Viscosity of Aqueous Solutions of a Triple-Helical Polysaccharide Schizophyllan

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ABSTRACT: Zero-shear viscosities η_0 of aqueous solutions of a rodlike polysaccharide schizophyllan were measured over a wide range of concentration c from high dilution to the critical concentration c^*, above which an ordered phase appeared. Three samples with molecular weights M covering both the rigid rod regime and semirigid rod regime were used. The reduced viscosity $\eta_0/[\eta]_0M\eta_s$ of the rigid rod samples at high concentrations was described as a function of a single variable cM, closely following the equation proposed by Doi. Here, $[\eta]_0$ is the zero-shear intrinsic viscosity and η_s the solvent viscosity. The variable c/c^* could not be utilized to superpose the viscosity data, because c^*M depends on M for the present polymer + solvent system. The reduced viscosity deviated upward from the theoretical curve at lower concentrations corresponding to $\eta_0 < 25\eta_s$, where the theory was no longer valid. The value of $\eta_0/[\eta]_0M\eta_s$ of the sample in the semirigid rod regime was much lower than that of the rigid rod at a given cM. Comparison among polymers having different main-chain structures suggests that solution viscosities are affected by strong intermolecular interactions in addition to the hard-core interaction assumed in the Doi theory.

When a solution of a rodlike polymer is very dilute, polymer molecules in the solution can move almost independently. However, such an independent movement of the polymer molecules may not be allowed above some critical concentration, where the molecules are entangled and cannot pass through each other; the molecules are randomly oriented and the solution is isotropic. This situation continues up to another critical concentration c^*, above which the random orientation is no longer allowed, eventually resulting in the appearance of an ordered phase. The concentration range between these two critical concentrations is referred to as the semidilute concentration regime, which is defined in terms of number polymer density n (number of polymer molecules in unit volume) by[1]

$$1/L^3 \ll n \ll 1/dL^2 \tag{1}$$

where L and d stand for the length and diameter of the molecule, respectively. The upper boundary of the regime may be close to the critical concentration c_A, above which the liquid crystal phase begins to appear.

Doi[1] formulated relaxation processes in this concentration regime by means of the tube model and derived an expression for the zero-shear viscosity η_0 of isotropic solutions of rodlike polymers. It reads

$$\eta_0 \propto kT\frac{\eta_s n^3 L^9}{\ln (L/d)}(\alpha - ndL^2)^{-2} \tag{2}$$

where k is the Boltzmann constant, T the absolute temperature, η_s the solvent viscosity, and α a numerical constant. It has been shown that eq 2 describes characteristic features of the viscosity of solutions of rodlike polymers, e.g., the sharp increase of viscosity with concentration in the concentration range just below c_A.[1-4]

An extracellular β-1,3-D-glucan schizophyllan produced by a fungus *Schizophyllum commune* is known to exist in aqueous solution as a trimer, in which three glucan chains form a three-stranded helix, taking a rodlike shape.[5,6] Thus schizophyllan seems to be an interesting model polymer, with which we can study various aspects of solutions of rodlike polymers, particularly at high concentrations. Indeed we recently found that aqueous solutions of schizophyllan form a cholesteric mesophase at high concentrations.[7-9]

Although the triple helix of schizophyllan is remarkably rigid at low molecular weight, it exhibits detectable flexibility at high molecular weight.[5,6] Thus schizophyllan provides us with the possibility of investigating the effect of increasing flexibility as well as rodlike nature on concentrated solution properties by the use of samples with appropriate molecular weights. Another advantage of this polysaccharide is its good solubility in water. This is in sharp contrast with many other rodlike polymers,[4,10] for which it is not necessarily easy to find solvents suitable for solution studies.

In this study, we investigated the viscous properties of concentrated solutions of schizophyllan in water with two purposes: to test the Doi theory with experimental data for the well-established schizophyllan helix and to examine the effect of reduced rigidity on solution viscosity. For the former purpose two samples in the rigid rod regime were used. One sample of higher molecular weight in the semirigid regime was added for the latter study.

Experimental Section

Three fractionated schizophyllan samples SPG-4, E-51, and F-52 were used. They were obtained as described elsewhere[5] and their viscosity-average molecular weights M_v were determined from the intrinsic viscosity–molecular weight relation established by Yanaki et al.,[6] yielding 128 000, 460 000, and 960 000, respectively. It can be considered from previous experience[9] that the fractionated samples SPG-4 and E-51 may be relatively narrow in molecular weight distribution, with a polydispersity index M_z/M_w of about 1.2. The molecular weight distribution of F-52 may be somewhat broader than this. When examined by intrinsic viscosity according to Yanaki et al.,[6] the former two samples may be rigid and straight under the experimental conditions employed, but the highest molecular weight sample exhibits significant flexibility.

Solutions were made by mixing the required amounts of a given sample and water in a stoppered flask. The weight fraction w of the polymer was determined gravimetrically. The mass concentration c (g cm^{-3}) was calculated from w with the solution density data reported elsewhere.[8]

Viscosity measurements were made at 30 °C on a concentric viscometer of the Zimm–Crothers type, which had been designed so that the solution could be diluted successively in the viscometer.[11] The apparent viscosity of the test solutions was calculated from the ratio of the torque applied to the rotor to the speed of angular rotation of the rotor. Here, the relation between the torque and the electric current, which caused an eddy current in the drag cup fixed to the rotor, was obtained from a preliminary experiment on glycerin and glycerin solutions in water for which viscosities had been determined with a capillary viscometer. In practice, after each measurement the polymer solution was diluted with water in the viscometer for the next measurement. In some

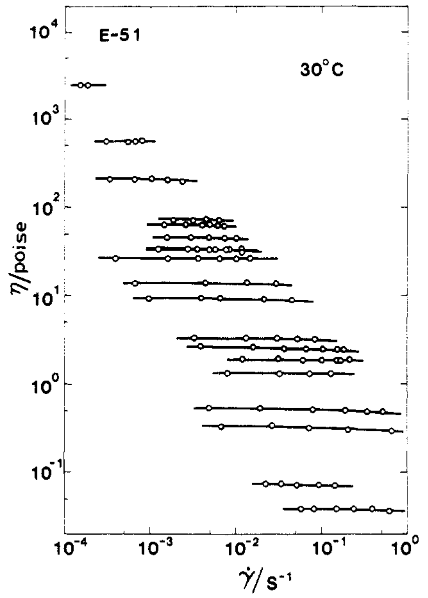

Figure 1. Shear rate dependence of viscosity for sample E-51 in water at 30 °C. The polymer concentrations c are 0.0569, 0.0487, 0.0426, 0.0379, 0.0364, 0.0341, 0.0319, 0.0300, 0.0297, 0.0257, 0.0223, 0.0197, 0.0171, 0.0151, 0.0152, 0.0107, 0.00884, 0.00454, and 0.00305 g cm^{-3}, from top to bottom.

cases, the solutions were heated at about 45 °C and/or filtered through a Millipore filter of pore size 0.45 μm to ensure complete dissolution. Solutions of SPG-4 showed no viscosity decrease on these treatments. On the other hand, these treatments brought about small viscosity decrease for solutions of E-51 and F-52. In no case, however, was the viscosity decrease greater than 20%. Thus we concluded that there would be no aggregation, which might seriously affect viscosity.

Aqueous solutions of either sample became birefringent above some critical concentration, indicating the appearance of the cholesteric phase at high concentrations. Most viscosity measurements were performed at concentrations below their critical concentrations, i.e., for isotropic solutions.

Results

Figure 1 shows viscosity data for the medium molecular weight sample E-51, where the solution viscosity η is plotted against shear rate $\dot{\gamma}$ on a double-logarithmic scale. It can be seen that η depends only slightly on $\dot{\gamma}$ within the range of relatively low shear rate studied; high $\dot{\gamma}$ could not be achieved on our viscometer. On the other hand, η varies remarkably with polymer mass concentration c; η increases by a factor greater than 10^4 from the solvent water to the solution with $c = 0.0487$. Figure 2 shows viscosity data for the lowest molecular weight sample SPG-4. Here again η is almost independent of $\dot{\gamma}$. The filled circles refer to a birefringent solution with $c = 0.211$. A slightly more dilute solution with $c = 0.199$ is isotropic but more viscous than this birefringent solution. Thus the boundary between the isotropic and biphasic regions is located at $c = 0.209$. The solution was found to be completely isotropic below this critical concentration. It can be seen that η increases with increasing c in the isotropic region but tends to decrease in the biphasic region. This is the well-known viscosity behavior of rodlike polymers forming a mesophase.[2-4]

Similar viscosity measurements were also made for isotropic solutions of F-52, which exhibited appreciable deviation from the rigid rod nature in dilute solution properties. The data are shown in Figure 3; measurements were limited to c up to 0.0306 g/cm^3 because of high viscosity. The features of this family of curves are essentially the same as those for E-51.

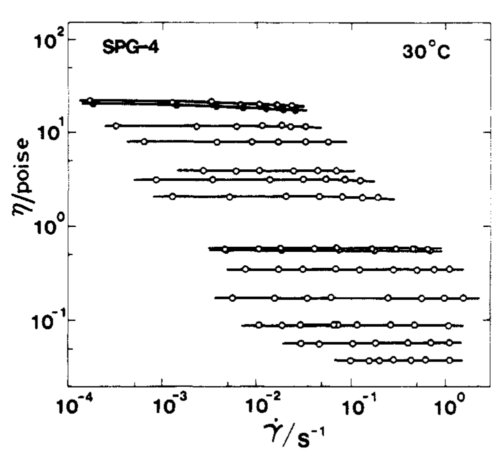

Figure 2. Shear rate dependence of viscosity for sample SPG-4 in water at 30 °C. The polymer concentrations c are 0.199, 0.211, 0.185, 0.175, 0.154, 0.148, 0.130, 0.100, 0.0946, 0.0803, 0.0616, 0.0456, 0.0362, and 0.0270 g cm^{-3}, from top to bottom. The filled circles refer to a bisphasic solution.

Table I
Zero-Shear Viscosities of Aqueous Solutions of Schizophyllan at 30 °C

c/g cm^{-3}	η_0/P	c/g cm^{-3}	η_0/P
	Sample SPG-4		
0.211	21	0.0803	0.344
0.199	22	0.0616	0.171
0.185	11.9	0.0456	0.089
0.175	8.0	0.0362	0.057
0.154[a]	3.90	0.0270	0.038
0.148	3.11	9.59×10^{-3}	0.014
0.130	2.05	6.39×10^{-3}	0.012
0.100	0.580	4.79×10^{-3}	0.011
0.0946	0.563		
	Sample E-51		
0.0569	2450[d]	0.0197[c]	3.22
0.0487	560	0.0171	2.68
0.0426	210	0.0152	1.31
0.0379	74.0	0.0151	1.90
0.0364	63.9	0.0107	0.535
0.0341	46.0	8.84×10^{-3}	0.339
0.0319	36.0	4.54×10^{-3}	0.076
0.0300	33.8	3.05×10^{-3}	0.039
0.0297[b]	26.2	1.21×10^{-3}	0.015
0.0257	13.7	9.06×10^{-4}	0.013
0.0223	9.40	7.25×10^{-4}	0.012
	Sample F-52		
0.0306	1345[d]	6.97×10^{-3}	1.85
0.0256	854	5.26×10^{-3}	0.84
0.0201	190	3.19×10^{-3}	0.22
0.0175	86.0	2.14×10^{-3}	0.11
0.0138	32.2	1.65×10^{-3}	0.075
0.0103	7.80	3.44×10^{-4}	0.0128
8.92×10^{-3}[a]	3.30	2.58×10^{-4}	0.0114
8.86×10^{-3}	3.93	1.72×10^{-4}	0.0101

[a] Filtered through a Millipore filter of 0.45-μm pore size. [b] Warmed at 44–46 °C for 2 days. [c] Warmed at 44–46 °C for 2 days and filtered through a Millipore filter of 0.45-μm pore size. [d] Values to be taken with reservations.

As seen in Figures 1–3, the shear rate dependence of η is almost negligible for all solutions studied, and the values at the lowest shear rate were regarded as the zero-shear viscosity η_0. All of the data for η_0 are summarized in Table I. Figure 4 illustrates how η_0 depends on polymer mass concentration c (in g cm^{-3}). It is appropriate to summarize the features of these data before attempting a molecular theoretical interpretation of them.

(1) Within the low shear rate range studied, essentially Newtonian behavior is observed for all the solutions studied.

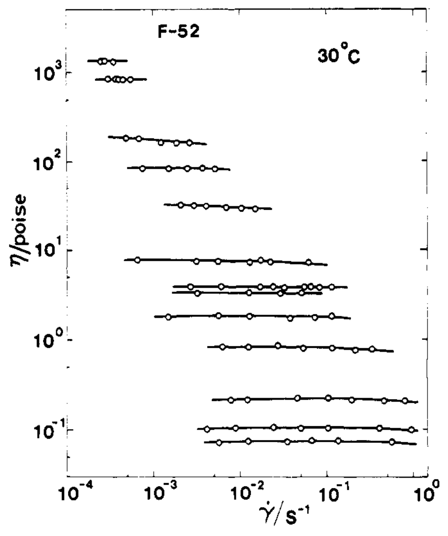

Figure 3. Shear rate dependence of viscosity for sample F-52 in water at 30 °C. The polymer concentrations c are 0.0306, 0.0256, 0.0201, 0.0175, 0.0138, 0.0103, 0.00886, 0.00892, 0.00697, 0.00526, 0.00319, 0.00214, and 0.00165 g cm^{-3}, from top to bottom.

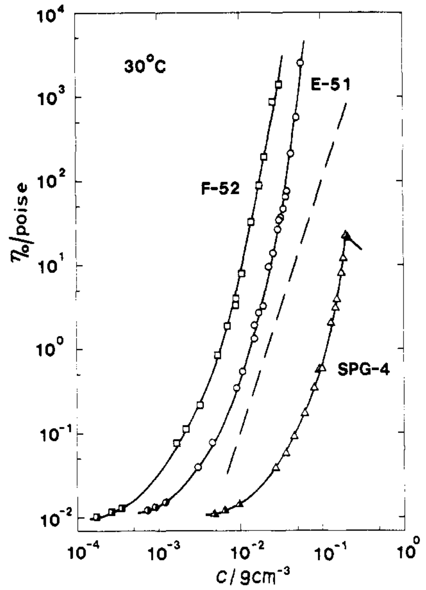

Figure 4. Concentration dependence of zero-shear viscosity η_0 for three schizophyllan samples in water at 30 °C. Squares, F-52 (M_v = 960 000); circles, E-51 (M_v = 460 000); triangles, SPG-4 (M_v = 128 000). The filled triangle refers to a biphasic solution. The half-filled marks indicate the data obtained by a capillary viscometer. The dashed line indicates a slope of 3.

(2) A finite maximum η_0 value is obtained at the highest concentration in the isotropic region for the lowest molecular weight sample SPG-4. No such a maximum is seen for the other samples.

(3) The dashed line in Figure 4 is drawn to indicate a slope of 3. It can be seen that there is only a small concentration range where η_0 increases linearly with c^3 for any of the samples. At higher concentrations, η_0 increases with c more rapidly than c^3.

(4) When compared at a fixed concentration, η_0 increases with M_v more rapidly than M_v^4, although the comparison can be made only for a limited concentration range and for the two higher molecular weight samples.

It appears that all these features are almost common to viscous properties of isotropic solutions of rodlike polymers so far studied.[2-4] For η_0 larger than 10^3 P, the observed shear rate was too small to be determined with reasonable accuracy on our viscometer, and hence the corresponding data will be omitted in the discussion to follow.

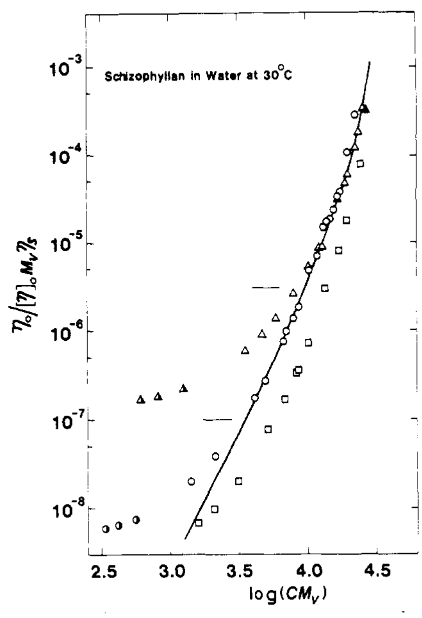

Figure 5. Relation between the reduced viscosity $\eta_0/[\eta]_0M_v\eta_s$ and the product cM_v for three schizophyllan samples in water at 30 °C. The marks are the same as in Figure 4. The heavy line is the theoretical curve calculated by eq 3 with $K = 2.12 \times 10^{-18}$ cm^6 g^{-6} mol^4 and $\alpha = 12.7$. The upper horizontal segment represents the ordinate value corresponding to $\eta_0 = 25\eta_s$ for sample SPG-4 and the lower one for sample E-51.

Discussion

Analysis of Experimental Data. In terms of mass concentration c and molecular weight M of the polymer, eq 2 can be recast in the form

$$\frac{\eta_0}{[\eta]_0M\eta_s} = K\frac{(cM)^3}{(1-\beta cM)^2} \tag{3}$$

with

$$\beta = N_Ad/\alpha M_L^2 \tag{4}$$

where $[\eta]_0$ is the intrinsic viscosity at zero shear rate, M_L is the molecular weight per unit length, and N_A is the Avogadro number. K and α are numerical constants independent of M and c for a homologous series of polymer samples. Equation 3 predicts that η_0 can be expressed as a single function of the product cM.

Figure 5 shows the η_0 data plotted according to eq 3; M_v is used for M. The solid curve in the figure represents the theoretical values calculated according to eq 3 with $K = 2.12 \times 10^{-18}$ cm^6 g^{-6} mol^4 and $\alpha = 12.7$; note that the theory does not give K and α. It can be seen that the data points for SPG-4 and E-51 closely follow the theoretical curve at concentrations corresponding to $\eta_0 > 25\eta_s$. Since both SPG-4 and E-51 are in the rigid rod regime, this result substantiates the validity of eq 3. Chu et al.[12] have found that eq 3 can well describe their viscosity data for several polymer + solvent systems.

Assuming that c_A is proportional to $1/M$ according to Flory's theory[13] of rodlike polymers, Doi[1] derived a viscosity equation expressing η_0 as a single function of c/c^*, with $c^* \sim c_A$. Figure 6 shows a plot of c_A against M_v^{-1} for aqueous schizophyllan at 25 °C; the filled circle represents the present data and open circles represent those reported by Itou et al.[9] It can be seen that the plot is linear but has a finite ordinate intercept. As concluded by Itou et al.,[9] this implies that the Flory theory does not hold for this system. Thus it follows that the superposition ob-

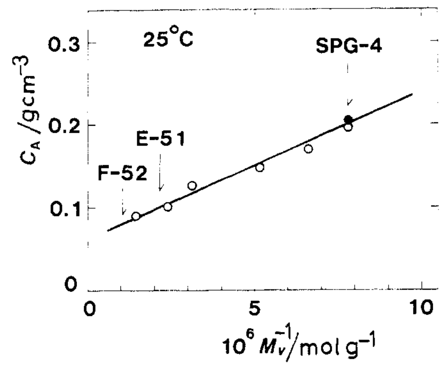

Figure 6. Relation between the critical concentration c_A and molecular weight M_v for schizophyllan in water at 25 °C. Closed circle, present data; open circles, Itou et al.[9] The vertical arrows give estimates of c_A for the samples used in the viscosity measurements.

Table II
Comparison of Critical Concentrations (g cm^{-3})

	lower boundary		upper boundary	
sample	eq 1 ($1/L^3$)	c' (η_0 = $25\eta_s$)	eq 1 ($1/dL^2$)	c^* ($c^* \simeq c_A$)
SPG-4	9.95×10^{-4}	0.066	2.30×10^{-2}	0.209[a]
E-51	7.72×10^{-5}	7.6×10^{-3}	6.36×10^{-3}	0.098[b]
F-52	(1.75×10^{-5})	3.0×10^{-3}	(3.05×10^{-3})	0.080[b]

[a] Determined from viscosity measurements. [b] Estimated from Figure 6.

tained by using c/c^* may not be applied to the present data. Indeed, we attempted to analyze the present data on the basis of this idea to find that the data points did not fall on a single curve.

The upward deviation of the data points for $\eta_0 < 25\eta_s$ corresponds to the crossover region from the semidilute to the dilute regime, where the Doi theory ceases to be valid. The validity of eq 3 is limited to the concentration range specified by eq 1. In physical terms, this may be the concentration range in which η_0 is much larger than η_s and the polymer molecules are entangled together but the liquid crystal phase is still unstable. Therefore, we may conclude that the lower boundary of the range is located at the concentration c' at which $\eta_0 = 25\eta_s$.

Table II compares the experimental critical concentrations with those predicted by eq 1; the latter were calculated with M_L = 2140 nm^{-1} and d = 2.6 nm.[6] It is clear that the prediction by eq 1 is too low compared with the observed values. Similar discrepancies are also found in other rodlike polymers.[12] This is taken to mean that quantitative significance of eq 1 should not be emphasized because of the lack of the proportionality factors to $1/L^3$ and $1/dL^2$.

Effect of Chain Flexibility. Figure 5 shows that the data points for sample F-52 deviate significantly downward from the theoretical curve. This can be seen more clearly by plotting the ratio of η_0 to the viscosity η_D calculated according to eq 3. In Figure 7 η_0/η_D is plotted against cM_v on a double-logarithmic scale. While the η_0/η_D values for SPG-4 and E-51 scatter around unity as expected, those for F-52 are much smaller than unity and almost independent of polymer concentration. This is attributed to the fact that in terms of dilute solution properties, the former samples are in the rigid rod regime, but the last one shows significant deviation from the rigid rod behavior. Indeed, an analysis according to Yanaki et al.[6] indicates that the $[\eta]_0$ values for SPG-4 and E-51 are about equal to those expected for straight rigid rods, but that for F-52 is 25% smaller than that for the straight rod of the same contour length. It should be noted that this relatively small effect of flexibility on $[\eta]_0$ is greatly amplified in η_0.

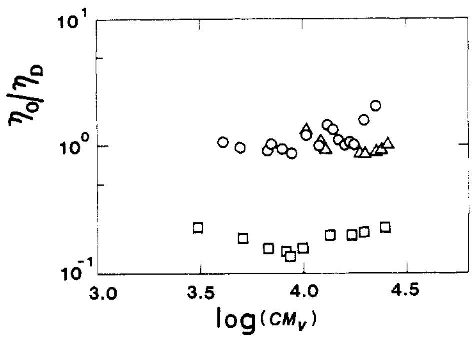

Figure 7. Ratio of zero-shear viscosity η_0 to the value η_D calculated by eq 3, η_0/η_D, plotted against the product cM_v for three schizophyllan samples in water at 30 °C. The marks have the same meaning as in Figure 4.

We may speculate that the viscosity behavior depends on the chain flexibility and deviates from the rigid rod behavior with increasing flexibility, eventually approaching the well-known $M^{3.4}$ law for highly entangled systems of flexible polymers. To confirm this, it is important to collect systematic data covering wide ranges of cM and flexibility.

Comparison among Different Polymers. Since eq 2 lacks a proportionality factor on the right-hand side, it does not tell us how to compare absolute values of η_0 for different polymers. To solve this problem, Berry et al.[14] introduced an empirical numerical factor γ^* defined by

$$\gamma^* = c^*L/M_L \tag{5}$$

and recast eq 2 in the form

$$\frac{\eta_0}{[\eta]_0 M \eta_s \gamma^{*3}} = K' \frac{X^3}{(1 - BX)^2} \tag{6}$$

with

$$X = cL/M_L\gamma^* \tag{7}$$

where K' and B are constants independent of c and M.

It must be noted that eq 6 is based on the assumption due to the Flory theory that c^*L is a constant independent of M; here c^* may be approximated by c_A. Furthermore, it is implicit in eq 5 that γ^* should be proportional to d/M_L in accordance with the Flory theory. However, Berry et al.[14] regarded γ^* as an adjustable parameter specific to a given polymer without regard to the constancy of c^*L, pointing out possible reasons for this adjustment. Actually, they have shown that a single composite curve is obtained when the γ^* values calculated by eq 5 from experimental c^* values are used. However, the calculated γ^* differ significantly from those estimated according to the Flory theory with the d/M_L for the individual polymers.

As mentioned above, c^*L is not constant for aqueous schizophyllan, and hence eq 6 cannot be applied. Therefore we have attempted to superpose viscosity data for different polymers according to eq 3 and 4, using the values of d and M_L determined directly from their dilute solution data. The results is shown in Figure 8, where the heavy line represents the theoretical curve fitting the data for aqueous schizophyllan in the rigid rod regime and dash-dot line the data for F-52 in the semirigid rod regime. This figure compares the reported η_0 of polymers divided into two groups: one consisting of helix-forming polymers, i.e., schizophyllan and poly(γ-benzyl L-glutamate) (PBLG),[15] and the other consisting of main-chain heterocyclic poly-

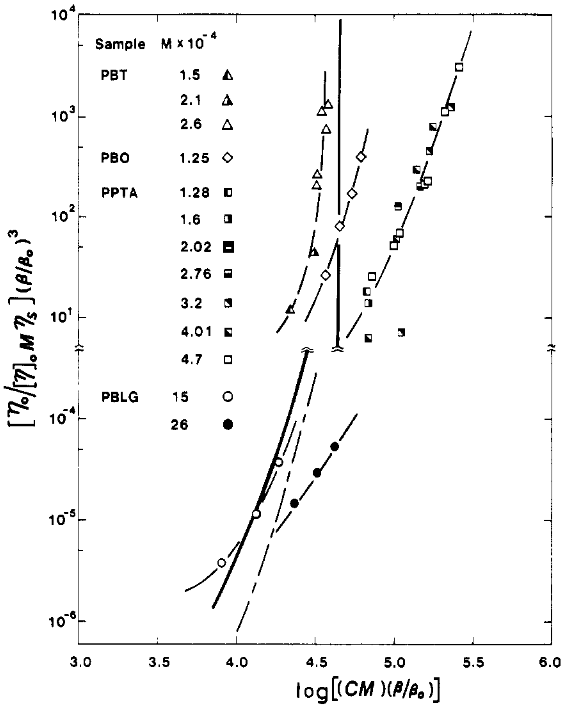

Figure 8. Relation between $[\eta_0/[\eta]_0 M\eta_s](\beta/\beta_0)^3$ and $(cM)(\beta/\beta_0)$ for various polymer + solvent systems. The heavy line corresponds to the curve shown in Figure 5. The dash–dot line is the curve fitted to the data for sample F-52. Various marks represent literature data for different polymer + solvent systems indicated. PBT in methanesulfonic acid (MSA), PBO in MSA, and PPTA in MSA (open squares), Chu et al.;[12] PPTA in 100% sulfuric acid, Baird and Ballman;[16] PBLG in *m*-cresol, Onogi and Asada.[15] β_0 is the value of β for aqueous schizophyllan (β/β_0 is unity for the heavy and the dash–dot lines).

mers, i.e., poly(*p*-phenylene-2,6-benzobisthiazole) (PBT),[12] poly(*p*-phenylene-2,6-benzobisoxazole) (PBO),[12] and poly(*p*-phenyleneterephthalamide) (PPTA).[12,16]

It can be seen that the data points for PBLG of lower molecular weight cross the theoretical curve, whereas those for the higher molecular weight appear definitely below the theoretical curve. This downward deviation is consistent with the finding from dilute solution data that the α-helix of PBLG is intact and straight at molecular weights lower than ca. 200 000 but appears flexible above this molecular weight;[17] the lower molecular weight sample is in the rigid rod regime but the higher molecular weight one in the semirigid rod regime.

When compared among the main-chain heterocyclic polymers, the curve for PBT is the steepest, and below it appear those for PBO and PPTA with smaller slopes. This trend may be interpreted in terms of the difference in chain stiffness among these polymers, which, as determined from dilute solution data,[18] decreases in the order PBT > PBO > PPTA.

It is noted that the data points for the heterocyclic polymers appear plotted far above those for the helical polymers. The difference in the ordinate value amounts to a factor larger than 10^4 when compared at the same abscissa value. This is due to the enormously large η_0 of these heterocyclic polymers. The theoretical curve is almost vertical in this range of ordinate value and does not allow a meaningful comparison with the experimental data. Berry et al.[19] suggested that solutions of these polymers are stabilized by strong intermolecular interactions of the electrostatic type added to the hard-core interaction, which may be one of the possible reasons for the enormous viscosity. It may be suggested that there might be some factor missing in eq 3 to account for the different viscosity behavior between the different groups of rigid rod polymers.

All these findings lead us to conclude that the heavy curve in Figure 8 can be a good approximate description of the viscosity of rodlike polymers in semidilute solutions, provided they are in the rigid rod regime and dissolve without any strong intermolecular interactions.

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Registry No. Schizophyllan, 9050-67-3.

References and Notes

(1) Doi, M. *J. Phys.* (*Paris*) **1975**, *36*, 607.
(2) Hermans, J., Jr. *J. Colloid Sci.* **1962**, *17*, 638.
(3) Papkov, S. P.; Kulichikin, V. G.; Kalmykova, V. D.; Malkin, A. Y. *J. Polym. Sci., Polym. Phys. Ed.* **1974**, *12*, 1753.
(4) Morgan, P. W. *Macromolecules* **1977**, *10*, 1381.
(5) Norisuye, T.; Yanaki, T.; Fujita, H. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 547.
(6) Yanaki, T.; Norisuye, T.; Fujita, H. *Macromolecules* **1980**, *13*, 1462.
(7) Van, K.; Norisuye, T.; Teramoto, A. *Mol. Cryst. Liq. Cryst.* **1981**, *78*, 123.
(8) Van, K.; Teramoto, A. *Polym. J.* **1982**, *14*, 999.
(9) Itou, T.; Van, K.; Teramoto, A. *J. Appl. Polym. Sci.*, in press.
(10) Miller, W. G. *Annu. Rev. Phys. Chem.* **1978**, *29*, 519.
(11) Einaga, Y.; Miyaki, Y.; Fujita, H. *J. Soc. Rheol. Jpn.* **1977**, *5*, 188.
(12) Chu, S. G.; Venkatraman, S.; Berry, G. C.; Einaga, Y. *Macromolecules* **1981**, *14*, 939.
(13) Flory, P. J. *Proc. R. Soc. London, Ser. A* **1956**, *234*, 73.
(14) Berry, G. C.; Venkatraman, S.; Einaga, Y. "Proceedings of the IUPAC 28th Macromolecular Symposium, 1982", p 790.
(15) Onogi, S.; Asada, T. *J. Appl. Polym. Sci.*, in press.
(16) Baird, D. G.; Ballman, R. L. *J. Rheol.* **1979**, *23*, 505.
(17) Itou, S.; Nishioka, N.; Norisuye, T.; Teramoto, A. *Macromolecules* **1981**, *14*, 904.
(18) Metzger, P. Ph.D. Thesis, Carnegie-Mellon University, 1979.
(19) Berry, G. C.; Metzger, P.; Chu, S. G. *Br. Polym. J.* **1981**, *13*, 47.