Colloid Chemical Studies of Starching Materials. V. Rheological Properties of Concentrated Polyvinyl Alcohol Solutions

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In a previous paper,[1] the dynamic viscosity and rigidity of starch solutions measured by a top-drive coaxial rheometer have been reported, and the results have been discussed[2] on the basis of Rouse's theory[3] as modified to take the intermolecular association into account. On the other hand, the structural viscosity of dilute solutions of polyvinyl alcohol has also been reported on previously[4]. These papers have, however, been chiefly interested in the anomalous viscosity due to the intermolecular association.

In the present paper, the viscoelastic behaviour of concentrated solutions of polyvinyl alcohol will be studied by means of a rotation viscometer, together with the rheometer previously used for starch solutions, and the results will be discussed on the basis of Rouse's theory, considering the change in intermolecular association in the solutions.

Experimental

Sample.—The polyvinyl alcohols used in these experiments are the same as those used in a previous paper.[5] They are Gohsenol GH-17 (degree of saponification $S=88.1\%$, average degree of polymerization $P=1700$), GH-23 ($S=87.5\%$, $P=2300$), NH-17 ($S=98.8\%$, $P=1700$), and NH-26 ($S=99.4\%$, $P=2600$).

To prepare aqueous solutions of polyvinyl alcohol, 90 g. of the polymer was put in 600 g. of distilled water, together with 0.18 ml. of Shinetsu Silicone Antifoaming Agent KM-65, and the whole was heated at 95°C for 30 min. (in the case of NH-17 and NH-26) or 1 hr. (in the case of GH-17 and GH-23) while being stirred well with a glass rod. After the solution had cooled to room temperature, the film which had formed on the surface of the solution was removed and kept in a closed vessel. The concentration was determined by measuring the weight of the polymer which remained after a known weight of the solution had been dried.

For the dynamic measurement, a solution put in the rheometer was covered with liquid paraffine and the measurements were made for the same solution 20, 60 and 110 hr. after the preparation of the solution. For the measurement of the steady-flow viscosity, a solution kept in a closed vessel for 20, 60 and 110 hr. was put in the rotation viscometer for each measurement.

Oscillation Rheometer.—A top-drive coaxial rheometer used was the same as has been reported on in a previous paper.[1] All measurements have been made in a thermostat at 30°C.

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[1] M. Nakagaki and K. Muragishi, This Bulletin, 34, 316 (1961).

[2] M. Nakagaki, ibid., 35, 606 (1962).

[3] P. E. Rouse, *J. Chem. Phys.*, 21, 1272 (1953),

[4] M. Nakagaki and A. Shimazaki, This Bulletin, 29, 60 (1956).

[5] M. Nakagaki and K. Goto, ibid., 35, 791 (1962).

Rotation Viscometer.—A coaxial rotation viscometer of the Couette type was newly constructed. An inner cylinder 30 mm. in diameter ($2r_1$), 75 mm. long, and weighing 461.72 g. was hung in an outer cylinder 42 mm. in inner diameter ($2r_2$) and 90 mm. deep with a steel wire 490 mm. long, the torsional constant of which was $k_0=1.036\times10^5$ (dyn. cm.). The sample solution was put into the gap between the inner and outer cylinders, and the inner cylinder was held to dip into the solution by $h=65$ mm. The outer cylinder set in a thermostat at 30°C was rotated. The rate of the rotation, Ω (r. p. m.), was variable between 6 r. p. m. to 190 r. p. m. by means of thirty combinations of gears. The velocity gradient, g (sec^{-1}), was calculated by the following relation:

$$g=\frac{2\pi r_2}{60(r_2-r_1)}\quad\Omega=0.367\,\Omega \tag{1}$$

By measuring the angle of the deflection of the inner cylinder, θ (degree), the steady-flow viscosity of the solution can be calculated by the equation:

$$\eta=\left(\frac{k_0}{24\,\pi\,h}\right)\left(\frac{1}{r_1^2}-\frac{1}{r_2^2}\right)\quad\frac{\theta}{\Omega} \tag{2}$$

All data are given in c. g. s. units.

Theoretical

In a previous paper,[2)] the viscoelastic behavior of starch solutions has been discussed on the basis of a modified Rouse equation:

$$\left.\begin{aligned}\eta&=(F/\sqrt{\omega})\,\alpha\\ G&=G_0+F\sqrt{\omega}\,\beta\end{aligned}\right\} \tag{3}$$

where ω is the angular frequency, τ is the relaxation time, F is a constant, and α and β are functions depending on $\omega\tau$ only. The values of the functions have been given in that previous paper.[2)]

In the case of polyvinyl alcohol solutions, however, the viscoelastic behaviour is different from that of starch solutions, especially in the low frequency region, where the polyvinyl alcohol solutions showed the following features: (1) The dynamic viscosity, η, is almost constant (except for NH-26), and (2) the dynamic rigidity, G, is nearly equal to zero; that is, $G_0\fallingdotseq0$.

Since the α function tends to the following value when $\omega\tau\ll1$,

$$\alpha=(\sqrt{2}\,\pi/3)\sqrt{\omega\tau}=1.48020\sqrt{\omega\tau} \tag{4}$$

the value of η at $\omega\rightarrow0$, designated by η_0, is given by:

$$\eta_0=1.48020\;F\sqrt{\tau} \tag{5}$$

Therefore, the following equations can be used for polyvinyl alcohol solutions:

$$\left.\begin{aligned}\eta/\eta_0&=A(\omega\tau)\\ G/\eta_0&=B(\omega\tau)/\tau\end{aligned}\right\} \tag{6}$$

where $G_0=0$ was used. Here, A and B are the functions of $\omega\tau$ only, as defined by the following:

$$\left.\begin{aligned}A&=\alpha/1.48020\sqrt{\omega\tau}\\ B&=\sqrt{\omega\tau}\,\beta/1.48020\end{aligned}\right\} \tag{7}$$

The theoretical relations of $\log(\eta/\eta_0)$ and $\log(G/\eta_0)$ relative to $\log\omega$ can be drawn for various values of τ (sec.), as shown in Fig. 1.

In order to compare the experimental with the theoretical values, the experimentally-obtained values were plotted on $\log\eta$ and $\log G$ vs. a $\log\omega$ chart with the same scale as the theoretically-drawn Fig. 1, and the chart was superposed on Fig. 1 by sliding it along the ordinate. In order to obtain the best fit, attention must be paid to the values of η at low frequencies. The values of η_0 can then be read off from the position of the ordinate at the best fit, and the value of τ (sec.) can

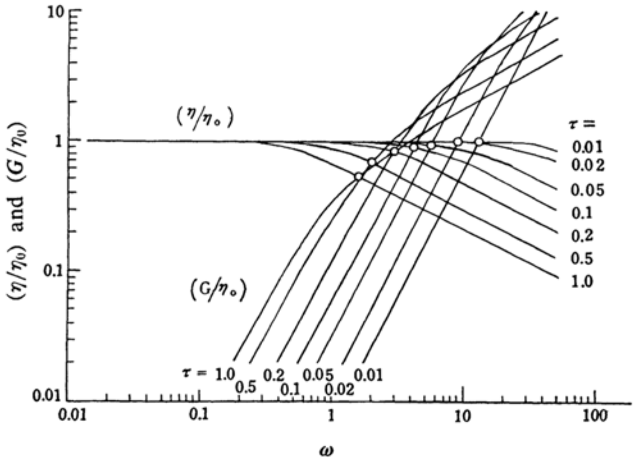

Fig. 1. Theoretical relations calculated for various τ (sec.) values.

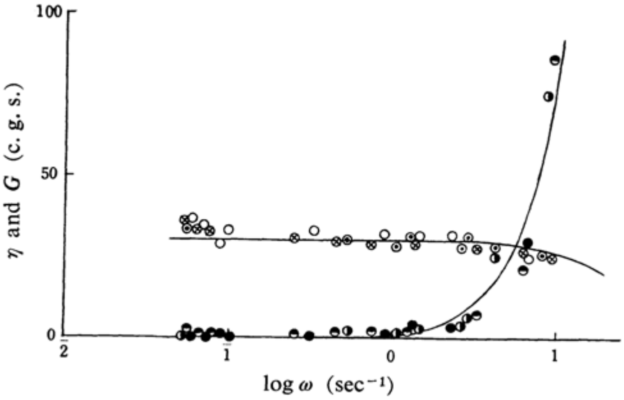

Fig. 2. Dynamic measurements for GH-17. η after 20 hr. (○), 60 hr. (⊗), 110 hr. (⊙), G after 20 hr. (●), 60 hr. (◓) and 110 hr. (◑).

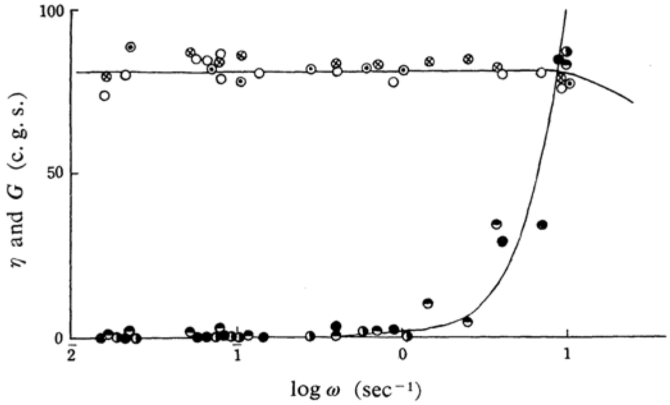

Fig. 3. Dynamic measurements for GH-23. η after 20 hr. (○), 60 hr. (⊗), 110 hr. (⊙), G after 20 hr. (●), 60 hr. (◓) and 110 hr. (◑).

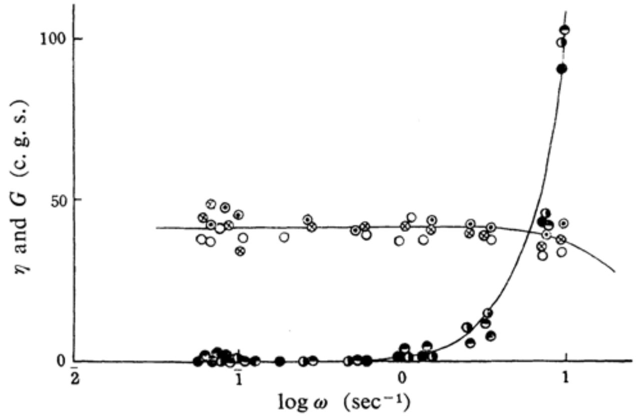

Fig. 4. Dynamic measurements for NH-17. η after 20 hr. (○), 60 hr. (⊗), 110 hr. (⊙), G after 20 hr. (●), 60 hr. (◓) and 110 hr. (◑).

TABLE I. PARAMETER VALUES (in c. g. s. units).

Sample	Dynamic measurement				Steady-flow measurement		
	η_0	τ	F	$\eta_0/P^2\times 10^5$	η_N	Time, hr.	G_y
GH-17	30	0.05	91	1.04	28	20	10
						60	60
						110	240
GH-23	81	0.02	387	1.53	87	20	150
						60	740
						110	1310
NH-17	41	0.05	124	1.41	40	20	60
						60	150
						110	190
NH-26	100	0.015	551	1.48	95	20	950
						60	1320
						110	1650

be obtained from the location of the experimental $\log\eta$ and $\log G$ curves, paying attention especially to the point of intersection of these curves, that is, the points marked by open circles in Fig. 1.

Results and Discussion

Dynamic Viscosity and Dynamic Rigidity.—The experimental values of η and G obtained by the oscillation rheometer at 30°C are shown in Fig. 2 for a 11.51% GH-17 solution, in Fig. 3 for a 12.38% GH-23 solution, and Fig. 4 for a 11.09% NH-17 solution. All these correspond well with the theoretical curves drawn by Eq. 6 with the parameter values cited in Table I. The length of time between the preparation of the solutions and the measurement did not make much difference in the η and G values.

The viscoelastic behavior of NH-26 was fairly different from that of other samples. The viscosity changed with the time which elapsed from the preparation of solutions to the measurement. If one pays attention to the frequency value at which the curves of η and G intersect, the values $\eta_0=100$ and $\tau=0.015$ are obtained, as is cited in Table I. The theoretical η and G curves for these parameter values, calculated by Eq. 6 and shown in Fig. 6 by broken lines, do not however, correspond well with the experimental values, especially at the small ω values, where the experimental η values are much greater than the η_0 value, probably because of the association of polymer molecules. If it is assumed that the degree of association is the greater, and the η value is the greater, the smaller the frequency, ω, the fraction of the highly-associated component x_1 could, of course, be calculated for various frequency values by using the method already described in a previous paper.[2] In the present paper, however, it is assumed that, because of the existence of the highly-associated component, the average τ value is the greater, the smaller the ω value. The ω dependency of τ is calculated as follows. It can be shown that the following equation should be used when $\omega\tau\ll 1$;

$$\tau \doteqdot (\eta/1.48020\, F)^2 \tag{8}$$

where F is a constant which is believed to be independent of ω and τ. The value of $F=551$ is obtained from Eq. 5 on the basis of $\eta_0=100$ and $\tau=0.015$. The frequency dependence of τ obtained by Eq. 8 for NH-26 is shown in Fig. 5. By using the τ values corresponding to the solid lines in Fig. 5 drawn by assuming that the $\tau-\log\omega$ relation is linear for $\omega\leqq 1$, the values of η and G calculated from Eq. 6, instead of from the approximate Equation 8, are shown in Fig. 6 by solid lines. Thus, it is concluded that the "structure" due to the intermolecular association is developed in the NH-26 solution; that the average relaxation time, τ, and, therefore, the dynamic viscosity, η, are increased with the lapse of time after the preparation of the solution, and that the structure is destroyed and that η is decreased with the increase in the frequency, ω.

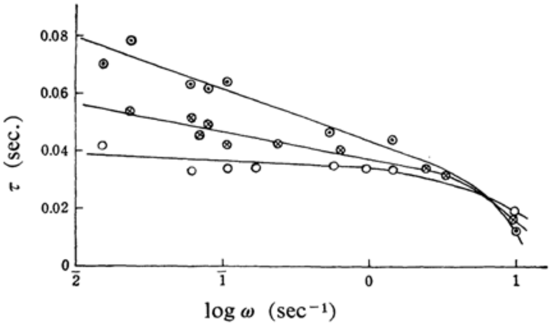

Fig. 5. Apparent relaxation time of NH-26 after 20 hr. (○), 60 hr. (⊗) and 110 hr. (⊙).

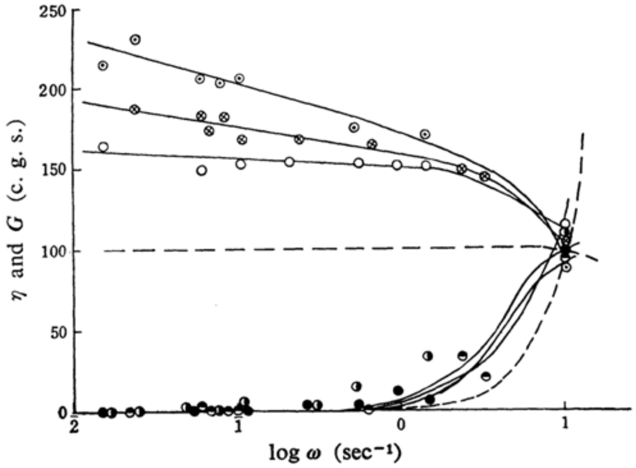

Fig. 6. Dynamic measurements for NH-26. η after 20 hr. (○), 60 hr. (⊗, 110 hr. (⊙), G after 20 hr. (●), 60 hr. (◓) and 110 hr. (◑). Broken curves are for $\eta_0=100$, $\tau=0.015$.

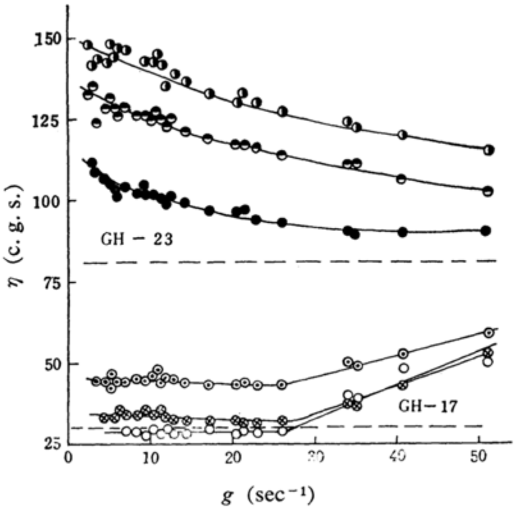

Fig. 7. Steady-flow measurements of GH-17 after 20 hr. (○), 60 hr. (⊗), 110 hr. (⊙) and of GH-23 after 20 hr. (●), 60 hr. (◓), and 110 hr. (◑).

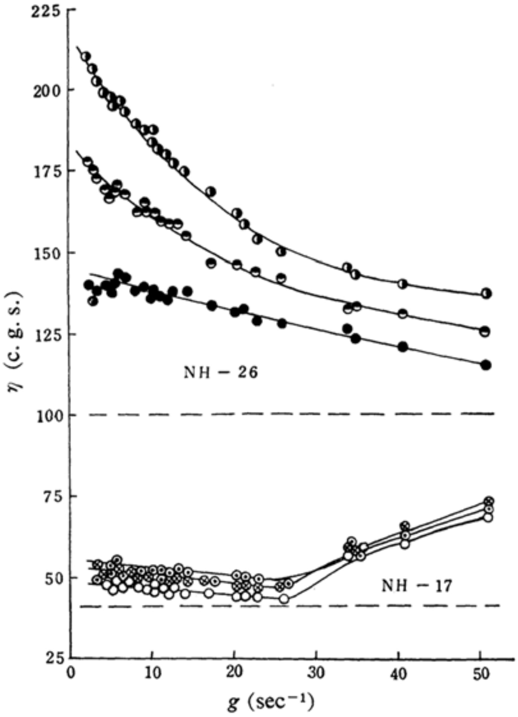

Fig. 8. Steady-flow measurements for NH-17 after 20 hr. (○), 60 hr. (⊗) and 110 hr. (⊙) and for NH-26 after 20 hr. (●), 60 hr. (◓) and 110 hr. (◑).

Steady-flow Viscosity.—The steady-flow viscosities measured by a coaxial rotational viscometer at 30°C are shown in Fig. 7 for GH-17 and GH-23 and in Fig. 8 for NH-17 and NH-26. The order of magnitude of the steady-flow viscosity values agrees with the values of η_0 in Table I obtained dynamically by the oscillation rheometer and shown in Figs. 7 and 8 by horizontal broken lines. There are, however, several important points of disagreement between the dynamic and steady-flow measurements.

The discussions in the present paper are essentially based on Rouse's theory, a theory which is presumed by some people⁽⁶⁾ to be applicable to the steady-flow viscosity, too, if one substitutes the frequency, ω, in the dynamic measurement as is in the original Rouse equation with the velocity gradient, g, in the steady-flow measurement. The present authors, however, do not agree with this conventional substitution; they believe that the steady-flow

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6) E. g., J. D. Ferry, M. L. Williams and D. M. Stern, *J. Phys. Chem.*, **58**, 987 (1954).

viscosity is equal to η_0. The steady flow viscosity should, therefore, be Newtonian except in the case of NH-26, for which the structural change with ω is observed in the course of dynamic measurement.

The solution of NH-26 showed structural viscosity as expected and as shown in Fig. 8. However, the steady-flow viscosities of GH-17, GH-23 and NH-17 also showed dependencies not only on the velocity gradient but also on the time after the preparation of the solution, as Figs. 7 and 8 show. Neither of these dependencies could be expected on the basis of the dynamic measurements reported in the preceding paragraph.

The steady-flow viscosity of the relatively low molecular weight samples, GH-17 and NH-17, increase with the velocity gradient, g, when the g value exceeds 30 sec^{-1}. In this region of g, the solutions, therefore, behave as if they are dilatant. This dilatant behavior might be due to a certain unexpected factor involved in the method of measurement, although the authors can not think of any fault in the experiment.

As for the structural viscosity of polyvinyl alcohol solutions, it has been reported[4] that the apparent viscosity is linear to the reciprocal of the rate of flow ($1/Q$), and that the limiting value of viscosity, η_N, extrapolated to ($1/Q\rightarrow 0$) is independent of the history of the solution; The empirical relation translated to the present notation is:

$$\eta=\eta_N+G_y/g \tag{9}$$

For the concentrated solutions discussed here, however, this relation holds not over the whole range of $1/g$, but only in the range of small $1/g$ values, excluding the dilatant behavior of GH-17 and NH-17. The results are shown in Fig. 9, while the values of the parameters, η_N and G_y, are given in Table I. The value of η_N is independent of the time which has elapsed before the measurement and is in good agreement with the dynamically-obtained η_0 value. The G_y has the dimension of rigidity and corresponds to the yield value of Bingham flow, although the behavior of the solution is not Bingham-like because the value of η is smaller than that expected from Eq. 9 in a high ($1/g$) region. The increase in G_y with time suggests the development of structure in the solutions.

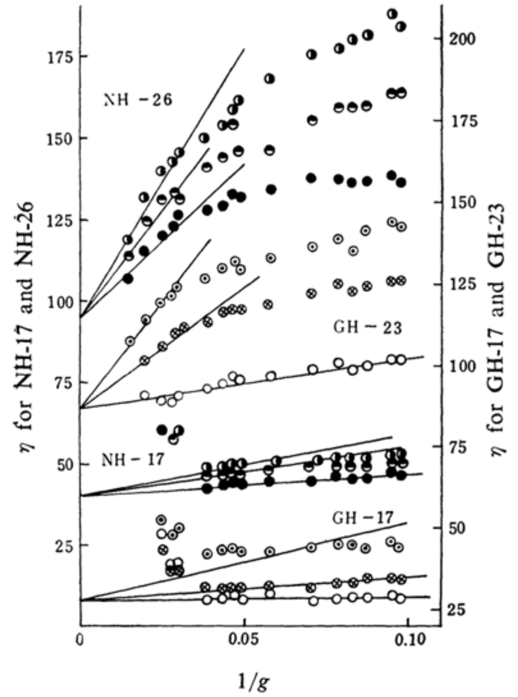

Fig. 9. Relation between η and $1/g$ for the samples after 20 hr. (○, ●), 60 hr. (⊗, ◓) and 110 hr. (⊙, ◑).

An Examination of Parameter Values.—As has been shown in a previous paragraph, the viscoelastic behavior of polyvinyl alcohol solutions may be described fairly well with Eq. 6, which is essentially based on Rouse's theory. On examining the values of parameters, however, it appears that the theory is not very good in explaining all the results. First of all, the value of F calculated by Eq. 5 and given in Table I is a constant throughout the experiments any on one sample, but it is not a constant common to all the samples. The same has been observed in the case of starch solutions reported on before.[2] On the other hand, the theoretical expression of F is, as has already been shown in a previous paper:[2]

$$F=nN\sigma\sqrt{kT}/4\sqrt{3}\sqrt{B} \tag{10}$$

where n is the number of molecules in a unit volume of the solution, N is the number of segments contained in one polymer molecule, σ is the length of the segment, and B is the mobility of the end of a segment. If the polymer molecules aggregate in the solution, and if the average number of molecules to form one aggregate is m, then n and N in Eq. 10 should be replaced by (n/m) and (mN) respectively, but this replacement does not make any difference in Eq. 10 because $(n/m)\cdot(mN)$ is equal to nN. Therefore, F should be a constant independent of the degree of intermolecular association, and it should be a constant for various samples of the polymer composed of the same monomeric unit. Contrary to this theoretical expectation, however, the experimental values of F for various samples do not equal each other. This is probably due to the change in $\sigma/\sqrt{B}$. However, the situation is supposed to be complicated in concentrated polymer solutions because of various reasons such as are, for example, described below: (1) The manner of the intermolecular aggregation might be different. If the molecules associated head to tail to form a linear aggregate, Rouse's theory may be applied without further modification, but if the molecules associate with intermediate segments to form a "star"-shaped aggregate, the viscoelastic behavior will be different from that expected by Rouse's theory derived for linear molecules. (2) If the possibility of intramolecular interaction can be expected, the interaction will change not only $\sigma/\sqrt{B}$ but also the effective number of segments, N. These changes will, of course, explain the variation in the value of F.

At any rate, it seems to be necessary to presume that the molecular aggregates are formed in the solutions of all samples, and that the aggregation is the cause of the non-Newtonian behavior of the steady-flow viscosity, but that the structural change of the aggregates is not dominant, except for NH-26, within the extent of the range of the frequency used for the dynamic measurement. Although this view still can not explain why the time dependence of η was not observed in the dynamic measurement, one of the reasons might be that the solution kept in the apparatus was used for successive measuments in the case of the dynamic experiment, while a part of a solution kept in a reservoir was placed in the apparatus for each steady-flow experiment.

Although it is not clear whether it is theoretically valuable or not, it may be worthwhile to point out here the entirely empirical fact that the value of η_0/P^2 is fairly constant, as is shown in Table I, where P is the degree of polymerization of the polymers.

Summary

The dynamic viscosity, dynamic rigidity and steady-flow viscosity at 30°C have been measured for 11～12% solutions of four specimens of polyvinyl alcohol, GH-17, GH-23, NH-17 and HN-26, 20, 60 and 110 hr. after the preparation of the solutions.

In the dynamic measurement by a top-drive coaxial oscillation rheometer, the relations of η and G vs. ω did not depend on time and have all been explained by Rouse's theory except for NH-26, the latter showing time and ω dependencies of the structure. In the steady-flow measurement by a coaxial rotation viscometer, the viscosity of all the polymers showed both time and velocity gradient dependencies.

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