nm², respectively. Also the molecular weights of the comb backbone and single branch were 5.8×10^5 and 1.13×10^4, respectively. From these data, we estimated that $f = 27$ and $\rho = 0.04$. Since at 35 °C, the squared radius of linear polystyrene is proportional to the molecular weight, the expected squared radius of a linear polymer having the same molecular weight as in comb-branched polymer is $214 \times 5.80/2.75 = 451$ nm². Hence, the g factor is evaluated as $214/451 = 0.576$, in good agreement with the value of 0.587, obtained from eq 6 with the g_θ^* from Figure 5.

Triple Helix of *Schizophyllum commune* Polysaccharide in Dilute Solution. 4. Light Scattering and Viscosity in Dilute Aqueous Sodium Hydroxide

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ABSTRACT: In previous work, it was deduced from sedimentation equilibrium and hydrodynamic measurements that an extracellular β-1,3-D-glucan schizophyllan is dissolved in water as a trimer assuming a triple-helical structure. The study reported in this paper was undertaken to estimate the pitch and stiffness of this helix from radius of gyration data obtained by a light scattering experiment. In the actual measurement, 0.01 N aqueous NaOH instead of pure water was used as the solvent because it was found that the molecular weights expected for the trimer were obtained only when a small amount of NaOH was added but that this operation did not destroy the helical structure of the trimer. The data for $\langle S^2 \rangle^{1/2}$ (the radius of gyration) as a function of molecular weight agreed with the prediction that the triple helix should behave like a semiflexible rod. The corresponding data for $[\eta]$ (the intrinsic viscosity) in 0.01 N NaOH also exhibited features characteristic of a semiflexible rod. These data were analyzed in terms of the known theories for unperturbed wormlike chains, with the result that the pitch per glucose residue and the persistence length of the schizophyllan triple helix are 0.30 ± 0.01 and 180 ± 30 nm, respectively. These values are in agreement with those derived in previous work from viscosity and sedimentation velocity in pure water.

Schizophyllan is an extracellular polysaccharide produced by the fungus *schizophyllum commune*; it consists of linearly linked β-1,3-D-glucose residues with one β-1,6-D-glucose side chain for every three main chain residues.[1,2] As was found in part 1[3] from viscosity and sedimentation equilibrium measurements, this polysaccharide shows very characteristic solubility behavior. Thus it disperses in water as a rodlike trimer with a triple-helical structure, while it disperses in dimethyl sulfoxide (Me_2SO) as a single randomly coiled chain. In part 3,[4] the pitch, diameter, and stiffness (expressed in terms of the persistence length) of the triple helix were estimated from viscosity and sedimentation velocity data, using appropriate hydrodynamic theories for rigid rods[5,6] and wormlike cylinders.[5,7] Here we report a light scattering study undertaken to evaluate the pitch and stiffness of the schizophyllan triple helix from radius of gyration data as a function of molecular weight. Actually, the experiment was done with water containing 0.01 N sodium hydroxide, rather than pure water, as the solvent for the reason mentioned in the Experimental Section. We also obtained viscosity data in this solvent and used them to estimate the pitch, diameter, and stiffness of the triple helix.

Experimental Section

Samples. Three schizophyllan samples, designated below as K ($[\eta] = 7 \times 10^2$ cm³ g⁻¹ in water at 25 °C), G ($[\eta] = 4.7 \times 10^2$ cm³ g⁻¹), and H ($[\eta] = 2.1 \times 10^2$ cm³ g⁻¹), were supplied by Taito Co. They were prepared by sonication of a native schizophyllan and purified by the method described in part 1.[3] By fractional precipitation and extraction with water as a solvent and ethanol as a precipitant, six fractions were separated from sample K, ten fractions from sample G, and eight fractions from sample H. An appropriate middle fraction of each sample was further divided into several parts, and five fractions, designated below as K-4, G-6, G-8, H-3, and H-5, were chosen for the present study. They were reprecipitated from aqueous solutions into acetone and freeze-dried from aqueous solutions.

Six more samples were used; four of them were a native sample N-1 and sonicated samples S-65-2, S-45-4, and S-164-3, all used in our previous studies[3,4] of this series, and the rest were samples S-100-2 and E-4b chosen from our stock.

Each of these eleven samples was dried overnight in vacuo at room temperature before use.

Preliminary Experiments. When we commenced the present light scattering study with pure water solutions, we anticipated that the measurement would give weight-average molecular weights, M_w, consistent with the values calculated from intrinsic viscosities, $[\eta]$, of the same solutions, using the $[\eta]$ vs. M_w relation established in part 3.[4] However, the actual values of M_w were 10–50% higher than the expected ones, and the discrepancy was greater for higher M_w. We suspected that this was due primarily to our insufficient optical clarification of the solutions and tried more intensive purification by repeating filtration and centrifugation. However, no substantial change occurred in the measured M_w.

At this stage we abandoned the use of pure water solutions and turned to testing the idea that the major source of the anomaly was the presence of microgels impossible to remove by ordinary means; if so, the problem should be eliminated or minimized by addition of a solubility-enhancing reagent which allows dissociation of those gels. The point is that such a reagent should not be strong enough to break the triple-helical structure of schizophyllan trimers or even to degrade the polymer. We tried to check this idea with potassium chloride and Me_2SO, but the results were discouraging. Eventually, we tried 0.01 N sodium hydroxide (NaOH) and found M_w approaching the values expected for trimers. This was encouraging, but we wondered if the stiffness of the helical structure of the trimer was impaired by the alkali. To examine this point we measured $[\eta]$ of several samples in aqueous NaOH of different concentrations. The experimental results delineated in Figure 1 suggest that the triple helix which schizophyllan would assume in pure water is maintained in aqueous NaOH if the alkali concentration does not exceed 0.02 N. From these observed facts we chose 0.01 N NaOH as the solvent for the present light scattering characterization of the schizophyllan triple helix.

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Table I
Results from Light Scattering and Viscosity Measurements on Schizophyllan Samples in 0.01 N NaOH at 25 °C

sample	$10^{-4}M_w$	10^4A_2/ cm³ mol g⁻²	$\langle S^2\rangle^{1/2}$/ nm	M_w(0.01 N NaOH)/ M_w(Me_2SO)	$10^{-2}[\eta]$/ cm³ g⁻¹	k'
N-1	568	3.29	333	3.5	120	0.40
S-65-2	400	1.71	251	2.9	74.5	0.44
S-45-4	285	1.91	205	2.9	43.8	0.41
S-100-2	151	2.56	147	3.3	19.2	0.40
K-4	62.0	4.89	72.3	3.6	5.80	0.40
G-6	46.1	4.72	57.5	3.3	4.55	0.40
G-8	41.3	4.76	51.0	3.2	3.30	0.41
H-3	35.3	4.95	44.8	3.0	2.95	0.40
	35.6[a]	1.34[a]	49.8[a]			
H-5	25.9	5.45	34.7	2.9	1.66	0.42
E-4b	17.0	5.99	22.1	2.8	0.791	0.42
	17.7[a]	2.04[a]	22.5[a]			
S-164-3	10.7	7.37	14.6	2.9	0.384	0.39

[a] In 0.001 N NaOH at 25 °C.

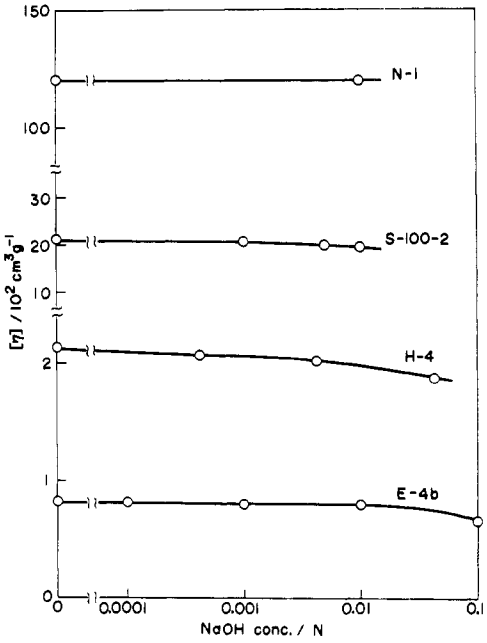

Figure 1. Dependence of $[\eta]$ on NaOH concentration for the indicated schizophyllan samples in aqueous NaOH at 25 °C.

Though the results are not displayed here, we extended the viscosity measurements in aqueous NaOH to a concentration as high as 4 N and observed that $[\eta]$ at high NaOH concentrations decreased appreciably with time, and $[\eta]$ at a fixed time dropped sharply in a concentration range near 0.15 N. These facts suggest that both dissociation and degradation of the triple helix occur in concentrated aqueous NaOH.

Light Scattering. Intensities of light scattered from schizophyllan in 0.01 N NaOH at 25 °C were measured on a Fica 50 automatic light scattering photometer in an angular range from 22.5 to 150°. Vertically polarized incident light of 436-nm wavelength was used for lower molecular weight samples and that of 546 nm was used for higher molecular weight samples. The angular dependence of scattered intensities was analyzed by use of a Zimm plot, i.e., Kc/R_θ vs. $\sin^2(\theta/2)$, while the concentration dependence was analyzed by use of Berry's square root plot,[8] i.e., $(Kc/R_\theta)^{1/2}$ vs. c. Here K is the optical constant, c the polymer mass concentration, and R_θ the reduced scattering intensity at scattering angle θ. None of the radius of gyration data obtained were corrected for polydispersity.

The instrument was calibrated by the usual method, with benzene at 25 °C as the reference liquid. Rayleigh ratios of benzene at 25 °C at 436 and 546 nm were taken to be 46.5×10^{-6} and 16.1×10^{-6} cm⁻¹, respectively.[9] The depolarization ratio of benzene was estimated to be 0.41 for 436 nm and 0.40 for 546 nm by the method of Rubingh and Yu.[10]

Optical clarification of aqueous NaOH solutions of schizophyllan was made by filtration through a membrane filter followed by 4 h of centrifugation at about $4 \times 10^4 g$ in a Sorvall RC2-B centrifuge. Use was made of Millipore's GSWP 047 00 for samples S-164-3 and E-4b, PHWP 047 00 for samples H-5 and H-3, HAWP 047 00 for samples G-8 and G-6, DAWP 047 00 for sample K-4, EAWP 047 00 for sample S-100-2, and SSWP 047 00 for samples S-45-4, S-65-2, and N-1. A central portion of the supernatant of the solution in the centrifuge tube was sucked into a pipet and directly transferred into a light scattering cell. The cell and pipet had been rinsed with refluxing acetone vapor for 6–12 h.

Samples S-164-3, H-3, and G-6 in 0.01 N NaOH at 25 °C were investigated at a fixed scattering angle of 90° with a polarizer oriented in the vertical direction. The scattered intensity measured for any of these samples with an analyzer set in the horizontal direction did not exceed 0.5% of the intensity measured with the analyzer set in the vertical direction. Furthermore, when the light scattering envelopes of sample S-164-3 for vertically polarized incident light and unpolarized incident light were compared, no difference was detected. Hence, we considered it unnecessary to correct the present light scattering data for optical anisotropy.

The specific refractive index increments of schizophyllan in 0.01 N NaOH at 25 °C were 0.144_4 cm³ g⁻¹ at 436 nm and 0.142_3 cm³ g⁻¹ at 546 nm. These were in agreement with the previously determined values[3] in pure water at the corresponding wavelengths.

Viscometry. Zero-shear-rate viscosities for samples N-1 and S-65-2 in 0.01 N NaOH at 25 °C were measured in a rotational viscometer of the Zimm–Crothers type[11] and those for samples S-45-4, S-100-2, K-4, G-6, G-8, and H-3 in four-bulb capillary viscometers.[12] For samples H-5, E-4b, and S-164-3 conventional capillary viscometers of the Ubbelohde type were used.

Results

Molecular Weights. Figure 2 illustrates the light scattering envelopes for sample K-4 in 0.01 N NaOH at 25 °C. Panels A and B show, respectively, the concentration dependence of $(Kc/R_\theta)^{1/2}$ for fixed θ and the angular dependence of Kc/R_θ for fixed c. The data points for each θ in panel A are fitted by a straight line, permitting the infinite-dilution values of Kc/R_θ to be determined accurately. These extrapolated values are shown by larger circles in panel B. The larger circles in panel A indicate the zero-angle values $(Kc/R_0)^{1/2}$, which were obtained by extrapolating the data points in panel B.

Figure 3 displays $(Kc/R_0)^{1/2}$ plotted against c for all the samples studied. The values of M_w and A_2 (the second virial coefficient) evaluated from the intercepts and slopes of the indicated straight lines are presented in Table I, together with those for samples H-3 and E-4b obtained with 0.001 N NaOH at 25 °C as the solvent. The agreement of M_w values for samples H-3 and E-4b in 0.01 and 0.001 N NaOH is quite good. Furthermore, our M_w values for samples S-164-3, H-3, S-45-4, S-65-2, and N-1 in 0.01 N NaOH are close to those determined previously by

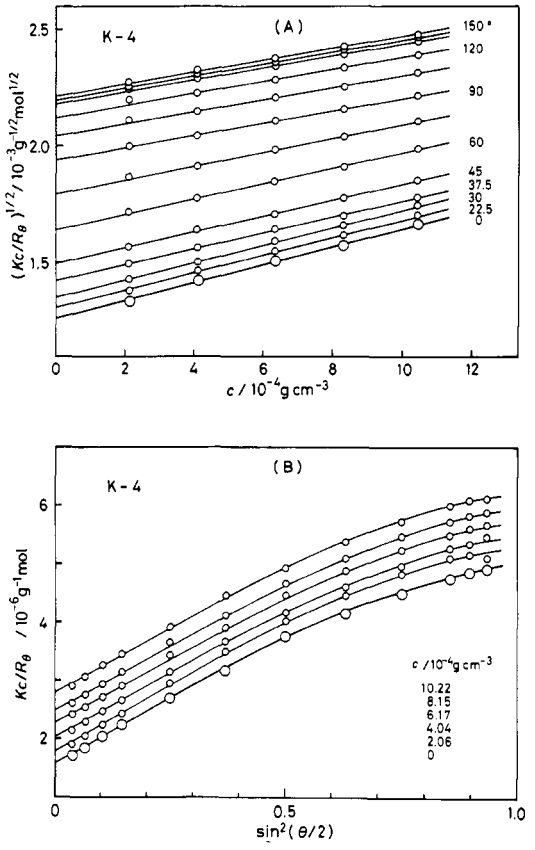

Figure 2. Light scattering envelopes for schizophyllan sample K-4 in 0.01 N NaOH at 25 °C.

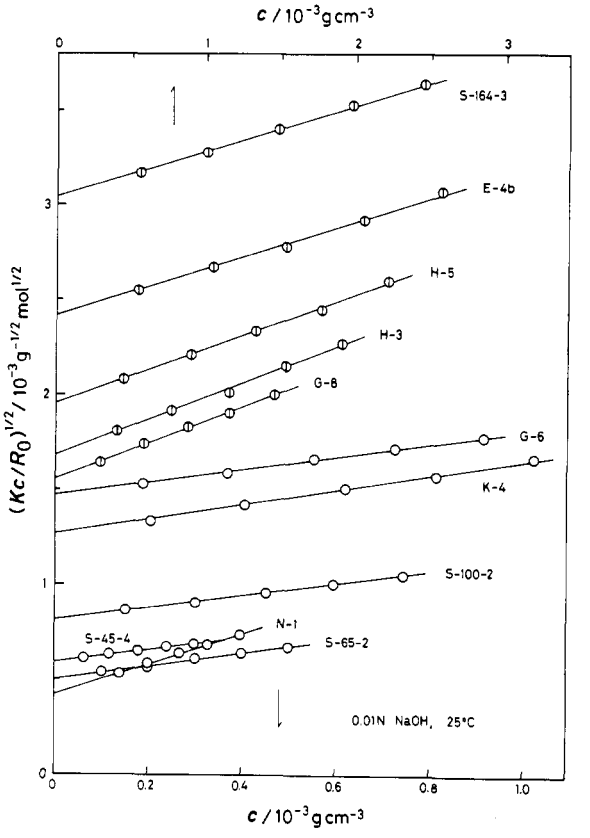

Figure 3. Concentration dependence of $(Kc/R_0)^{1/2}$ for schizophyllan samples in 0.01 N NaOH at 25 °C.

sedimentation equilibrium in pure water (see ref 3 and 4). These results suggest that the effect of preferential adsorption of NaOH on the schizophyllan molecule is negligible.

The fifth column of Table I gives the ratios M_w(0.01 N NaOH)/M_w(Me_2SO) computed from the present data and our unpublished data in Me_2SO. They are close to 3 and substantiate that the predominant species of schizophyllan in 0.01 N NaOH is a trimer, as was found to be the case in pure water.[3]

Radius of Gyration. Figure 4 depicts the particle scattering functions $P(\theta)$ for all the samples in 0.01 N NaOH. The curves fitting the data points are more convex upward for higher molecular weight. The values of $\langle S^2\rangle^{1/2}$ (the radius of gyration) evaluated from the slopes of the indicated dashed lines are presented in the fourth column of Table I, together with those for samples H-3 and E-4b in 0.001 N NaOH. The agreement of $\langle S^2\rangle^{1/2}$ for samples H-3 and E-4b in 0.01 and 0.001 N NaOH confirms our conviction that the triple-helical structure of schizophyllan should suffer no change at these low concentrations of NaOH.

In Figure 5, the values of $\langle S^2\rangle^{1/2}$ in 0.01 N NaOH and our unpublished data in Me_2SO are plotted double logarithmically against M_w. The curves for the two solvents display distinctly different behavior and intersect at $M_w \sim 1.3 \times 10^5$. The curve for 0.01 N NaOH in the range of M_w below 3×10^5 is linear and has a slope of 1.0. Since this slope agrees with the theoretical prediction for straight rods, it can be concluded that the schizophyllan triple helix in this molecular weight region behaves as a rigid, straight rod. In the higher molecular weight region, however, the slope of the curve decreases continuously with increasing M_w and reaches 0.6 at $M_w \sim 5 \times 10^6$. This behavior can be ascribed to a gradual bending of the rod. The line for Me_2SO is straight and has a slope of 0.58, indicating that schizophyllan in this solvent is a random coil swollen by an excluded-volume effect.

Intrinsic Viscosity. The values of $[\eta]$ and the Huggins constant k' for all the samples in 0.01 N NaOH are summarized in the sixth and seventh columns of Table I, and these $[\eta]$ values are plotted double logarithmically against M_w in Figure 6, together with our previous[3] and unpublished data for Me_2SO solutions. The data in Me_2SO can be fitted by a straight line with slope 0.69 over the entire range of M_w studied. This slope is also typical of linear flexible polymers in good solvents. The curve for 0.01 N NaOH is distinctly different from the line for Me_2SO, and both intersect at $M_w \sim 2 \times 10^5$. We have already seen similar behavior for $\langle S^2\rangle^{1/2}$ in these solvents. The slope of the curve for 0.01 N NaOH is about 1.8 in the region of M_w below 5×10^5 and about 1.1 at $M_w \sim 5 \times 10^6$. The value 1.8 is the theoretical prediction for long rigid rods[6] and is consistent with the conclusion from $\langle S^2\rangle$ that the schizophyllan triple helix with an M_w lower than about 3×10^5 is straight. The lower slope 1.1 at $M_w \sim 1.1 \times 10^6$ suggests that the helix can be modeled as a semiflexible chain for M_w above 5×10^5. The $[\eta]$ vs. M_w curve for 0.01 N NaOH is quite close to that reported in part 3[4] for schizophyllan in pure water, in which the slopes in the lower and higher molecular weight regions were 1.7 and 1.2, respectively.

Discussion

Determination of the Wormlike Chain Parameters. The Benoit–Doty expression[13] for $\langle S^2\rangle$ of the Kratky–Porod wormlike chain,[14] a typical model chain for semiflexible polymers, is

$$\langle S^2\rangle = \frac{qL}{3} - q^2 + \frac{2q^3}{L}\left[1 - \frac{q}{L}(1 - e^{-L/q})\right] \quad (1)$$

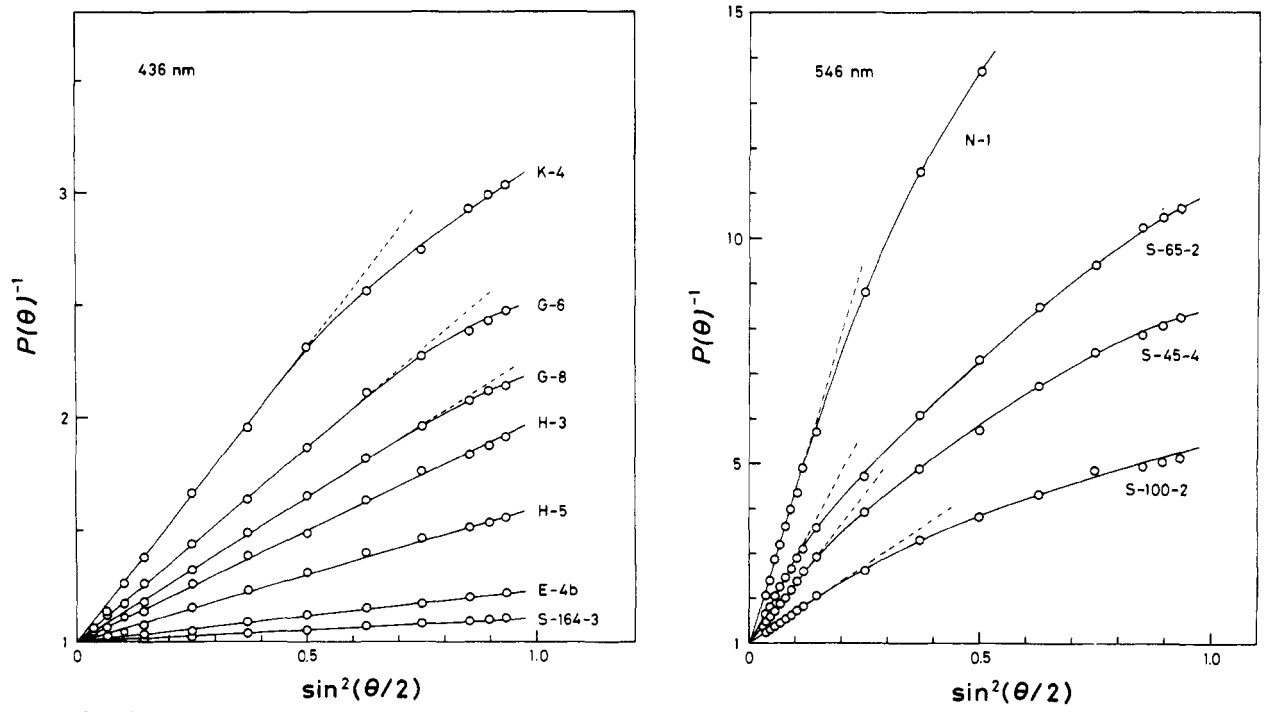

Figure 4. Particle scattering functions for schizophyllan samples in 0.01 N NaOH at 25 °C.

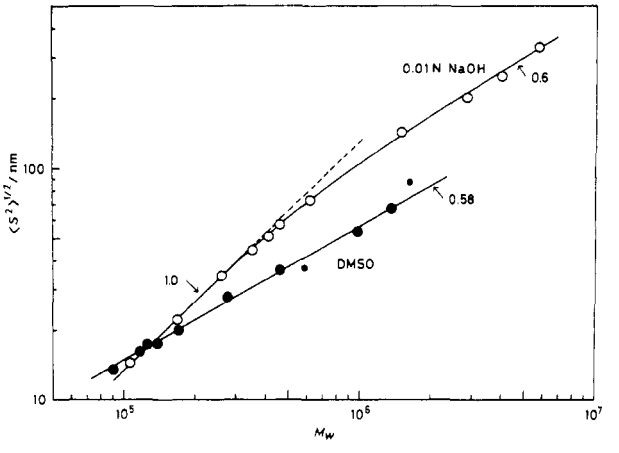

Figure 5. Double-logarithmic plots of $\langle S^2\rangle^{1/2}$ vs. M_w for schizophyllan in 0.01 N NaOH (○) and in dimethyl sulfoxide [(•) previous data;[3] (●) unpublished data] at 25 °C.

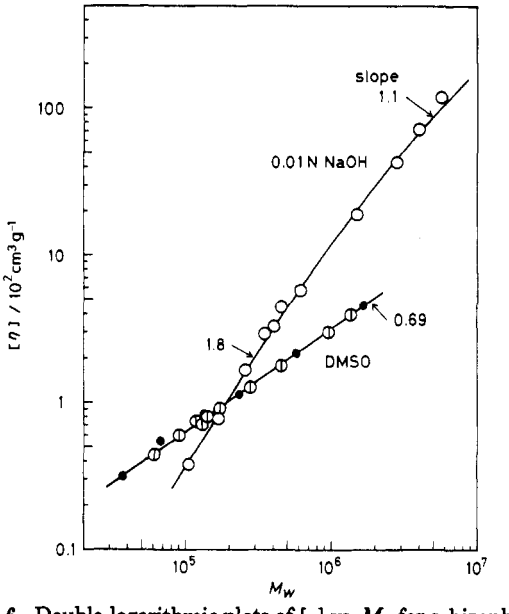

Figure 6. Double-logarithmic plots of $[\eta]$ vs. M_w for schizophyllan in 0.01 N NaOH (○) and in dimethyl sulfoxide [(•) previous data;[3] (⊕) unpublished data] at 25 °C.

where L and q are the contour length and the persistence length of the chain, respectively. The contour length is related to the molecular weight M of the chain by

$$L = M/M_L \tag{2}$$

with M_L the molar mass per unit contour length. Equation 1 indicates that $\langle S^2\rangle^{1/2}/L$ is a function of a reduced contour length $L/2q$, which decreases monotonically from $1/\sqrt{12}$ to zero as $L/2q$ increases from zero to infinity. Another feature of eq 1 is that $\langle S^2\rangle^{1/2}/L$ is $1/2\sqrt{12}$ at $L/2q = 6.394$, regardless of q and M_L. Thus, we have

$$H \equiv \lim_{L/2q\to 0} \langle S^2\rangle^{1/2}/M = 1/\sqrt{12}M_L \tag{3}$$

and

$$M^* = 12.79qM_L \tag{4}$$

where M^* is the molecular weight at which $\langle S^2\rangle^{1/2}/M$ is equal to $H/2$. Equations 3 and 4 allow us to evaluate q and M_L if H and M^* can be determined by experiment.

Figure 7 shows a plot of $\langle S^2\rangle^{1/2}/M_w$ vs. log M_w constructed from our data in 0.01 N NaOH. The points for M_w below 3×10^5 are approximately fitted by a horizontal line, allowing H to be determined without extrapolation. The curve intersects the horizontal line for $H/2$ at an M_w of 4.2×10^6. From the values of H and M^* so obtained we find 2170 ± 50 nm^{-1} for M_L and 150 ± 30 nm for q.

In Figure 8, the points are the measured values of $\langle S^2\rangle^{1/2}$ for schizophyllan in 0.01 N NaOH and the lines represent the values computed from eq 1 with $M_L = 2170$ nm^{-1} for $q = 100$, 150, 200 nm, and ∞. The data points agree most satisfactorily with the theoretical curve for $q = 150$ nm.

The Yamakawa-Yoshizaki theory[7] for $[\eta]$ of the wormlike cylinder involves three parameters, q, M_L, and d (the hydrodynamic diameter of the cylinder). The unique evaluation of these three unknowns from viscosity data alone is not a simple matter. However, as was done in part 3,[4] M_L and d of the schizophyllan triple helix may be

Table II
Pitches of Triple-Helical Polysaccharides

polysaccharide	solvent	h/nm	method	ref
schizophyllan	0.01 N NaOH	0.30 ± 0.01	light scattering	this work
		0.30 ± 0.01	viscosity	this work
	water	0.30 ± 0.02	viscosity and sedimentation	4
		0.30	molecular model	3
β-1,3-D-xylan (right handed)	crystalline state	0.306	X-ray	17
lentinan (right handed)	crystalline state	0.29	X-ray	18
lentinan (left handed)	crystalline state	0.33		
curdlan (right handed)	crystalline state	0.294	X-ray	19

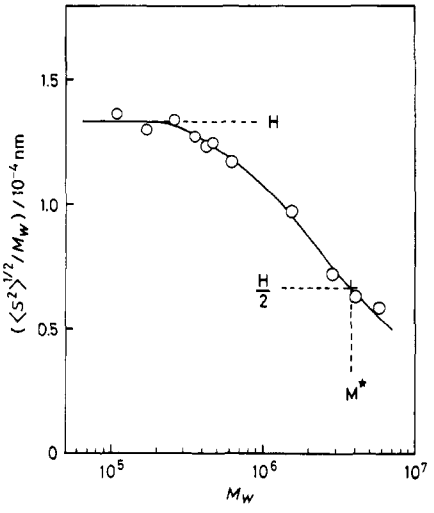

Figure 7. Plot of $\langle S^2\rangle^{1/2}/M_w$ vs. log M_w for schizophyllan in 0.01 N NaOH. See the text for the definitions of H and M^*.

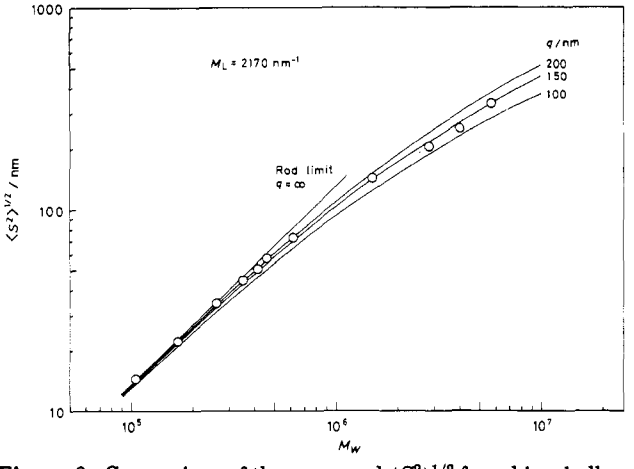

Figure 8. Comparison of the measured $\langle S^2\rangle^{1/2}$ for schizophyllan in 0.01 N NaOH with the theoretical values calculated from eq 1 with M_L = 2170 nm^{-1} for q = 100, 150, 200 nm, and ∞.

evaluated by utilizing the experimental fact that the molecular weight dependence of our $[\eta]$ below 5×10^5 is compatible with the prediction from Yamakawa's theory[6] for long straight cylinders. Once M_L and d are known, the third parameter, q, may be determined by seeking a q value which allows the Yamakawa–Yoshizaki theoretical curve to fit our $[\eta]$ data over as broad a range of molecular weight as possible.

In Figure 9, the values of $M_w^2/[\eta]$ for the six lowest molecular weight samples in 0.01 N NaOH are plotted against log M_w, according to Yamakawa's theory,[6] which yields the relation

$$M^2/[\eta] = (45M_L^3/2\pi N_A)[\ln M - 0.6970 - \ln (dM_L)] \quad (5)$$

where N_A is Avogadro's constant. If the data points are

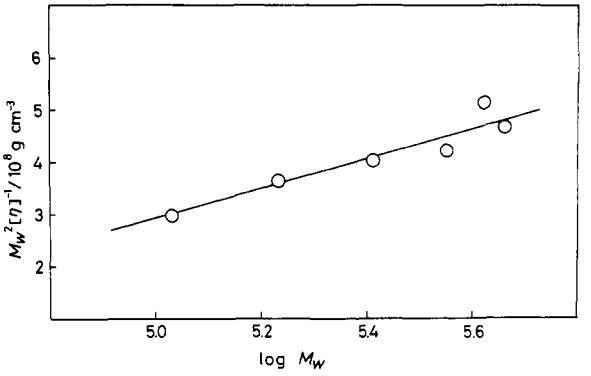

Figure 9. Plot of $M_w^2/[\eta]$ vs. log M_w for schizophyllan in 0.01 N NaOH.

fitted by a straight line as indicated, M_L and d are determined to be 2190 ± 50 nm^{-1} and 2.2 ± 0.6 nm, respectively. The M_L value of 2190 nm^{-1} is very close to 2170 nm^{-1} determined above from $\langle S^2\rangle^{1/2}$. The large uncertainty in d reflects the fact that Yamakawa's theory is insensitive to d. If this fact is taken into account, our d values are considered to be consistent with 2.6 ± 0.6 nm, which was estimated by Yanaki et al.[4] from $[\eta]$ in pure water at 25 °C.

With M_L and d fixed at 2190 nm^{-1} and 2.2 nm, respectively, we computed $[\eta]$ for different q from the Yamakawa–Yoshizaki theory.[7] The results are compared with the measured values for 0.01 N NaOH solutions in Figure 10, in which the solid curves represent the theoretical values for q = 150, 200, 300 nm, and ∞. The curve for q = 200 nm gives the best agreement between theory and experiment. We made similar analyses by allowing M_L and d to vary within the ranges of uncertainty indicated above and found that all q fell in the range between 230 and 170 nm. The q values in this range are comparable with 200 ± 30 nm estimated by Yanaki et al.[4] from $[\eta]$ and sedimentation coefficient in pure water but are slightly larger than 150 ± 30 nm determined above from $\langle S^2\rangle^{1/2}$ in 0.01 N NaOH. This difference in q is probably immaterial because, as can be seen from the theoretical curves in Figures 8 and 10, values of log $\langle S^2\rangle^{1/2}$ and log $[\eta]$ are insensitive to q in the ranges of M and q examined. Thus, we conclude that q of the schizophyllan triple helix in both 0.01 N NaOH and water is 180 ± 30 nm. This q value is larger than 130 nm for triple-helical collagen[15] and 60 nm for double-stranded DNA,[16] both being typical stiff macromolecules.

Helix Pitch. The pitch h of the schizophyllan triple helix per β-1,3-D-glucose residue is related to M_L by

$$h = (M_0/3)/(M_L/3) \quad (6)$$

with M_0 the molar mass of the schizophyllan repeat unit (=648). We note that each repeat unit of the main chain of schizophyllan contains three β-1,3-D-glucose residues. The values of h calculated from our M_L values are presented in Table II, together with the reported pitches for

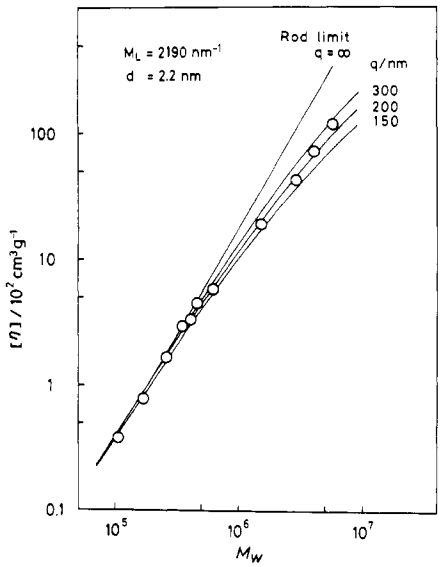

Figure 10. Comparison of the measured $[\eta]$ for schizophyllan in 0.01 N NaOH with Yamakawa and Yoshizaki's theoretical values for wormlike cylinders calculated for q = 150, 200, 300 nm, and ∞ with M_L and d fixed at 2190 nm^{-1} and 2.2 nm, respectively.

schizophyllan in water,[4] the model triple helix of schizophyllan,[3] and triple helices of other polysaccharides[17–19] in the crystalline state. Our pitches from light scattering and viscosity in 0.01 N NaOH agree not only with Yanaki et al.'s values[4] from sedimentation velocity and viscosity but also with the value estimated from the molecular model for schizophyllan. They are also close to the values for a β-1,3-D-xylan,[17] lentinan (β-1,3-D-glucan),[18] and curdlan (β-1,3-D-glucan),[19] leading to the conclusion that the triple-helical structure of schizophyllan in 0.01 N NaOH and water is very similar to that of these other polysaccharides in the crystalline state.

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Development of a Linear Helical Conformation from Its Cyclic Correlate. β-Spiral Model of the Elastin Poly(pentapeptide) $(VPGVG)_n$

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ABSTRACT: Mathematical methods of obtaining linear helical correlate structures from a given cyclic conformation are applied to the case of the linear poly(pentapeptide) poly(L-Val-L-Pro-Gly-L-Val-Gly), $(VPGVG)_n$, of elastin, leading to the derivation of low-energy β-spiral models of the polymer from the known structure of its cyclic correlate, *cyclo*-$(VPGVG)_3$.

The relevance of studies on cyclic peptides from the standpoint of biomolecular conformation and function is well reviewed.[1] The interest in cyclic peptides has been additionally enhanced by a recent proposal[2] that they may, in some cases, serve as instructive models for *linear* helical peptides. By small changes in torsion angles of a cyclic peptide, an acceptable linear conformation can be obtained. Thus one can expect to find linear sequential polymers having conformational features similar to those of the cyclic molecules with the same sequence. The linear and the "corresponding" cyclic molecules may then be viewed as "correlates" of each other. This idea, referred to as cyclic conformations with linear conformational correlates,[2] has recently found a fascinating application in the conformational studies of oligopeptides with the pentamer repeat sequence L-Val-L-Pro-Gly-L-Val-Gly, VPGVG, which is found in tropoelastin.[3–5] For instance, a detailed study[6] on the series of cyclic peptides *cyclo*-$(VPGVG)_n$, with n = 1–6, shows that *cyclo*-$(VPGVG)_3$ has NMR spectral properties strikingly similar to those of the linear polymer, $(VPGVG)_n$. The solid-state conformation of *cyclo*-$(VPGVG)_3$ has been determined by X-ray diffraction,[7] and the conformation in solution has been inferred from the combined analyses of NMR studies and

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