Non-Newtonian Viscosity of Dilute High Polymer Solutions. II. Measurements on Polystyrene Fractions in Toluene*

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(Received September 9, 1956)

Introduction

During recent years it has been recognized by several investigators that the non-Newtonian behavior of polymer solutions can no longer be ignored in the evaluation of the intrinsic viscosity (limiting viscosity number), $[\eta]$, in some cases. As the result, various investigators[1–8] have recently examined the shear-rate dependence of viscosity of dilute polymer solutions and some have proposed the methods of extrapolating the viscosity data to the limit of zero rate of shear.

Most of the empirical equations[9–12] that have been proposed to express the shear dependence of $[\eta]$ or reduced viscosity, η_{sp}/c, show the velocity gradient entering to the first power. For example, Fox, Fox and Flory[9] have proposed the empirical relationship:

$$\ln \eta_{sp}=[\ln \eta_{sp}]_0-(\phi/100)q, \qquad (1)$$

where $[\ln \eta_{sp}]_0$ is the value of $\ln \eta_{sp}$ at zero rate of shear, ϕ is a constant which is independent of concentration in a given solvent, and q denotes the velocity gradient. These equations are in marked disagreement with the prediction of the theory of Kuhn and Kuhn[13] according to which $[\eta]$ should decrease

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* Presented at the 9-th Annual Meeting of the Chemical Society of Japan held in Tokyo, April, 1956.

[1] P. Alexander and K. A. Stacey, *Trans. Faraday Soc.*, **51**. 299 (1955).

[2] J. Schurz, *Makromol. Chem.*, **12**, 127 (1954).

[3] M. A. Golub, *J. Polymer Sci.*, **18**, 27, 156 (1955).

[4] F. Patat and J. Hartmann, *Makromol. Chem.*, **18/19**, 422 (1956).

[5] T. Hotta, *Chem. High Polymers*, **12**, 276 (1955).

[6] M. A. Golub, *J. Phys. Chem.*, **60**, 431 (1956).

[7] T. Kuroiwa, This bulletin, **29**, 164 (1956).

[8] See also the literatures cited in the previous paper (7) 1—16), 20) for this subject.

[9] T. G. Fox, Jr., J. C. Fox and P. J. Flory, *J. Am. Chem. Soc.*, **73**, 1901 (1951).

[10] H. T. Hall and R. M. Fuoss, ibid., **73**, 265 (1951).

[11] G. de Wind and J. J. Hermans, *Rec. trav. Chim. Pay-Bas*, **70**, 521 (1951).

[12] S. Newman, L. Loeb and C. M. Conrad, *J. Polymer Sci.*, **10**, 463 (1953).

[13] W. Kuhn and H. Kuhn, *Helv. Chim. Acta*, **28**, 1533 (1945).

initially with q^2, and accordingly $[\eta]$ vs. q curve should have horizontal tangent at $q=0$.

Kuhn and Kuhn[13] have suggested that the non-Newtonian character of polymer solution depends on the ease with which the chain molecule is deformed. Thus for a fairly rigid molecule, since the orientation of the chain molecule in the direction of flow increases as the gradient field increases and since the frictional resistance of the chain decreases with increasing orientation, $[\eta]$ decreases with increasing q. For a completely flexible or soft molecule, on the other hand, which can change its shape in flow and become stretched in the gradient field, $[\eta]$ is independent on q because of the complete compensation of stretching and orientation effects.

The viscous resistance which must be overcome by a force, which tends to change the end-to-end distance of a molecule, consists not only of the usual resistance of the surrounding medium but also of an additional resistivity-the inner viscosity of Kuhn and Kuhn-which is inherent in the molecular chain.

The resistance force due to the inner viscosity, K_2, can be written as follows:

$$K_2=-B\mathrm{d}h/\mathrm{d}t, \tag{2}$$

where h is the end-to-end distance of the molecule, and B may be called " the coefficient of stiffness " of the chain.

These authors have deduced for the limiting case of $B\gg \lambda\eta_0 L$ the following expression[14]:

$$[\eta]_q/[\eta]_0=1-2\xi^2+\frac{473}{16}\xi^4-\cdots\cdots \tag{3}$$

where

$$\xi=q\overline{h_0^2}/16\,D_{\rm rot}, \tag{3$'$}$$

and L is the so-called hydrodynamic length, i.e., the fully extended legnth of the chain, η_0 is the solvent viscosity and λ a numerical factor which is approximately equal to $3\pi/16$, $[\eta]_q$ is the intrinsic viscosity at a shear rate q and $[\eta]_0$ is the one at $q=0$, $D_{\rm rot}$ represents the rotational diffusion constant of the chain in the solution and $\overline{h_0^2}$ is the mean square end-to-end distance of the chain at rest. Moreover, it has been shown that the approximate value of ξ for a given polymer can be evaluated according to the equation:

$$\xi=[\eta]_0 M\cdot 10^3\eta_0 q/mRT \tag{4}$$

where M and m are the molecular weight (MW) of the polymer and the monomer, respectively.

Real polymer chains are neither quite stiff nor completely soft, and the dependence of $[\eta]$ on q should lie somewhere between these limiting cases. Furthermore, according to the theory[15], B decreases with MW as $1/M$ owing to the increase of the number of links where a rotation can take place. Hence the shear rate effect should become progressively less pronounced with increasing MW, and this means that $[\eta]_q/[\eta]_0$ vs. ξ curve for real polymer should approach to $[\eta]_q/[\eta]_0=1$ (for $B\ll \lambda\eta_0 L$) with increasing MW and to the curve according to Eq. (3) with decreasing MW[16].

In order to determine whether the increase in viscosity persists up to the region of very low rates of shear in accordance with the proposed empirical relations such as Eq. (1) or it vanishes in a range of small q as has been demanded by the theory, most of the existing data are of little avail because they are concerned only with regions of rather high q. It is worthy of notice that a few recent works[1,7,17] in which the measurements have been extended down to very low q appear to show the quadratic dependence of viscocity on q and thus to support the above-mentioned theory[18].

In the present paper the results of measurements on the shear dependences of several polystyrene fractions in toluene are presented and the effect of non-Newtonian behavior on the evaluation of $[\eta]$ and Huggins' slope constant k' are discussed from these data and some remarks are made as to $[\eta]$-MW relationship and the effect of polydispersity of polymer on the shear dependence of viscosity. Finally, a comparison is made between the above-mentioned theory and the results of the present investigation on the basis of $[\eta]_q/[\eta]_0$ vs. ξ relation.

Experimental

The original polystyrene was prepared by polymerizing the pure monomer at 60°C. The procedures for purification of the monomer and for polymerization of the monomer were described in the previous paper[7].

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[14] Kuhn and Kuhn treated the problem only in the two-dimensional motion on the xy-plane. The three dimensional treatment will change the numerical factors but not affect the functional dependence.

[15] W. Kuhn and H. Kuhn, *Helv. Chim. Acta*, **29**, 609 (1946).

[16] Of course, in a simple $[\eta]_q/[\eta]_0$ vs. q plot, such a tendency cannot be expected and the variation of $[\eta]_q/[\eta]_0$ with q is larger, the larger the MW is, as has been pointed out several investigators.

[17] E. Wada, *J. Sci. Res. Inst.*, **47**, 159 (1953); *J. Polymer Sci.*, **14**, 305 (1954).

[18] On the other hand, non-vanishing increase of viscosity at very small q was found to be real for some polymers. From this fact, Schurz has considered that the shear dependence is mainly caused by molecular interactions (formation of temporary structure), and that the contributions of the single molecules only play a role of minor importance. See the literature 19) for the further details.

[19] J. Schurz, *Makromol. Chem.*, **10**, 194 (1953).

The fractionation of the polymer was carried out by precipitating the polymer from a mixture: polystyrene-methylethylketone-n-butanol. Methylethylketone was slowly evaporated at constant temperature by suction until precipitation began. The mixture was then heated until the precipitate redissolved and was allowed to stand overnight, after which time a fraction reprecipitated to gel at the original temperature. A fraction separated from the mixture was then dissolved in benzene to make up about 1% solution and reprecipitated in a large excess of methanol. This precipitate was washed with methanol and dried by pumping in vacuum at about 70°C for six hours. 22 fractions were obtained in this way[20].

Molecular weight (*MW*) of the original polymer (*UF*) and the fractions used in this study were determined by light scattering measurements of toluene solutions of these samples[21] and are listed below together with the viscosity data obtained by an Ostwald viscometer.

fraction	$MW\times 10^{-4}$	$[\eta]$ (100 cc./g.) in toluene at 30°C	k'
F- 4	410	5.49	0.39
F-10	308	4.53	0.37
F-16	194	3.27	0.34
F-20	100	2.07	0.38
UF	283	4.01	0.33

The apparatus used in this work consists of a manostat system, a manometer and a horizontal viscometer. These were already described in detail in the previous paper[7] together with the experimental procedure employed, and are not repeated here.

The maximum rate of shear at the wall of the capillary was calculated by the equation[22]:

$$q=4Q/\pi R^3 t\times(1-1/4t\times \mathrm{d}(Pt)/\mathrm{d}P), \qquad (5)$$

and the relative viscosity, η_r, which corresponds to the above value of q was evaluated by the equation[22]:

$$\eta_r=t/t_0\times(1-1/4t\times \mathrm{d}(Pt)/\mathrm{d}P)^{-1}, \qquad (6)$$

where R is the radius of the capillary, P is the driving pressure and t and t_0 are the efflux times for a given volume, Q, of the solution and the solvent, respectively.

Results and Discussion

Figs. 1 and 2 show the products of applied pressure and efflux time, Pt, for these fractions, measured at several concentrations at 25°C, plotted against P, where t is the efflux time for unit volume of flow (Pt is nearly proportional to η_r). On casual inspection, the more concentrated the solution, the larger the shear dependence of viscosity. An examination of these results, however, reveals that

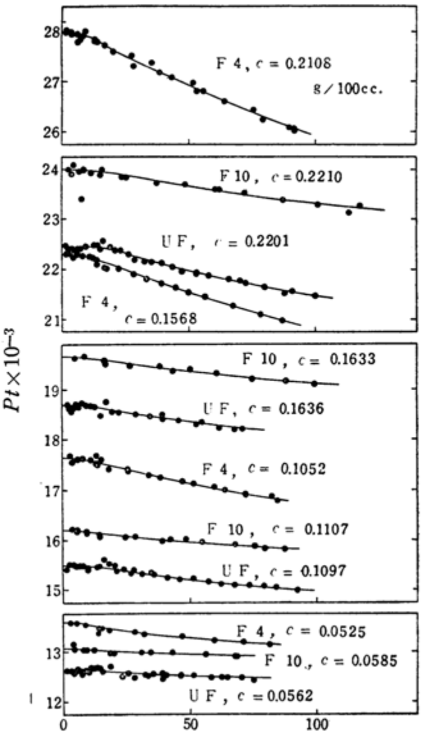

Fig. 1. Product of applied pressure and efflux time for unit volume of flow, Pt vs. applied pressure, P for F 4, F 10 and UF, measured at several concentrations at 25°C by a horizontal viscometer No. 1 (R=0.01440 cm, L=30.3 cm).

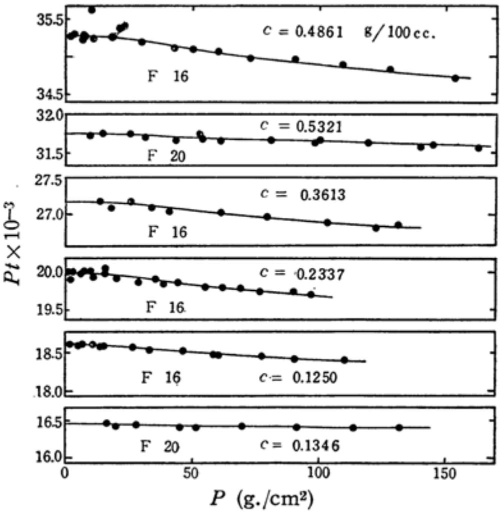

Fig. 2. Product of applied pressure and efflux time for unit volume of flow, Pt vs. applied pressure, P for F 16 and F 20 measured at 25°C. Results for F 16, c=0.1250 and F 20 were obtained by a horizontal viscometer No. 2 (R=0.01362 cm, L=30.1 cm) and the other by a horizontal viscometer No. 1.

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[20] Details of these procedures were described already in the *Annual Reports of Fiber Science Research Institute* (*Osaka University*), No. 9, p. 30 (1956), by K. Kawahara of this laboratory.

[21] This author is indebted to T. Oyama and K. Kawahara of this laboratory for these measurements. Details of these will be published in near future.

[22] T. Hotta, *Reports of Laboratory of High Polymer Research, Nagoya University*, No. 3, 22 (1951).

MW of the polymer has the most pronounced effect on degree of shear dependence; for example, the shear effect is quite small in the case of F 20 even when concentration is as high as 0.53%, but it is fairly large for F 4 even when concentration is ten times smaller than that of the solution of F 20.

It may be seem from these figures that these curves have horizontal tangents at the origin instead of showing sharp rises in the neighborhood of zero pressure, although this is somewhat ambiguous for the fractions of low *MW* owing to the rather large scattering of points in this region. Breadth of initial horizontal part seems to be roughly independent on concentration for a given fraction and it extends toward a high pressure as *MW* of fraction decreases. The tendency for solution viscosity to be constant at low pressures may be found also in Fig. 3, which shows ratios of efflux times of solution and solvent measured by a specially designed multi-bulb viscometer[23] which is essentially similar to that designed by Schurz[2] as a function of the mean pressure head of the viscometer.

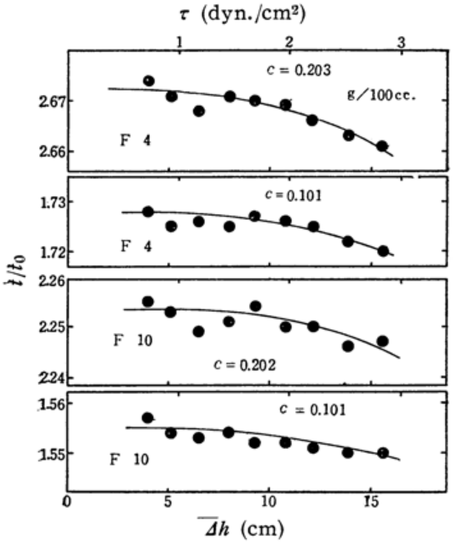

Fig. 3. Ratio of efflux times of solution and solvent, t/t_0, measured at 35°C by a multi-bulb viscometer (see foot-note (23)). $\overline{\Delta h}$ denotes the mean pressure head of the viscometer. For the upper abscissa, τ, see Eq. (7).

Included in Fig. 1 are the results obtained previously for UF, of which a description was already given in the earlier paper[7]. It is interesting to note that these solutions of UF exhibits the more pronounced shear dependences than the solutions of F 10 despite the fact that the average *MW* of F 10 is somewhat higher than that of UF and the concentration range covered by these two are approximately equal to each other. The characteristic feature of *Pt* vs. *P* relation also seems to be somewhat different between these two. This can be presumably ascribed to the presence of high *MW* components in UF. In this connection, it is very attractive to compare the shear dependences of viscosities of several solutions at the same concentration, the solute polymers of which are comparable to each other in average *MW* but different in patterns of *MW* distribution.

The results of measurements on two kinds of mixtures of two fractions and on single fractions are illustrated in Fig. 4, as *Pt* vs. *P* plots and these samples measured are tabulated in Table I. From these results, it seems that the shear effect should be considered dependent on patterns of *MW* distribution and is markedly affected by the presence of high *MW* components in the polymer mixture. This means that it might be possible to find somewhat smaller shear dependences of polystyrens fractions than those found in the present investigation if better fractionated samples were used, and so too quantitatively distinct interpretation of the present

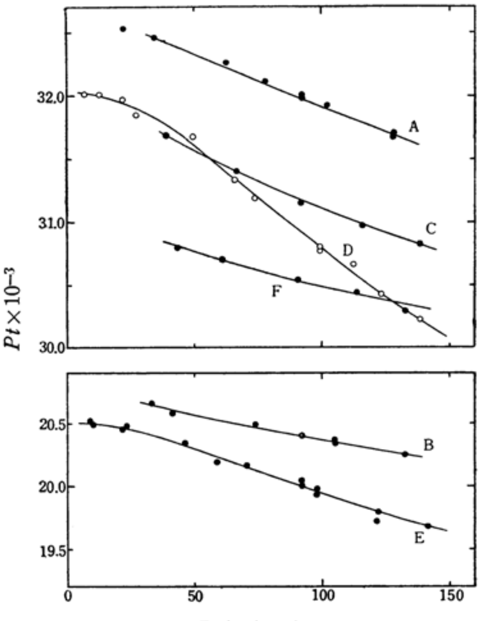

Fig. 4. Product of applied pressure and efflux time for unit volume of flow, *Pt* vs. applied pressure, *P* for the solutions shown in Table I, measured at 30°C by the viscometer No. 2 (see foot-note of Fig. 2). For A, B, C etc., see the last column of Table I.

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[23] The design of the viscometer ($R=0.0131$ cm, $L=30$ cm) and results for the other solutions obtained by the viscometer will be published in this bulletin in near future.

TABLE I

SAMPLES USED IN THE MEASUREMENTS RESULTS OF WHICH ARE SHOWN IN FIG. 3

Sample	Component, Weight%	$[\eta]^a$	Concentration in g./100 cc.	
F- 12	——	3.98	0.3022	A
			0.1510	B
MF-1	F 8 ($[\eta]^a=4.91$), 36.2 F 16 ($[\eta]^a=3.27$), 63.8	3.86^b (calc'd)	0.3022	C
MF-2	F 4 ($[\eta]^a=5.49$), 52.2 F 20 ($[\eta]^a=2.07$), 47.8	3.85^b (calc'd)	0.3022 0.1512	D E
F- 13	——	3.76	0.3022	F

a measured by an Ostwald viscometer in toluene at 30°C.
b calculated from $[\eta]$ of each component assuming contribution of components to the viscosity of mixture by their weight fractions.

results must be abandoned.

For each of these solutions, η_r was calculated as a function of q by the use of Eqs. (5) and (6) from the results in Figs. 1 and 2, and from the data for the dimensions of the viscometer. A typical set of η_r vs. q curves for F 4 is shown in Fig. 5. Values of η_{sp}/c were interpolated from these η_r vs. q relations at various q and plotted against the concentration for F 4 and F 10 as shown in Fig. 6.

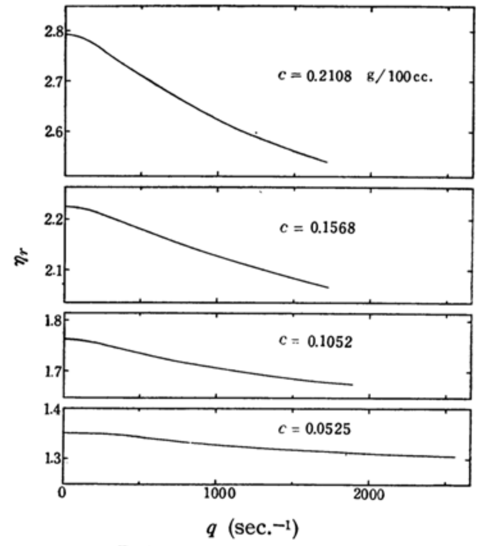

Fig. 5. Relative viscosity, η_r, vs. shear-rate, q, for F 4.

In the usual viscometry carried out by the ordinary Ostwald-type viscometer, measurements are made at constant shearing *stress* rather than at constant q by operating the viscometer at a standard driving pressure[24]. Moreover, it is customary to calculate η_r according to $\eta_r=t/t_0$ which is only the apparent η_r owing to the neglect of the second term in the bracket of Eq. (6). Accordingly, it is pertinent to find η_{sp}/c vs. c relation at constant stress using $\eta_r'=(Pt)/(Pt)_0$ at constant P in order to see the influences of non-Newtonian behavior on the results of the usual viscometry. Some of these curves thus obtained, η_{sr}'/c vs. c, are inserted in Fig. 6 for the convenience of comparison, where shearing stress τ was calculated by the equation:

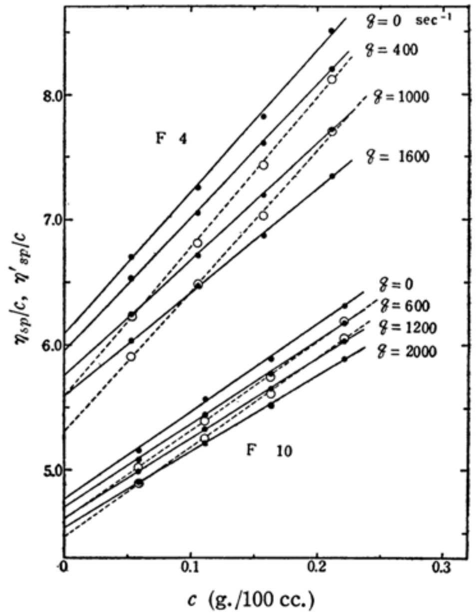

Fig. 6. Iso-shear η_{sp}/c vs. c (—●—) and iso-stress η_{sp}'/c vs. c (- - -○- - -) for F 4 and F 10. The upper iso-stress curve for each fraction is for τ=9.4 dyn./cm² and the lower for τ=18.8 dyn./cm².

$$\tau=PR/2L \tag{7}$$

which is the expression for the maximum stress at the capillary wall.

It can be seen from Fig. 6 that the tangent of iso-stress η_{sp}'/c vs. c curve is always larger than that of iso-shear η_{sp}/c vs. c curve. This means that Huggins' constant k' evaluated

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[24] Strictly speaking, driving pressure is not constant owing to small differences of densities amongst solutions and solvent.

from the data of the usual viscometry is generally greater than that from iso-shear η_{sp}/c vs. c relation except when τ is zero when the shear effect is appreciable. This is merely the natural consequence of the fact that q increases as the concentration of solution is decreased owing to the decrease in viscosity when τ is kept constant.

$[\eta]_q$ and $[\eta]_\tau$, obtained by linear extrapolation of these η_{sp}/c vs. c and η_{sp}'/c vs. c relations respectively to $c=0$, are shown in Fig. 7 as a function of q and τ, respectively.

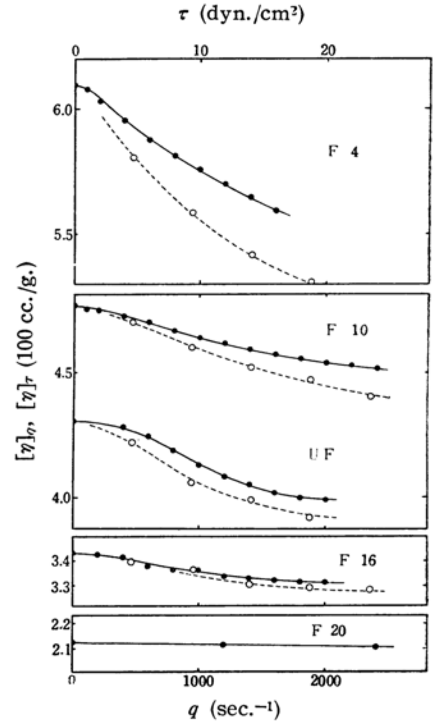

Fig. 7. $[\eta]_q$ vs. q (—●—) and $[\eta]_\tau$ vs. τ (- - -○- - -). For the upper abscissa, τ, see Eq. (7).

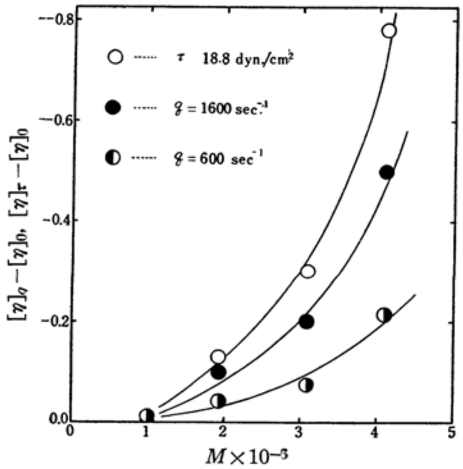

Fig. 8. $[\eta]_q-[\eta]_0$ vs. MW and $[\eta]_\tau-[\eta]_0$ vs. MW.

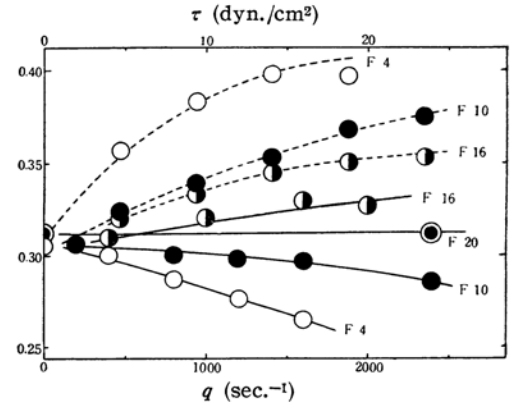

Fig. 9. k'_q vs. q and k'_τ vs. τ.
For the upper abscissa, τ, see Eq. (7).

It can be easily shown[2] that the dependence of shear-viscosity relation on MW distribution cannot take place if the shear dependence of viscosity is proportional to the first power of MW. Thus the existence of the effect of MW distribution on shear dependence such as has been noted above suggests a nonlinear dependence of shear effect on MW, and in fact this seems to be brought out in Fig. 8, which shows $[\eta]_q-[\eta]_0$ and $[\eta]_\tau-[\eta]_0$ as a function of MW for a few values of q and τ.

k'_q and k'_τ, obtained from the slopes of η_{sp}/c vs. c and η'_{sp}/c vs. c curves divided by the square of each intersept, respectively, appear plotted against q and τ, respectively in Fig. 9. Although the uncertainty of k' value is large owing to the sensitiveness of k' to the experimental error, it may be safely concluded that k'_q decreases to some extent with increasing q while k'_τ increases rather rapidly with increasing τ. A small increase of k'_q with q for F 16 may simply reflect the experimental error. Fig. 10 shows k'_q and k'_τ at some values of q and τ as a function of $[\eta]_0$. It is interesting to note that $k'_{q=0}$ $(=k'_{\tau=0})$ seems to be independent on MW,

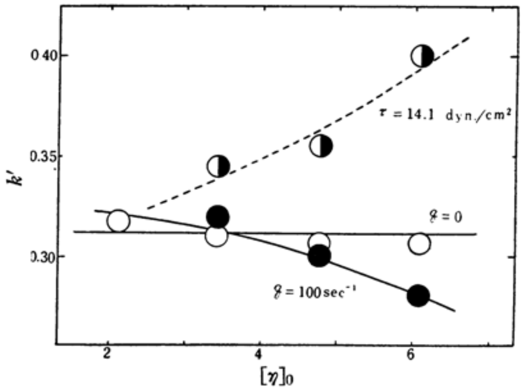

Fig. 10. k'_q vs. $[\eta]_0$ and k'_τ vs. $[\eta]_0$.

while k'_q at finite q decreases slowly and k'_τ at finite τ remarkably increases as MW is increased.

The relations between $[\eta]_\tau$ and MW are shown in log-log plot for $\tau=(q=)0$ and for $\tau=18.8$ dyn./cm^2 in Fig. 11. For the present case, reliable determinations of K and α in $[\eta]=KM^\alpha$ as a function of τ may be hampered by the small number of fractions measured and by the possible effect of MW distribution on shear dependence of $[\eta]$ mentioned above. These results of Fig. 11 may be sufficient only to get a rough idea of the relation between α and τ. The tangents of these two lines drawn in Fig. 11 are 0.74 and 0.66, respectively.

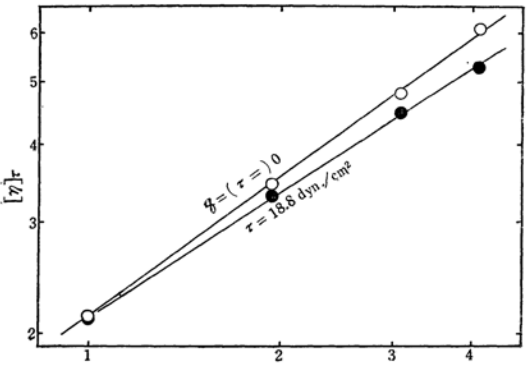

Fig. 11. $\log[\eta]_\tau$ vs. $\log M$.

Turning to the comparison with the theory, $[\eta]_q/[\eta]_0$ of these fractions are plotted against ξ, which was calculated for each fraction by the use of Eq. (4) putting $m=104$ and $\eta_0=0.552\times10^{-2}$ poise, as shown in Fig. 12. The theoretical dependence of $[\eta]_q/[\eta]_0$ for $B\gg\lambda\eta_0L$ as given by Eq. (3) is represented by the broken line in Fig. 12.

As may be seen from Fig. 12, the tendency for $[\eta]_q/[\eta]_0$ vs. ξ relation to approach to the theoretical curve for $B\gg\lambda\eta_0L$ with decreasing MW of the polymer cannot be observed for the present case, which is not in line with what would be expected from the theory of Kuhn and Kuhn mentioned above. This should not seem, however, to be regarded as a conflict with the theory.

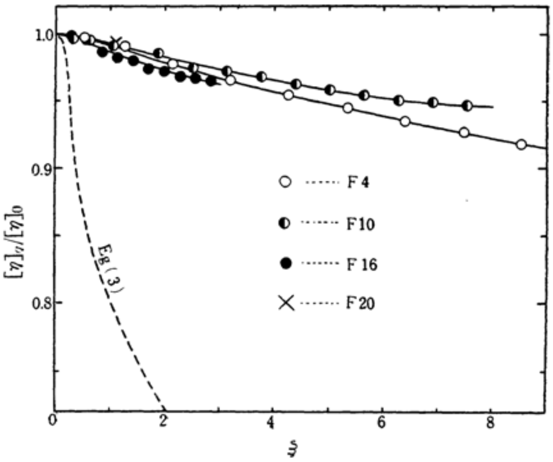

Fig. 12. $[\eta]_q/[\eta]_0$ vs. ξ for the fractions.

Kuhn and Kuhn[25] have suggested on the basis of the results of streambirefringence measurements by Signer and Gross, that the inner viscosity of a polystyrene molecule is fairly small already at MW of 44×10^4. And in this region of such high MW as have been studied in this work, the inner viscosity may be significantly small as would be expected from the theoretical relation $B\propto1/M$. The same information regarding the stiffness of the polymer molecule may be obtained from the fact that all the experimental curves lie near to the curve $[\eta]_q/[\eta]_0=1$ being apart from the theoretical curves in Fig. 12.

The apparent disaccord with the theory may be merely due to the fact that the further decrease in B with increasing MW from the order of 100×10^4 to higher values can cause only an indistinguishable change in $[\eta]_q/[\eta]_0$ vs. ξ relation within experimental error.

It appears that, in order to make a more critical test of the theory, the similar measurements should be made in the range of lower MW and over a wider range of q or on polymer of more stiff nature.

This author should like to express his gratitude to Prof. S. Murahashi and Prof. S. Akabori of this university for their kind encouragements and to Prof. W. Kuhn of the University of Basel for his kind instruction and information.

The financial asistance of the Tekkōsha Company is also gratefully acknowleged.

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[25] W. Kuhn and H. Kuhn, *Ergeb. exakt. Naturwiss.*, 25, 8 (1951).