equations may also be applicable to molten polymers. In this case, η^* is zero, Eq. 5 is then reduced to:

$$\eta_{\mathrm{app}}/\eta_0=\exp(-S) \qquad (7)$$

Figure 4 shows the plots of $1/S$ versus $1/\tau$ for the present samples under the conditions of normal flow. It may be seen that Eqs. 6 and 7 are approximately valid for these molten polymers. The rheological values obtained from the relation between $1/S$ and $1/\tau$ are listed in Table III, where S_∞^{cal} and $\eta_\infty^{\mathrm{cal}}$ are estimated to be as follows. Denote by $S_{\mathrm{inf}}^{\mathrm{exp}}$ the value of S at the inflection point on the curve of $\log\tau$ versus $\log D$. The

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7) O. H. Clark and M. L. Deutsch, *J. Appl. Phys.*, **21**, 713 (1950).

TABLE III. RHEOLOGICAL VALUES FOR DIFFERENT POLY(DIMETHYL SILOXANES)

Degree of polymerization of samples (Z)	S_∞^{exp}	S_∞^{cal}	$\eta_\infty^{\mathrm{exp}}$ poise	$\eta_\infty^{\mathrm{cal}}$ poise	β cm²/dyn.	βS_∞ (cm²/dyn.) from $1/\tau\sim 1/S$	from Eq. 10	from Eq. 11
3.23×10^2	0.703	0.86	1.1	1.02	5.2×10^{-7}	3.7×10^{-7}	3.1×10^{-7}	4.1×10^{-7}
5.00×10^2	1.14	1.56	1.3	1.07	6.6×10^{-7}	7.5×10^{-7}	4.1×10^{-7}	4.1×10^{-7}
8.70×10^2	1.77	1.89	1.5	1.46	7.2×10^{-7}	1.28×10^{-6}	6.9×10^{-7}	5.8×10^{-7}
1.15×10^3		2.45		2.11	6.7×10^{-7}	1.65×10^{-6}	7.7×10^{-7}	1.3×10^{-6}
1.41×10^3		2.80		2.95	6.4×10^{-7}	1.80×10^{-6}	1.9×10^{-6}	1.3×10^{-6}
1.66×10^3		3.30		2.97	6.5×10^{-7}	2.15×10^{-6}	2.3×10^{-6}	1.2×10^{-6}
2.63×10^3		5.13		2.47	1.0×10^{-6}	5.15×10^{-6}	6.0×10^{-6}	2.4×10^{-6}

ratios of S_∞ to $S_{\mathrm{inf}}^{\mathrm{exp}}$ may then be determined for our samples, e, f and g, the upper Newtonian region of which has been experimentally established (see Fig. 3). Thus, we find that $S_\infty/S_{\mathrm{inf}}^{\mathrm{exp}}\doteqdot 1.7$ independent of the degree of polymerization. The relations between S_∞ and $S_{\mathrm{inf}}^{\mathrm{exp}}$ of other polymer systems are available from the literature; they are shown in Fig. 5. This figure clearly suggests that the $S_\infty/S_{\mathrm{inf}}^{\mathrm{exp}}$ ratio is practically a constant, 1.7, independent of the polymer and solvent species. Accordingly, if the curve of $\log\tau$ versus $\log D$ is available up to its inflection point, S_∞ can be determined to be $1.7S_{\mathrm{inf}}^{\mathrm{exp}}$. The values of S_∞ thus obtained for the present samples are plotted in Fig. 6 against the degree of polymerization (Z). From the figure, we find that:

$$S_\infty = 3.62\times10^{-3}\times Z^{0.92} \tag{8}$$

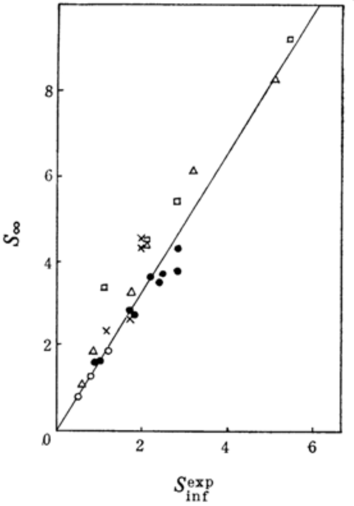

Fig. 5. Relations between S_∞ and $S_{\mathrm{inf}}^{\mathrm{exp}}$ for various polymer systems.
Molten polymer
○: poly (dimethyl siloxane)
Polymer solutions
●: polystyrene in diethyl phthalate at 20°C[1)]
△: polyisobutylene in dicaline at 25°C[8)]
□: cellulose nitrate in n-butyl acetate at 25°C[9)]
×: cellulose triacetate in ethylene chlorohydrine at 25°C[10)].

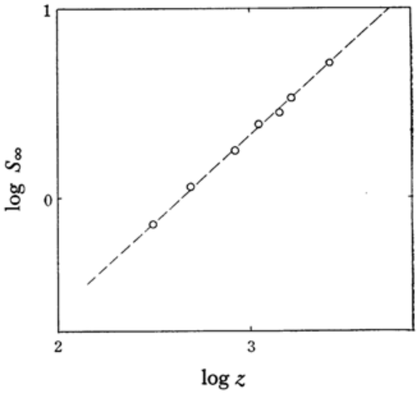

Fig. 6. Dependence of S_∞ on the degree of polymerization for poly(dimethyl siloxane).

Accordingly, by using Eq. 7 or Eq. 8 and the relations of η_0 and Z in Refs. 5 and 6, the η_∞ (upper Newtonian viscosity) value can be estimated from η_0 and S_∞, or directly from Z. The values of β are calculated from $S_\infty\beta$ by using $S_{\mathrm{inf}}^{\mathrm{exp}}$ for the siloxanes with degrees of polymerization from 3.23×10^2 to 8.70×10^2, and by using S_∞^{cal} for the siloxanes with degrees of polymerization from 1.15×10^3 to 2.63×10^3.

Shearing Strain, Pressure Loss and End Correction in the Capillary Flow.—From the theory[1-3)] previously proposed, the relations among strain (S), end correction (e), shear stress (τ), and pressure loss (P_{loss}) are:

$$2e=\sqrt{2}S/[1-(1-1/\beta\tau_c)S/S_\infty] \tag{9}$$

$$P_{loss}=\sqrt{2}\beta S_\infty\tau^2 \tag{10}$$

$$=(2\sqrt{2}e^2)/(\beta S_\infty)=(2e)^2/(\sqrt{2}\beta S_\infty) \tag{11}$$

Equations 9, 10, and 11 were examined for the present cases. The solid curves in Fig. 7 indicate the results calculated from Eq. 9 by using the β, τ_c, and S_∞ values obtained experimentally. The experimental results (various point marks) and the theoretical results (solid curve) are substantially in accordance with each other. Two kinds of

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

9) W. Philippoff, F. H. Gaskins and J. G. Brodnyan, *J. Appl. Phys.*, **28**, 1118 (1957).

10) J. Schurz and K. Windisch, *Kolloid-Z.*, **177**, 149 (1961).

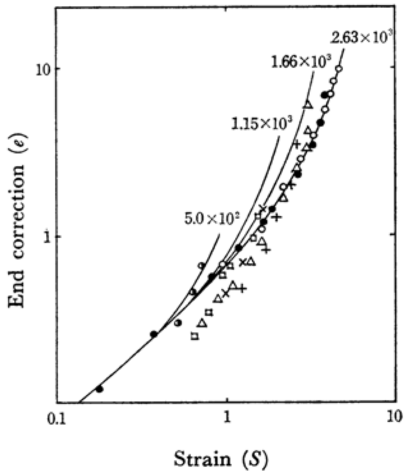

Fig. 7. Relations between e and S for poly(dimethyl siloxanes).
The solid curves indicate the results calculated from Eq. 9 by using β, τ_c, and S_∞ obtained. The numerals on the curves indicate the degrees of polymerization. The symbols represent the experimental values for the degree of polymerization as follows.
◑: 3.23×10^2 □: 5.00×10^2 ×: 8.70×10^2
+: 1.15×10^3 △: 1.41×10^3 ●: 1.66×10^3
○: 2.63×10^3

βS_∞ values, obtained graphically by using Eqs. 10 and 11, are given in Table III, together with the βS_∞ value obtained from the slope of the plot of $1/S$ versus $1/\tau$. These three kinds of βS_∞ values are in agreement with one another. These results show that the above relations proposed³⁾ for polymer solutions are also applicable to the molten state of poly(dimethyl siloxanes).

Summary

The non-Newtonian flow of poly(dimethyl siloxanes) of various mol. wts. has been studied with a short capillary viscosimeter. The experiment has covered a wide range of shear rate, from 10^{-1} to 3×10^6 sec^{-1}. The results are as follows:

1) The flow behavior of the sample changes with the degree of polymerization. For the siloxanes with degrees of polymerization less than 1.55×10^2, the flow of the fluid is Newtonian throughout the whole range of shear rates; in the cases of the siloxanes with degrees of polymerization from 3.23×10^2 to 2.63×10^3, however, the flow is non-Newtonian at moderate shear rates; it again becomes Newtonian at high shear rates. With degrees of polymerization of more than 3.31×10^3, the spiral flow rises to a high shear rate.

2) The flow behavior of the sample is expressed by modifying Shishido's equation proposed for non-Newtonian polymer solutions.

3) When the flow curve observed contains its inflection point, the upper Newtonian viscosity can be estimated by a new method proposed here.

4) The relations among the end correction of capillary, the pressure loss and the shear stress proposed by Shishido for polymer solutions are applicable to poly(dimethyl siloxane) also.

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