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Dynamics of Stiff-Chain Polymers in Isotropic Solution. 2. Viscosity of Aqueous Solutions of Xanthan, a Rigid Double-Helical Polysaccharide

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ABSTRACT: Zero-shear viscosities η_0 of aqueous solutions of a rigid double-helical polysaccharide xanthan with 0.1 M NaCl were measured over a wide range of polymer concentration c from dilute through isotropic concentrated using eight fractionated samples ranging in the number N of Kuhn's statistical segments from 0.25 to 11.6. The strong polymer concentration and molecular weight M dependences of η_0 measured could not be described by simple power laws. In contrast with concentrated flexible polymer solutions, the slope of the plot of log η_0 vs log M at fixed c exceeded 3.4 at high M. The data of η_0 for all the samples were compared with the viscosity equation for rodlike polymers previously derived. The viscosity equation could describe the data for the two lowest molecular weight samples ($N \leq 0.4$) but not for the other samples ($N > 0.8$). This was taken to show an importance of finite stiffness in the solution viscosity. In spite of the remarkable electrostatic interaction on thermodynamic properties, the viscosity underwent no such effect.

1. Introduction

The dynamics of rodlike or rigid polymers in concentrated solution have currently been of considerable interest. They have been studied by electric,[1,2] flow,[3] and magnetic[4] birefringence, dynamic light scattering,[5-8] viscosity,[9-17] viscoelasticity,[17-20] fluorescence recovery after photobleaching,[21,22] and rheooptical measurements.[12,13,23] With the accumulation of the experimental data, quantitative comparison between the Doi–Edwards theory[24] for rodlike polymer solutions and experiment has been undertaken, and several theoretical improvements have been presented. For example, the rotational diffusion coefficient D_r obtained from electric and flow birefringence and dynamic light scattering exhibited a large discrepancy with the Doi–Edwards theory in magnitude, and some investigators[25-27] tried to explain this discrepancy. Recently Teraoka and Hayakawa[28] formulated D_r of the rodlike polymer in dilute and semidilute solutions from a mean-field Green function method and showed that their theory agreed almost quantitatively with Mori et al.'s experimental data[2] of D_r for relatively low molecular weight poly(γ-benzyl L-glutamate) in dilute through semidilute solutions. Unfortunately, the experimental data of D_r are restricted up to the semidilute regime and also in a relatively narrow molecular weight range.

On the other hand, viscosity measurements were made over wider polymer concentration and molecular weight ranges than the D_r measurements. For example, Enomoto et al.[14] measured the zero-shear viscosity η_0 for aqueous solutions of seven fractionated samples of schizophyllan (a triple-helical polysaccharide) differing widely in molecular weight over the concentration from dilute through concentrated regimes. Their viscosity data for lower molecular weight samples in semidilute and concentrated isotropic regimes were successfully fitted by Doi's viscosity equation,[29] while those for higher molecular weight samples exhibited a substantial deviation from it, indicating a remarkable effect of the chain flexibility on η_0. In the previous paper[30] (Part 1 of this series), Sato and Teramoto have derived a new viscosity equation of rodlike polymer solutions applicable over a wide range of concentration *from dilute through concentrated isotropic* and showed that it describes the data for lower molecular weight schizophyllan well. There are many viscosity data for other rodlike and semiflexible polymer systems;[9-12,15-17] most of them, however, are not so detailed or not for well-characterized samples and would not be appropriate for molecular theoretical analysis.

In this paper, we present viscosity data of aqueous solutions of xanthan with added salt. Here xanthan is an ionic polysaccharide which exists as a rigid double-stranded helix in aqueous salt solution,[31,32] and this double helix is represented by a wormlike chain model whose parameters have been determined previously from dilute-solution study;[33] its persistence length was estimated to be about 120 nm irrespective of the ionic strength of the medium, which is smaller than that of schizophyllan (ca. 200 nm)[34] but much larger than those of typical synthetic stiff-chain polymers (<60 nm).[35,36] Although fragmental viscosity data for aqueous xanthan have already been reported by several authors,[15-17,20] they are not as extensive as those for schizophyllan by Enomoto et al. to use for a quantitative test of the viscosity equation obtained previously.[30] In this study, we used eight well-characterized and narrow-distribution xanthan samples with the molecular weights of 1.18×10^5–5.4×10^6 and made viscosity measurements over dilute through concentrated isotropic regions.

2. Experimental Section

Materials. A commercial xanthan sample (Kelco's Keltrol) was sonicated from 5 min to 72 h to reduce its molecular weight.[31] After purification by centrifugation, each of the sonicated samples was fractionated into 5–10 parts by the fractional precipitation with 0.5 M aqueous sodium chloride (NaCl) as the solvent and acetone as the precipitant. Middle fractions with similar intrinsic viscosities were combined and refractionated into 3–4 parts. The refractionation was repeated two to four times to obtain eight final samples designated as R-1, R-2, ..., R-8. Two low molecular weight samples were finally fractionated by isotropic–liquid crystal phase separation (liquid crystal fractionation),[37] yielding samples R-1 and R-3. The eight samples were converted to the Na salt form by the conventional method[31] and used for viscometry; the degree of pyruvation for out Keltrol samples was about 0.4, from which the charge density (in units of elementary charge) was estimated to be about 3 nm^{-1}.[38]

From experience, the polydispersity index M_z/M_w (M_z, the z-average molecular weight; M_w, the weight-average molecular weight) of a xanthan sample obtained from the liquid crystal fractionation is known to be smaller than 1.1,[39] while that for xanthan samples obtained from the repeated fractional precipitation is known to be about 1.2.[31]

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Table I
Molecular Characterization of the Xanthan Samples Used

sample	$[\eta]/(\mathrm{cm}^3\,\mathrm{g}^{-1})^a$	$M_v/10^4$	L/nm	N	$c_i/(\mathrm{g\,cm}^{-3})^a$
R-1	68.5	11.8	60.8	0.25	0.092
R-2	131	18.5	95.3	0.40	0.073
R-3	352	37.8	195	0.81	0.053
R-4	577	59.0	304	1.27	0.046
R-5	1570	125	644	2.68	
R-6	2520	190	979	4.08	
R-7	5500	410	2110	8.81	
R-8	7100	540	2780	11.6	

[a] In 0.1 M NaCl at 25 °C.

To effect complete dissolution, aqueous xanthan solutions with 0.1 M NaCl were prepared in the following manner. A dried xanthan sample was mixed with 0.01 M aqueous NaCl and stirred vigorously at about 25 °C overnight. Then 0.19 M aqueous NaCl was added to the solution to make the NaCl molar concentration C_s (in the solvent) 0.1 M. For samples R-4, R-6, and R-8, solution viscosities were measured also at C_s = 0.006 M (R-4) or 0.005 M (R-6 and R-8). For these measurements, the samples were dissolved directly into 0.005 M (or 0.006 M) aqueous NaCl below 25 °C in order to avoid possible thermal denaturation of the xanthan double helix.[40]

Viscometry. Most of solution viscosities η above 1 dyn cm^{-2} s were measured by a suspended ball rheometer[41,42] with a 0.5-mm-radius steel ball coated with polystyrene. The test solution contained in a stoppered test tube with the inner diameter of 10 mm was thermostated at 25 °C by circulating water. The rheometer was calibrated by use of a silicone oil (η = 9.6 dyn cm^{-2} s) and 95 wt % aqueous glycerin (η = 3.66 dyn cm^{-2} s). The shear rate $\dot{\gamma}$ was estimated by the equation

$$\dot{\gamma} = 3v/2a$$

where v is the velocity of the test solution and a the radius of the ball. Actually this $\dot{\gamma}$ is the maximum shear rate at the equator of the ball. Viscosity measurements were made under the condition that $3 < \eta\dot{\gamma}/(\mathrm{dyn\,cm}^{-2}) < 20$. Viscosities for solutions with $\eta < 1$ dyn cm^{-2} s, as well as intrinsic viscosities $[\eta]$ of samples R-4 through R-8, were measured using low-shear four-bulb capillary viscometers with suitable flow times; $[\eta]$ of samples R-1 through R-3 were measured on a conventional Ubbelohde-type capillary viscometer. All the viscosity measurements were made at 25 °C.

3. Results

Molecular Characterization. Intrinsic viscosities $[\eta]$ in 0.1 M aqueous NaCl at 25 °C and viscosity-average molecular weights M_v of samples R-1 through R-8 are listed in Table I. The values of M_v were determined from $[\eta]$ by using the $[\eta]$–M_w relation established.[32,33] Sato et al.[33] determined the wormlike cylinder parameters of the xanthan double helix in 0.1 M aqueous NaCl from data for the radius of gyration, limiting sedimentation coefficient, and $[\eta]$: the molecular weight per unit contour length M_L = 1940 nm^{-1}, the persistence length q = 120 nm, and the helix diameter d = 2.2 nm. These values of M_L and d are consistent with the molecular model for the xanthan double helix proposed by Okuyama et al.[43] By use of these parameters, the contour length L ($=M_v/M_L$) and the number of the Kuhn statistical segments N ($=L/2q$) for each sample were also calculated (see the fourth and fifth columns of Table I). From the values of N, it can be seen that lower molecular weight samples used in this study may be rodlike ($N < 1$), while higher molecular weight samples can be regarded as semiflexible chains ($N \gg 1$).

Steady-State Viscosity. Figure 1 shows the $\dot{\gamma}$ dependence of η for solutions of the highest molecular weight sample R-8 in 0.1 M aqueous NaCl with different polymer mass concentrations c. The values of the zero-shear viscosity η_0 were determined by extrapolation to $\dot{\gamma} = 0$ as shown by solid curves in the figure. The shear rate dependence of η was less remarkable for lower molecular weight samples. The η_0 values obtained for all the samples are summarized in Table II. For samples R-1 through R-5, the values of η_0 were obtained up to the vicinity of the phase boundary mass concentration c_i between isotropic and biphasic regions[39] (cf. the sixth column of Table I). On the other hand, viscosity measurements for the higher molecular weight samples were limited to significantly lower concentration than c_i, because η_0 in the vicinity of c_i for such samples was too high to be measured by our suspended ball rheometer.

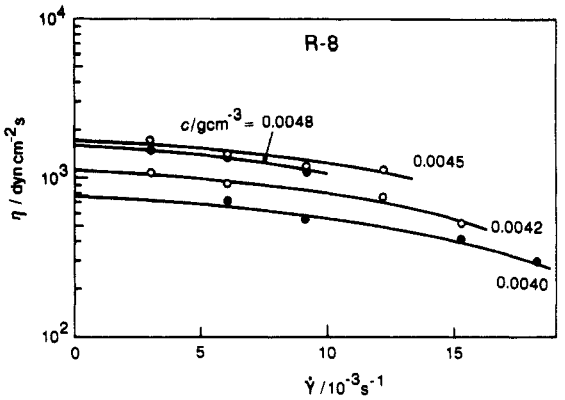

Figure 1. Shear rate dependence of η for aqueous solutions of the highest molecular weight samples R-8 with C_s = 0.1 M and different polymer concentrations.

Figure 2 illustrates double-logarithmic plots of η_0 vs c for the eight samples at C_s = 0.1 M and at 25 °C. For each sample, a sharp increase in η_0 with c is observed at high c, which cannot be described by a simple power low. At $c \sim c_i$, the slopes of the curves fitting data points for samples R-1 through R-3 are about 3, while those for samples R-4 and R-5 are 5.6 and 7.6, respectively. The curves for samples R-6 through R-8 have the slope of 6–7 around the highest concentrations examined. The Doi–Edwards prediction,[24] i.e., the c^3 dependence of η_0, holds only in a narrow concentration range, and this range does not necessarily correspond to the semidilute regime.

The molecular weight dependence of η_0 at fixed polymer concentrations and C_s = 0.1 M is shown in Figure 3. For each concentration, η_0 increases monotonously with increasing molecular weight, following a curve convex downward. Thus we see no simple power law also with respect to the molecular weight dependence. This is in contrast with the case of concentrated flexible polymer solutions where it is known that η_0 is proportional to $M^{3.4}$ at sufficiently high molecular weight M and c.[44] At high M_v, the molecular weight dependence of η_0 for aqueous xanthan is much stronger than those for flexible polymer solutions (cf. the segment with the slope 3.4 in Figure 3). A similar strong molecular weight dependence of η_0 has been reported for other stiff-chain polymer solutions.[10,14]

Figure 4 shows the double-logarithmic plot of η_c against $c[\eta]$ for four samples, where η_c is a reduced viscosity defined by

$$\eta_c = (\eta_0/\eta_s - 1)/(c[\eta]) \qquad (1)$$

with the solvent viscosity η_s. Looking at the data points critically, we find that η_c depends not only on $c[\eta]$ but also slightly on the molecular weight at $c[\eta] > 1$. Enomoto et al.[14] already noted a similar trend in the viscosity data for aqueous schizophyllan. This result does not agree with Milas et al.'s,[16] who measured η_0 for aqueous xanthan on the same solvent condition; their viscosity data for four

Table II
Values of the Zero-Shear Viscosity η_0 for Aqueous Solutions of Xanthan with 0.1 M NaCl at 25 °C

$c/(\mathrm{g\ cm^{-3}})$	$\eta_0/(\mathrm{dyn\ cm^{-2}\ s})$	$c/(\mathrm{g\ cm^{-3}})$	$\eta_0/(\mathrm{dyn\ cm^{-2}\ s})$
	Sample R-1		
0.090	0.548	0.020	0.0309
0.080	0.400	0.015	0.0233
0.070	0.287	0.010	0.0173
0.060	0.195	0.0060	0.0134
0.050	0.131	0.0040	0.0118
0.040	0.0845	0.0020	0.0103
0.030	0.0521		
	Sample R-2		
0.072	1.49	0.030	0.152
0.070	1.28	0.025	0.106
0.068	1.19	0.020	0.0716
0.065	1.05	0.015	0.0465
0.060	0.795	0.010	0.0287
0.055	0.652	0.0080	0.0233
0.050	0.494	0.0050	0.0167
0.045	0.384	0.0030	0.0132
0.040	0.287	0.0020	0.0116
0.035	0.212	0.0015	0.0109
	Sample R-3		
0.052	11.7	0.010	0.110
0.050	10.5	0.0080	0.0750
0.045	7.18	0.0050	0.0386
0.040	4.74	0.0040	0.0300
0.035	3.13	0.0030	0.0229
0.030	1.97	0.0020	0.0172
0.025	1.04	0.0015	0.0148
0.020	0.579	0.0010	0.0126
0.015	0.251	0.00050	0.0107
	Sample R-4		
0.045	104	0.018	1.82
0.040	49.4	0.015	0.983
0.038	44.4	0.010	0.337
0.035	25.0	0.0050	0.0800
0.032	15.5	0.00080	0.0139
0.030	11.4	0.00060	0.0126
0.025	5.97	0.00040	0.0113
0.020	2.57		
	Sample R-5		
0.032	17300	0.0080	4.65
0.030	11200	0.0060	1.74
0.025	2330	0.0050	0.890
0.022	1280	0.0030	0.228
0.020	521	0.0020	0.0972
0.018	250	0.0010	0.0346
0.015	82.4	0.00050	0.0187
0.012	27.5	0.00030	0.0142
0.010	12.0	0.00020	0.0122
0.0090	7.74	0.00010	0.0105
	Sample R-6		
0.018	8330	0.0050	4.80
0.016	3330	0.0040	2.00
0.014	1050	0.0020	0.274
0.012	436	0.0010	0.0670
0.010	120	0.00050	0.0275
0.0090	65.0	0.00020	0.0145
0.0080	40.0	0.00010	0.0116
0.0060	11.0	0.000070	0.0107
	Sample R-7		
0.0062	2800	0.0040	63.6
0.0060	1270	0.0010	0.366
0.0055	730	0.00080	0.231
0.0052	342	0.00060	0.126
0.0050	263	0.00040	0.0574
0.0048	196	0.00020	0.0250
0.0045	144	0.00015	0.0197
0.0042	95.9	0.00010	0.0153
	Sample R-8		
0.0048	1600	0.0012	2.04
0.0045	1700	0.0010	0.918
0.0042	1100	0.00080	0.456
0.0040	720	0.00060	0.285
0.0035	260	0.00050	0.174
0.0032	94.0	0.00040	0.103
0.0030	72.0	0.00020	0.0350
0.0028	62.0	0.00010	0.0184
0.0015	5.41	0.000050	0.0127

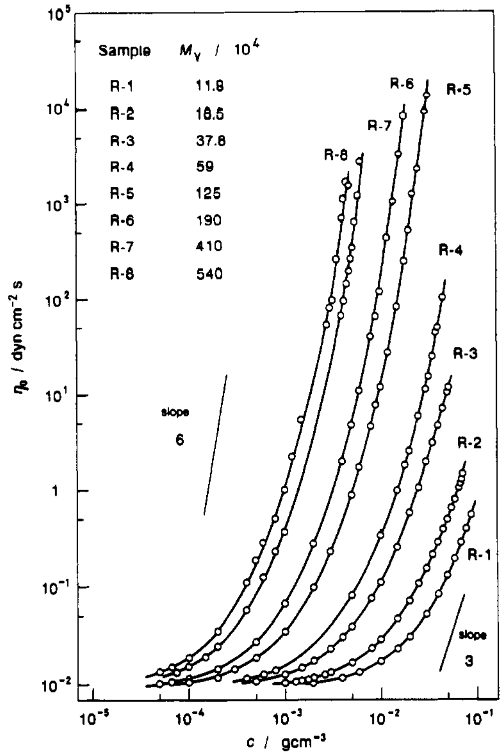

Figure 2. Double-logarithmic plot of η_0 vs c for aqueous solutions of xanthan with C_s = 0.1 M at 25 °C.

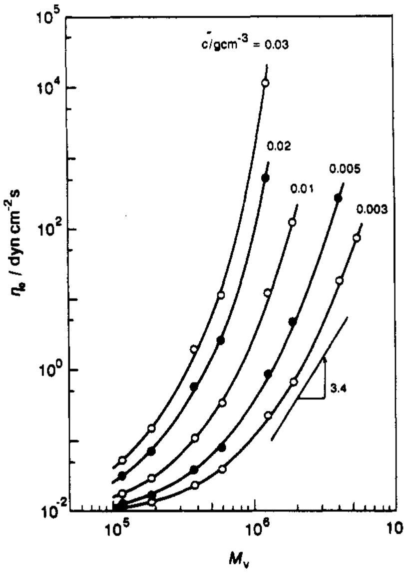

Figure 3. Molecular weight dependence of η_0 for aqueous xanthan with C_s = 0.1 M at the indicated polymer concentrations.

different molecular weight samples followed a single composite curve represented by the broken curve in Figure 4, which cannot fit our data at large $c[\eta]$. It should be noted that their viscosity measurements were limited to $c[\eta] < 20$.

Figure 5 compares the η_0 data at C_s = 0.1 M with those at C_s = 0.005 M (R-6 and R-8) or with those at C_s = 0.006 M (R-4). In spite of a large difference in the electrostatic screening length between C_s = 0.005 M (or 0.006 M) and 0.1 M, η_0 does not reflect such a difference. This result confirms the previous finding for sample R-4,[41] where η_0 showed almost no change over a wider C_s range from 0.006 to 1.0 M, and forms a remarkable contrast with η_0 of more flexible polyelectrolyte solutions.[45] In connection with these findings, we refer to Sho et al.'s[38] and Liu et al.'s[40] observations that $[\eta]$ and the radius of gyration of xan-

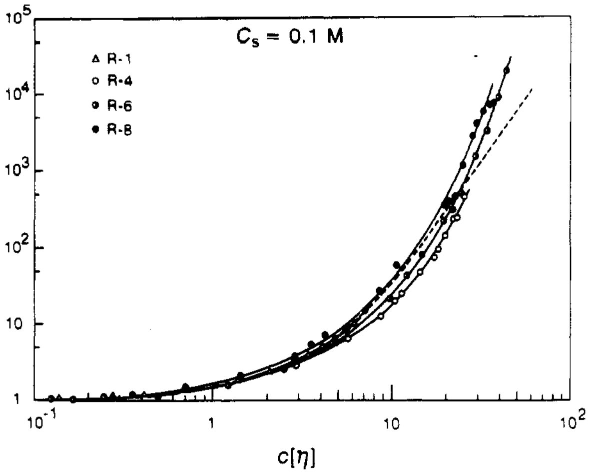

Figure 4. Double-logarithmic plot of η_c against c[η] for samples R-1, R-4, R-6, and R-8 in 0.1 M NaCl at 25 °C. η_c is defined by eq 1. The broken curve contains the values calculated from Milas et al.'s empirical viscosity equation[16] for aqueous xanthan on the same solvent condition.

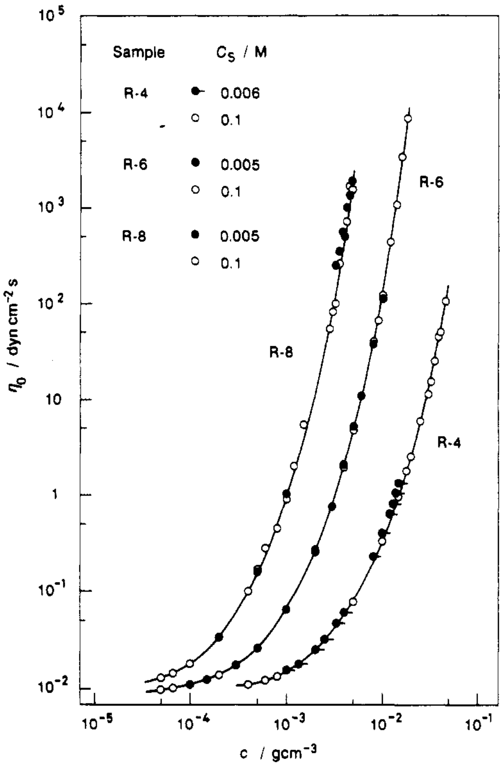

Figure 5. Comparison of the η_0 data for three samples at C_s = 0.1 M with those at C_s = 0.005 M (or 0.006 M).

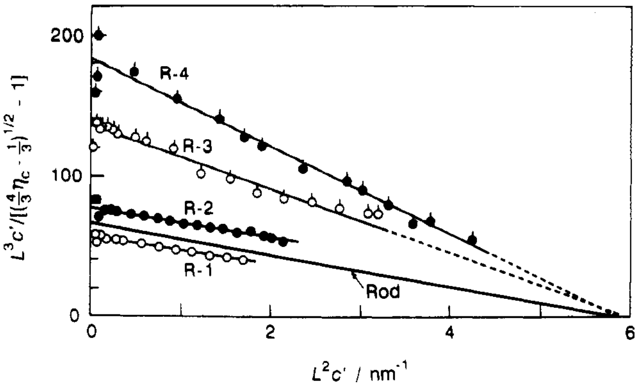

Figure 6. Plot of $L^3c'/\{[(4/3)\eta_c - 1/3]^{1/2} - 1\}$ vs L^2c' for low molecular weight xanthan samples R-1 through R-4 at C_s = 0.1 M. The heavy straight line labeled "Rod" contains the theoretical values for the rodlike polymer solution calculated from eq 5 with β = 4400 and α = 13.

than in dilute solution are quite insensitive to C_s at $C_s \geq$ 0.005 M. This insensitiveness means that the chain conformation of xanthan is hardly affected by the intramolecular electrostatic interaction owing to the intrinsic stiffness of the xanthan double helix. This is also in contrast with the case of flexible polyelectrolytes. Therefore, the remarkable difference in the C_s dependence of η_0 between xanthan and more flexible polyelectrolytes may be ascribed mainly to the difference in the C_s dependence of the chain conformation. We can say that the *intermolecular* electrostatic interaction does not contribute to the solution viscosity of the stiff-chain polymer in the C_s range examined.

4. Discussion

In the previous paper[30] (Part 1 of this series), Sato and Teramoto derived a viscosity equation for isotropic rodlike polymer solutions using a relation between η_0 and the rotational diffusion coefficient D_r[24] together with D_r formulated by a mean-field Green function method.[28] It is given as a function of the number density c' of the rods by

$$\eta_c = \frac{1}{4} + \frac{3}{4}\left(1 + \frac{B_0c'}{1 - A_0c'}\right)^2 \tag{2}$$

where A_0 and B_0 are

$$B_0 = \beta^{-1/2}L^3 \tag{3}$$

$$A_0 = \alpha^{-1}L^2d \tag{4}$$

with two numerical constants α and β (see eqs 14–16 in ref 30). We test this viscosity equation with the experimental data of η_0 for aqueous xanthan with C_s = 0.1 M. For the two lowest molecular weight samples R-1 and R-2, this test has already been made in Part 1, and the viscosity equation (2) has been demonstrated to describe well the polymer concentration and molecular weight dependences of η_0 for the two xanthan samples, as well as for low molecular weight samples of schizophyllan; the two constants α and β have been determined to be about 13 and 4400, respectively. Therefore, in this section, the comparison is extended to the other higher molecular weight samples of xanthan in the following manner.

Equations 2–4 are combined and rewritten as

$$\frac{L^3c'}{[(4/3)\eta_c - 1/3]^{1/2} - 1} = \beta^{1/2}[1 - (d/\alpha)L^2c'] \tag{5}$$

The left-hand side of this equation can be calculated by using experimental values of η_0 and [η]. If the viscosity equation (5) is applicable to all the xanthan samples, the plot of the left-hand side quantity vs L^2c' constructed with the data of all the samples should obey the single straight line given by eq 5. Figure 6 shows this plot for samples R-1 through R-4; different symbols represent data points for different samples, while the heavy straight line labeled "Rod" is drawn using eq 5 with β = 4400 and α = 13. The data points for samples R-1 and R-2 are close to this straight line, demonstrating the applicability of the viscosity equation to very rigid polymer solutions ($N \leq$ 0.4), as has been already shown in Part 1 in a different way. The data points for samples R-3 (N = 0.81) and R-4 (N = 1.27), however, follow different straight lines. These lines give β (from the ordinate intercept) larger than 4400, but α (from the abscissa intercept) almost equal to 13; β

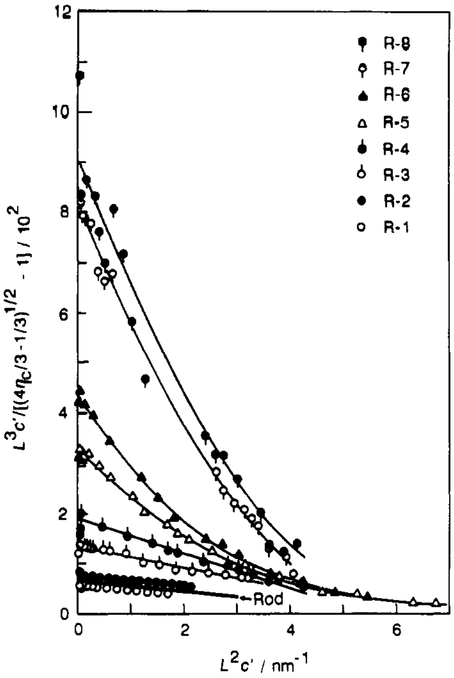

Figure 7. Same plot as in Figure 6 for all the samples studied at C_s = 0.1 M.

$= 1.8 \times 10^4$ for R-3 and $\beta = 3.4 \times 10^4$ for R-4. Therefore, we can say that β is very sensitive to the chain flexibility. This β is the proportionality constant appearing in the Doi–Edwards equation[24] for the rotational diffusion coefficient of the rigid rod. Some authors[8,25] have already pointed out that the chain flexibility affects β strongly and causes a large discrepancy in magnitude between the Doi–Edwards equation and experimental results for D_r of stiff polymers with a finite stiffness in the semidilute solution regime.

Figure 7 shows the plot of $L^3c'/\{[(4/3)\eta_c - 1/3]^{1/2} - 1\}$ against L^2c' constructed by the experimental data of η_0 for all the samples obtained in this study. The points for the higher molecular weight samples R-5 through R-8 with $N \geq 2.68$ do not follow straight lines any more but curves convex downward whose intercepts increase with increasing N. Thus eq 5 or the viscosity equation obtained in Part 1 cannot describe the concentration dependence of η_0 for $N \geq 2.68$.

The factor in the square bracket on the right-hand side of eq 5 is associated with the concentration dependence of the longitudinal diffusion coefficient of rigid rods (the jamming effect), which has been formulated on the assumption that the hindrance of the polymer longitudinal diffusion by end crashes with other polymers is released only by the longitudinal diffusion of the hindering polymers.[30,46] Therefore, the nonlinearity of the plot in Figure 7 for higher molecular weight samples implies that the hindrance of the longitudinal motion of semiflexible chains in concentrated solution may be released by a mechanism other than that mentioned above. It is possible that the end-crash hindrance of the longitudinal motion of a semiflexible chain (test chain) is released also by some suitable conformation changes of the test chain and/or hindering chains, which has not been considered in eq 5.

In conclusion, the polymer chain flexibility becomes an important factor in η_0 of aqueous xanthan, when N exceeds about 0.8. A similar conclusion was obtained by Enomoto et al.[14] from their data of η_0 for aqueous schizophyllan. An extension of the viscosity equation (2) with eqs 3 and 4 to semiflexible polymers wil be presented in the following paper.

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