Colloid Chemical Studies on Starching Materials. IV. Viscoelasticity and Structure Change of Starch Solutions

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Structural viscosity, that is, the apparent viscosity decreasing with an increasing velocity gradient, is due to the dispersion of highly associated colloidal particles or polymer molecules into smaller aggregates by the effect of the velocity gradient[1]. A structure change like this should obviously affect the dynamic viscosity and the dynamic rigidity of high polymer solutions. The viscoelastic properties of high polymer solutions have been discussed by Rouse[2]. Rouse's theory is satisfactory to the extent that the theory gives the value ($-1/2$) to the gradient of the relaxation spectra of high polymer solutions[3], but the actual behavior of high polymer solutions is much more complicated than the theory expects. Moreover, Rouse's theory cannot predict the existence of structural viscosity because the theory does not take into account any structure change in the solution.

In the preceding paper of this series[4], experimental data of dynamic viscosity and dynamic rigidity, obtained by using a top-drive coaxial rheometer, have been reported for 3 and 5% potato starch, 5% sweet potato starch and 5% rice starch solutions. Examination of the data, too, has been made on the basis of the modified Rouse equations:

$$\eta=\eta_0 f_1(\tau\omega) \tag{1}$$

$$G=G_0+(6/\pi^2)(\eta_0/\tau)f_2(\tau\omega) \tag{2}$$

where

$$\left.\begin{aligned} f_1&=(6/\pi^2)\sum_{p=1}^{N}[p^2/(p^4+\tau^2\omega^2)] \\ f_2&=\sum_{p=1}^{N}[\tau^2\omega^2/(p^4+\tau^2\omega^2)] \end{aligned}\right\} \tag{3}$$

Here, η is the dynamic viscosity, G is the dynamic rigidity, ω is the angular frequency, p is an integer, and η_0, G_0 and τ are constants. It has been suggested, in the same paper, that the experimental data can be explained satisfactorily if one assumes that there are in the starch solutions large aggregates of polymer molecules with large values of η_0 and G_0 when the frequency is small and that the aggregates change to smaller ones of smaller η_0 and G_0 with the increase of the frequency. In the present paper, the idea described in the preceding paper has been formulated and applied to the experimental data.

Theoretical

According to Rouse's theory, the parameters η_0 and τ in Eqs. 1 and 2 depend on the number N of segments (submolecules) contained in a high polymer molecule as follows:

$$\left.\begin{aligned} \eta_0&=(\pi^2/6)nkT\tau \\ \tau&=\sigma^2N^2/6\pi^2BkT \end{aligned}\right\} \tag{4}$$

where n is the number of molecules in a unit volume of the solution, τ is the longest relaxation time of the polymer molecule (τ_1 in Rouse's original paper), σ is the length of the segment, and B is the mobility of the end of a segment. Therefore, by introducing three parameters α, β and F, defined by:

$$\left.\begin{aligned} \alpha(\tau\omega)&=(2\sqrt{2}/\pi)\sqrt{\tau\omega} \\ &\quad\times\sum_{p=1}^{\infty}[p^2/(p^4+\tau^2\omega^2)] \\ \beta(\tau\omega)&=[(2\sqrt{2}/\pi)/\sqrt{\tau\omega}] \\ &\quad\times\sum_{p=1}^{\infty}[\tau^2\omega^2/(p^4+\tau^2\omega^2)] \end{aligned}\right\} \tag{5}$$

and

$$F=nN\sigma\sqrt{kT}/4\sqrt{3}\sqrt{B} \tag{6}$$

the modified Rouse equations 1 and 2 can be rewritten into the following equations:

$$\left.\begin{aligned} \eta&=(F/\sqrt{\omega})\alpha(\tau\omega) \\ G&=G_0+F\sqrt{\omega}\beta(\tau\omega) \end{aligned}\right\} \tag{7}$$

The points to be emphasized here are as follows: First, the parameter F is proportional to nN, that is, the total number of segments in a unit volume of the solution, or to the weight concentration, irrespective of the degree of molecular association. Second, the parameters α and β are functions of ($\tau\omega$) only and have the values cited in Table I. Both α and β approach zero when ($\tau\omega$) is small and

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TABLE I. THEORETICAL VALUES OF α AND β

$\tau\omega$	α	β	$\tau\omega$	α	β
0.0001	0.01480	0	0.5	0.9165	0.2807
0.0002	0.02093	0	1	1.0000	0.5211
0.0005	0.03310	0.00001	2	1.0000	0.6855
0.001	0.04682	0.00003	5	1.0000	0.7986
0.002	0.06620	0.00009	10	1.0000	0.8577
0.005	0.1047	0.00034	20	1.0000	0.8993
0.01	0.1480	0.00097	50	1.0000	0.9362
0.02	0.2093	0.00275	100	1.0000	0.9550
0.05	0.3310	0.01085	200	1.0000	0.9681
0.1	0.4649	0.03055	500	1.0000	0.9799
0.2	0.6459	0.08386	1000	1.0000	0.9858

approach unity when $(\tau\,\omega)$ is large. However, the manners of approach of α and β to these limiting values are widely different. Under a 1% allowance, α is equal to zero when $(\tau\,\omega)$ is smaller than 0.0001, but β is already zero when $(\tau\,\omega)$ is smaller than 0.05; α is already equal to unity when $(\tau\,\omega)$ is larger than 1, but β is equal to unity when $(\tau\,\omega)$ is as large as 1000.

In order to consider a mixture of highly associated molecules of N_1 segments and less associated (or not associated) molecules of N_2 segments $(N_2<N_1)$, the dynamic viscosity η and dynamic rigidity G of the mixture may be assumed to be:

$$\left.\begin{aligned}\eta&=(x_1\alpha_1+x_2\alpha_2)F/\sqrt{\omega}\\ G&=x_1G_0+(x_1\beta_1+x_2\beta_2)F\sqrt{\omega}\end{aligned}\right\}\qquad(9)$$

where x_1 and x_2 are the weight fractions of respective components $(x_2=1-x_1)$. α_1 and β_1 are the values of α and β for $(\tau_1\,\omega)$, and α_2 and β_2 are the values for $(\tau_2\,\omega)$, where the value of τ_1 is much larger than the value of τ_2 because the suffix 1 designates highly associated, and the suffix 2 less associated, molecules. The G_0 values of the less associated molecules are assumed to be zero.

In order to apply Eq. 9 to experimental values of η and G and to obtain an experimental $x_1-\omega$ relationship, the values of the four parameters F, G_0, τ_1 and τ_2 should be estimated. The choice of the four parameter values is not as arbitrary as it looks, because of the character of the ω dependency of the functions α and β, especially because α_1 should be equal to unity except when ω is very small, and β_2 should be equal to zero except when ω is very large. As a result, the relative value of x_1 (calculated by assuming that the value of x_1 is equal to unity for the smallest ω value used in the experiment) can be obtained without any arbitrariness. The results obtained for starch solutions will be shown later.

By way of application of Eq. 9, it has been recognized that the choice of the values of τ_1 and τ_2 does not affect the final $\log\eta-\log\omega$ relationship and $\log G-\log\omega$ relationship too much. Therefore, an approximate method is also used by assuming $\tau_1\gg1$ and $\tau_2\ll1$, or

$$\alpha_1=1,\quad \beta_1=1,\quad \alpha_2=0,\quad \beta_2=0\qquad(10)$$

In this case, Eq. 9 can be simplified to:

$$\left.\begin{aligned}\eta&=x_1F/\sqrt{\omega}\\ G&=x_1(G_0+F\sqrt{\omega})\end{aligned}\right\}\qquad(11)$$

This equation was also applied to starch solutions.

Discussion of Experimental Data

By using either Eq. 9 or 11, the variation of x_1 with the circular frequency ω was calculated for starch solutions, the dynamic viscosity and the dynamic rigidity experimental values of which have been reported in the preceding paper[4]. Results for the 3% potato starch solution are shown in Fig. 1, the 5% potato starch solution in Fig. 2, the 5% sweet potato solution in Fig. 3, and the 5% rice starch solution in Fig. 4. In these figures, the experimental values of $\log\eta$ (○), $\log G$ (●) and x_1 (both values obtained by Eq. 9 (□) and by Eq. 11 (△) are shown) are plotted. The values of the parameters adopted to calculate the values of x_1 are cited in Table II. The values of x_1 thus obtained are linear to $\log\omega$ for potato starch and sweet potato starch solutions, as is

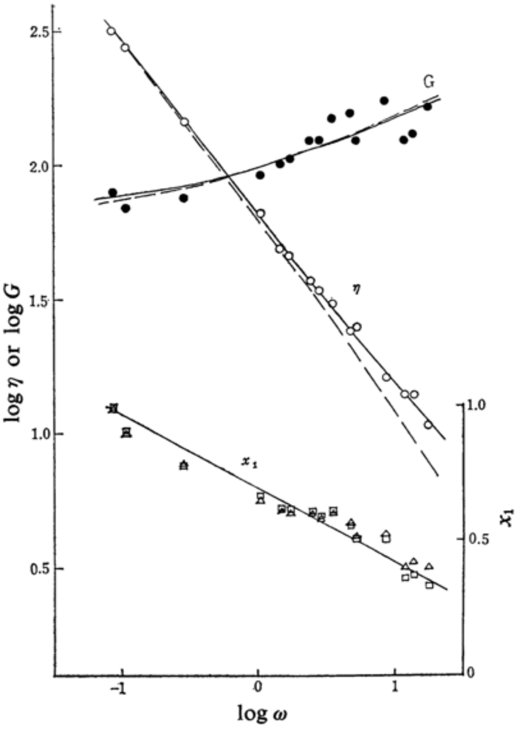

Fig. 1. $\log\eta$ (○), $\log G$ (●), and x_1 by Eq. 9 (□) and Eq. 11 (△) of 3% potato starch solution.

shown by the straight lines in Figs. 1—3. By using x_1 values corresponding to these straight lines, and also by using the parameter values cited in Table II, values of η and G were calculated and shown in these figures by solid lines for Eq. 9 and by broken lines for Eq. 11. Agreements between the experimental plots and the calculated curves are satisfactory for the potato starch solutions (Figs. 1 and 2). In the case of the sweet potato starch solution (Fig. 3), the analysis based on Eq. 9 gave the result that $\tau_1 \gg 1$ and $\tau_2 \ll 1$, so that Eq. 9 turned out to be the same as Eq. 11. The values of the parameter F (and G_0) for Eq. 9 and for Eq. 11 differ because in the case of Eq. 9 the experimental data at about $\log \omega = -1$ were respected highly, while in the case of Eq. 11 they were neglected. It is obvious that a better agreement can be obtained if one adopts for F and G_0 some values between those for Eqs. 9 and 11, if one discards the expectation to the linearity of x_1 to $\log \omega$ and if one adopts more suitable values for x_1 for each $\log \omega$ value. In the case of the rice starch solution (Fig. 4), the value of x_1 decreases linearly as far as

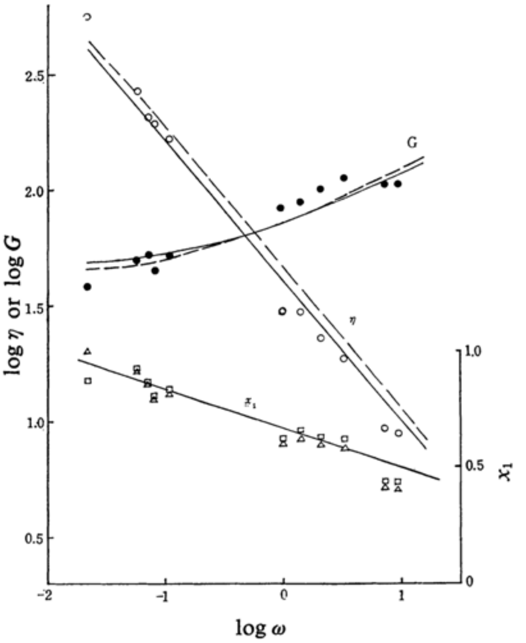

Fig. 2. $\log \eta$ (○), $\log G$ (●), and x_1 by Eq. 9 (□) and Eq. 11 (△) of 5% potato starch solution.

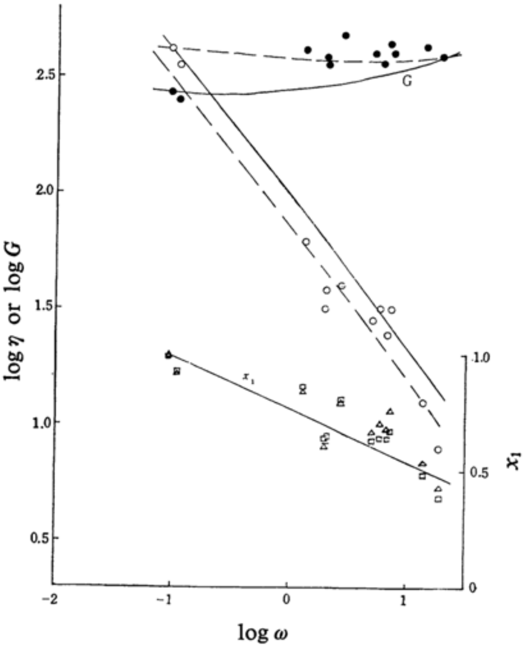

Fig. 3. $\log \eta$ (○), $\log G$ (●), and x_1 by Eq. 9 (□) and Eq. 11 (△) of 5% sweet potato starch solution.

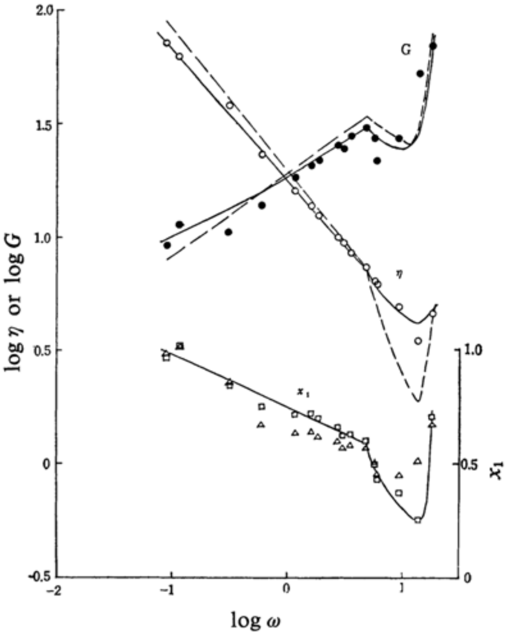

Fig. 4. $\log \eta$ (○), $\log G$ (●), and x_1 by Eq. 9 (□) and Eq. 11 (△) of 5% rice starch solution.

TABLE II. PARAMETERS OF EQS. 9 AND 11 (in c. g. s. units)

Starch	Concn. %	Eq.	F	G_0	τ_1	τ_2
Potato	3	9	93.1	50.9	≫1	0.0016
		11	99.5	44.1	≫1	≪1
Potato	5	9	63.5	47.8	37.2	≪1
		11	69.7	37.7	≫1	≪1
Sweet potato	5	9	127.3	231	≫1	≪1
		11	93.4	394	≫1	≪1
Rice	5	9	21.3	4.15	190	0.0135
		11	26.6	0	≫1	≪1

$\log \omega = 0.7$. However, if one attaches importance to the minimum of $\log \eta$ and $\log G$ at about $\log \omega = 1.1$, one should assume a minimum for x_1, too. The rapid increase of x_1 (and consequently of η and G) at high ω values might correspond to the entanglement of rice starch molecules due to mechanical work, a phenomenon familiar to Japanese people in the process of rice-cake making.

Summary

Modified Rouse's equations were applied to solutions consisting of a mixture of highly aggregated and less aggregated polymer molecules. The fraction of higher aggregates, x_1, was calculated for 3 and 5% potato starch solutions, a 5% sweet potato starch solution, and a 5% rice starch solution. The value of x_1 decreased linearly with the increase of $\log \omega$, except for the rice starch. The x_1 value of the latter increased rapidly when the $\log \omega$ became very large.

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