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Triple Helix of *Schizophyllum commune* Polysaccharide in Dilute Solution. 5. Light Scattering and Refractometry in Mixtures of Water and Dimethyl Sulfoxide

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ABSTRACT: Light scattering and differential refractive index measurements were made on a sonicated sample of schizophyllan in water + dimethyl sulfoxide (Me_2SO) mixtures over the entire composition range at 25 °C. When the water composition was diminished to about 13 wt %, the weight-average molecular weight M_w and the z-average mean-square radius of gyration $\langle S^2\rangle_z$ were found to decrease abruptly to the values in pure Me_2SO. This result directly checks the previous deduction from viscosity data that the triple helix of schizophyllan would dissociate to single randomly coiled chains at a water composition of about 13 wt %. Analysis of the M_w and $\langle S^2\rangle_z$ data indicated that the dissociation proceeds in all-or-none fashion. Specific refractive index increments for dialyzed and undialyzed solutions showed that the Me_2SO molecule adsorbs preferentially on schizophyllan in the region of water composition below about 40 wt %.

Schizophyllan is an extracellular polysaccharide consisting 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] In part 1,[3] we found that this polysaccharide dissolves in water as a rodlike triple helix, while it disperses in dimethyl sulfoxide (Me_2SO) as a single randomly coiled chain. We also found that the intrinsic viscosity $[\eta]$ of schizophyllan in mixtures of water and Me_2SO at 25 °C undergoes an almost discontinuous decrease when the water composition is decreased to about 13 wt %. This decrease in $[\eta]$ was taken as reflecting a sharp dissociation of the triple helix to single chains.

In part 2,[4] we explored thermal effects on the schizophyllan triple helix in the water + Me_2SO mixture at a water composition of 12.76 wt % by viscometry and ultracentrifugation. When the solution was heated, for example, at 30 °C, $[\eta]$ decreased slowly with time and virtually leveled off at a constant after about 24 h. Schlieren patterns for this final solution revealed the presence of the triple helix and the single chain but not any other species. When the solution was examined at a higher temperature of 45 °C, the schlieren peak corresponding to the triple helix disappeared and $[\eta]$ approached the value in pure Me_2SO. From these results we concluded that the schizophyllan triple helix melts into single chains in all-or-none fashion with increasing temperature.

This paper reports a light scattering study undertaken to see whether the isothermal solvent-induced dissociation of the schizophyllan triple helix in water + Me_2SO mixtures also proceeds in all-or-none fashion.

Experimental Section

Preparation of Solutions. A purified, sonicated fraction of schizophyllan chosen from our stock was used for all measurements. A weighed amount of the sample was dissolved in the water + Me_2SO mixture of a desired composition at a temperature below 25 °C, and the solution was left standing at 25 °C for 1 day. By diluting it with the same mixed solvent of 25 °C, we prepared a series of polymer concentrations.

Dimethyl sulfoxide was dehydrated with calcium hydrate and fractionally distilled in a reduced nitrogen atmosphere. Densities ρ_0 and refractive indices n_0 of water + Me_2SO mixtures at 25 °C were evaluated by interpolating or extrapolating the reported values[5] and our previously measured values.

Differential Refractometry. We constructed a dialyzer so designed that both the solution and solvent compartments can be stirred; their capacities were about 8 and 50 cm^3, respectively. The solution was separated from the mixed solvent by a Visking gel–cellophane membrane, and the entire system was thermostated at 25 ± 0.1 °C. Before setting, the membrane was conditioned by washing it successively with 0.01 N acetic acid, water, and the mixed solvent. Osmotic equilibrium was attained after 2–4 days.

Specific refractive index increments $(\partial n/\partial c)_{T,\mu}$ for dialyzed solutions and $(\partial n/\partial c)_{T,p,w_H}$ for undialyzed ones, both at 25 °C, were determined by using a differential refractometer of the modified Schulz–Cantow type calibrated with Kruis' data[6] on aqueous potassium chloride. Here, T and p have the usual meaning, and μ and w_H denote the chemical potentials of the diffusible components (i.e., water and Me_2SO) in the solution and the weight fraction of water in the mixed solvent, respectively. In the subsequent presentation, the subscripts T and p are omitted for simplicity.

Refractive index increments $(\partial n_0/\partial w_H)$ of water + Me_2SO mixtures at 25 °C were evaluated from the slope of n_0 vs. w_H or directly measured in the differential refractometer.

Light Scattering. Intensities scattered from schizophyllan solutions in water + Me_2SO mixtures at 25 °C were measured on a Fica 50 automatic light scattering photometer in an angular range from 22.5 to 150°. Instead of pure water solutions those containing 0.01 N sodium hydroxide (NaOH) were used, for the reason mentioned in part 4.[7] Vertically polarized incident light of 546-nm wavelength was used for most of the measurements. The photometer was calibrated in the same way as described previously.[7]

Solutions of $w_H = 0.1270$ and 0.1000 were investigated at a fixed scattering angle of 90° with an analyzer set in the vertical direction or the horizontal direction. The scattering intensity I_{Hv} relative to I_{Vv} was found to be virtually zero for any of the solutions, where I_{Hv} and I_{Vv} denote the intensities measured for vertically polarized incident light with the analyzer oriented in the horizontal direction and the vertical direction, respectively. Thus, the optical an-

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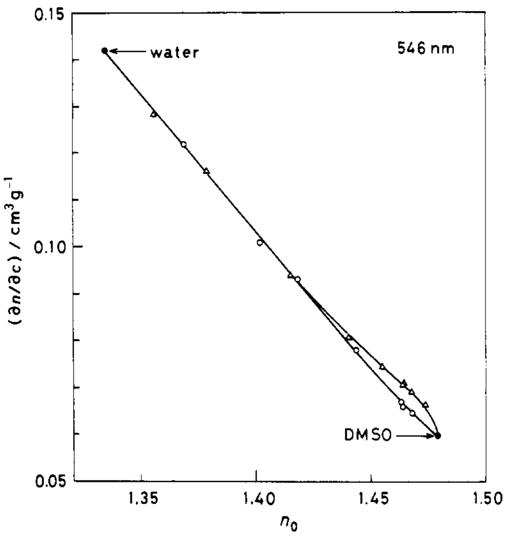

Figure 1. Specific refractive index increments of schizophyllan in water + Me_2SO mixtures at 25 °C. Triangles, $(\partial n/\partial c)_\mu$; circles, $(\partial n/\partial c)_{w_H}$.

isotropy of the schizophyllan sample at $w_H = 0.1270$ and 0.1000 was concluded to be negligible. Kashiwagi et al.[7] found that this was the case with schizophyllan in 0.01 N NaOH.

Each test solution was optically clarified by 4-h centrifugation at 25 °C and about $4 \times 10^4 g$ in a Sorvall RC2-B centrifuge. Its central portion in the centrifuge tube was sucked into a pipet and directly transferred into a light scattering cell. The pipet and the cell had been rinsed with refluxing acetone for 6–12 h. For 0.01 N NaOH solutions, optical clarification was made by the method established by Kashiwagi et al.[7]

If, as was concluded in part 2,[4] both the triple helix and the single chain coexist in schizophyllan solutions of $w_H \sim 0.13$ and if the specific refractive index increments of these two species are different, the light scattering parameters cannot generally be estimated by the conventional measurement. As the data presented in the Appendix show, both $(\partial n/\partial c)_\mu$ and $(\partial n/\partial c)_{w_H}$ are independent of whether schizophyllan is in triple helix, random coil, or other conformations, if any. Therefore, regardless of whether it contains more than one species different in conformation, our system can be treated optically as being composed of two solvents and one polymer, so that the desired light scattering parameters may be derived from intensity data on undialyzed solutions if $(\partial n/\partial c)_\mu$ is used in calculating the optical constant K.[8-10]

Results and Discussion

Refractive Index Increments and Preferential Adsorption. Values of $(\partial n/\partial c)_\mu$ and $(\partial n/\partial c)_{w_H}$ at 546 nm are plotted against n_0 in Figure 1. Below $n_0 \sim 1.43$ the two sets of data points can be fitted by a single straight line, whereas for $n_0 > 1.43$, $(\partial n/\partial c)_\mu$ are larger than $(\partial n/\partial c)_{w_H}$. These two refractive index increments can be related to each other, in a very good approximation, by

$$(\partial n/\partial c)_\mu = (\partial n/\partial c)_{w_H} - w_H \rho_0^{-1} \zeta (\partial n_0/\partial w_H) \qquad (1)$$

with the introduction of a preferential adsorption parameter ζ defined by[8]

$$\zeta = (\partial g_D/\partial g_S)_{\mu_D} \qquad (2)$$

provided that the solution is incompressible and the molecular weight of the sample is not too low. In eq 2, g_D and g_S denote, respectively, grams of Me_2SO and schizophyllan per gram of water in the solution at the limit of zero polymer concentration, and μ_D is the chemical potential of Me_2SO in the same solution.

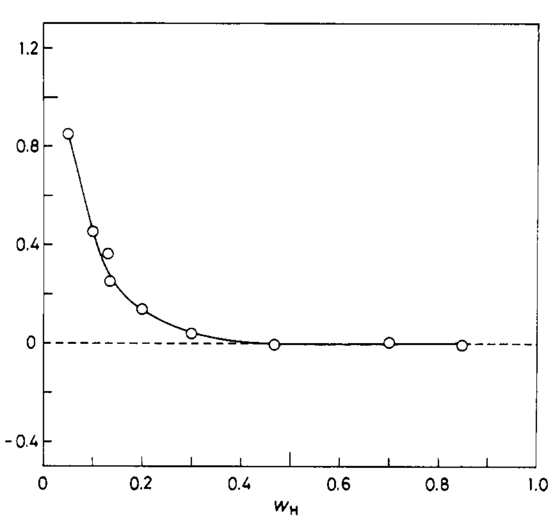

Figure 2. Values of the preferential adsorption parameter for the schizophyllan sample in water + Me_2SO mixtures at 25 °C.

The values of ζ obtained by use of eq 1 are plotted against w_H in Figure 2. In the region of w_H below about 0.40, ζ is positive, implying that schizophyllan interacts preferentially with Me_2SO; note that preferential adsorption does not necessarily mean the binding of solvent molecules onto polymer chains. On the other hand, approximately zero ζ values in the region of $w_H > 0.4$ indicate that neither Me_2SO nor water is adsorbed preferentially on schizophyllan in this composition region.

Recently, Straub and Brant[11] investigated preferential adsorption in the system of water + Me_2SO and amylose, pullulan, and dextran by gel permeation chromatography and found that all these glucans preferentially adsorb water above $w_H \sim 0.32$ and Me_2SO below $w_H \sim 0.32$. The w_H value of 0.32 for $\zeta = 0$ corresponds to the stoichiometric composition of the postulated complex[5] $Me_2SO \cdot 2H_2O$. On the basis of this finding, Straub and Brant conjectured that mixtures of w_H above and below 0.32 contain excess water and excess Me_2SO, respectively, relative to the stoichiometry of the complex and that these excesses are responsible for the characteristic adsorption behavior of the glucans examined. Interestingly, the w_H range in which they found preferential adsorption of Me_2SO is comparable to that we found in this work for schizophyllan. However, it should be noted that Straub and Brant's results are at variance with ours in regard to preferential adsorption of water.

Light Scattering Envelopes. Figure 3, a and b, illustrates the Zimm plots for the schizophyllan sample at $w_H = 0.1335$ and 0.1270. Here, R_θ is the reduced scattering intensity at scattering angle θ and c is the polymer mass concentration. The scattering envelope in Figure 3a is normal, whereas that in Figure 3b is anomalous in that each curve for fixed c has a negative initial slope. The curve for $\theta = 0$ in the latter graph is bent downward, indicating a negative third virial coefficient. This feature too seems to be unusual. Similar anomalies were also found at $w_H = 0.1250$ and 0.1000; at the latter composition the data yielded a normal angular variation at infinite dilution but a concentration dependence at $\theta = 0$, which was still indicative of a negative third virial coefficient.

Since virtually no optical anisotropy was detected for the schizophyllan sample in the mixtures of $w_H = 0.1270$ and 0.1000, the anomalous scattering envelopes in these solvents cannot be attributed to an optical anisotropy effect. Another schizophyllan sample with a molecular weight of 9×10^4 (in Me_2SO at 25 °C) was examined at $w_H = 0.1250$, with a similar anomalous scattering envelope. Hence, the anomalies encountered are not specific to the sample used in this work. Unusual scattering envelopes similar to ours were reported for styrene/methyl methacrylate block copolymers by Utiyama et al.[12] and Tanaka

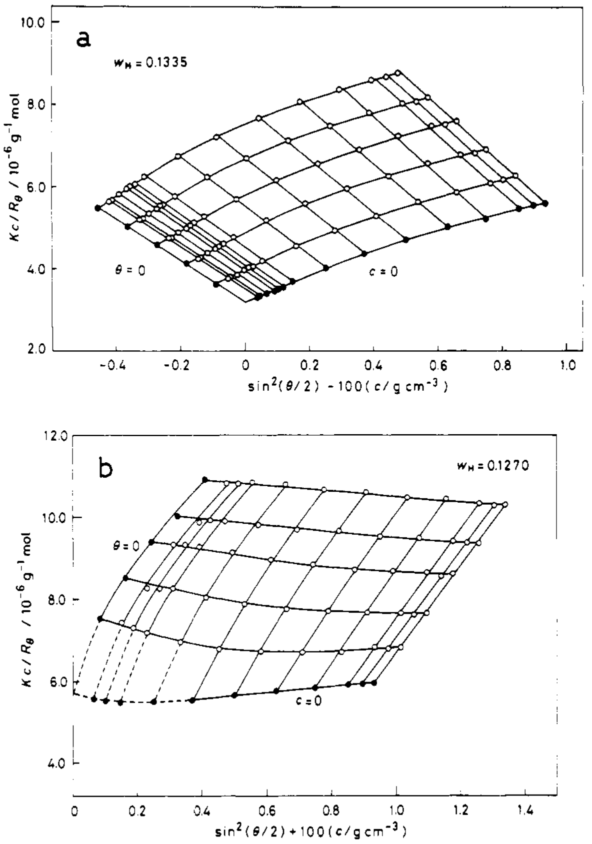

Figure 3. Zimm plots for the schizophyllan sample in the water + Me$_2$SO mixtures of w_H = 0.1335 (a) and 0.1270 (b) at 25 °C.

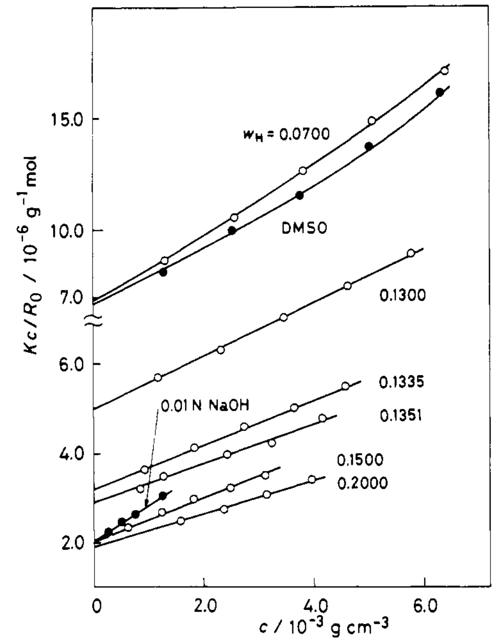

Figure 4. Concentration dependence of Kc/R_0 for the schizophyllan sample in Me$_2$SO, water + Me$_2$SO mixtures, and 0.01 N NaOH at 25 °C.

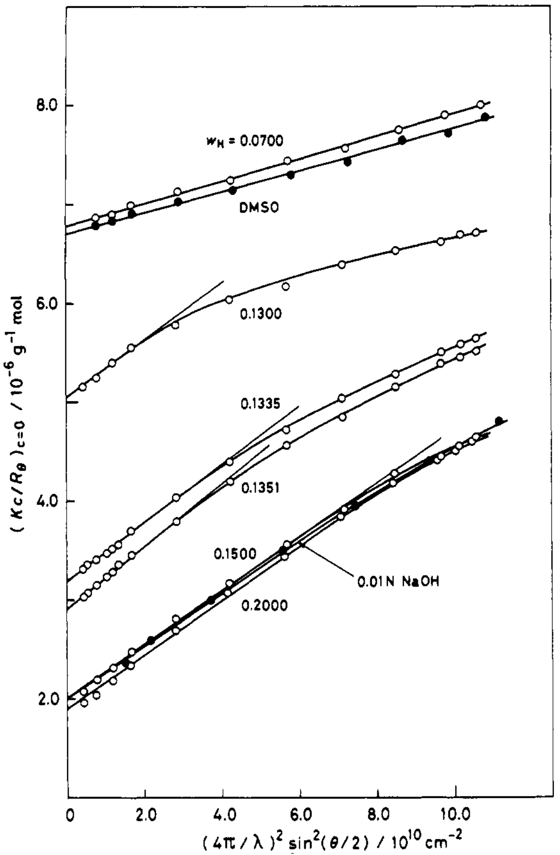

Figure 5. Angular dependence of $(Kc/R_\theta)_{c=0}$ for the schizophyllan sample in Me$_2$SO, water + Me$_2$SO mixtures, and 0.01 N NaOH at 25 °C. λ denotes the wavelength of incident light in solution.

et al.,[13] who ascribed them to intermolecular interference of scattering light. It is not as yet clear to us what was responsible for our anomalous Zimm plots. Leaving its pursuit for future work, we discard the data for w_H = 0.1270 and 0.1250 in the subsequent data analysis.

Figure 4 depicts the concentration dependence of Kc/R_0, the zero-angle value of Kc/R_θ, for the schizophyllan sample in pure Me$_2$SO, mixtures of different w_H, and 0.01 N NaOH. Weight-average molecular weights M_w and light scattering second virial coefficients A_2^{LS} were evaluated from the intercepts and initial slopes of the indicated curves; those in pure Me$_2$SO and the mixture of w_H = 0.0700 were determined by use of the plot of $(Kc/R_0)^{1/2}$ vs. c, since this type of plot was found to be more linear than the Kc/R_0 vs. c plot.

In Figure 5, the angular dependence of $(Kc/R_\theta)_{c=0}$ is displayed. From the slopes of the indicated thin lines z-average mean-square radii of gyration $\langle S^2\rangle_z$ were evaluated.

Composition Dependence of M_w, $\langle S^2\rangle_z^{1/2}$, and A_2^{LS}. The w_H dependence of M_w, $\langle S^2\rangle_z^{1/2}$, and A_2^{LS} is depicted in Figure 6, together with that of [η] determined for the same schizophyllan sample. The M_w value in 0.01 N NaOH is approximately 3 times as large as that in pure Me$_2$SO, which confirms the conclusion of Kashiwagi et al.[7] that the predominant species of schizophyllan in 0.01 N NaOH solutions is a trimer. However, the M_w values in mixtures of w_H between 0.8 and 0.2 are appreciably larger than that expected for the trimer. In the same composition range, $\langle S^2\rangle_z^{1/2}$ and [η] are also larger than the corresponding values in 0.01 N NaOH or in pure water. These results suggest that schizophyllan triple helices associate with one another in solutions of w_H between 0.8 and 0.2. In this connection, a few remarks may be made.

(1) Previously determined [η] for sample S-144-2 in mixtures of w_H ranging from 0.2 to 0.8 were approximately the same as that in pure water.[3] This result differs from the present observation. The discrepancy is presumably due to the difference that the previous data were determined at finite shear rates, while the present data refer to zero shear rate.

(2) For scleroglucan, which is a β-1,3-D-glucan having essentially the same chemical structure as schizophyllan, Yanaki et al.[14] recently observed that [η] in water + Me$_2$SO

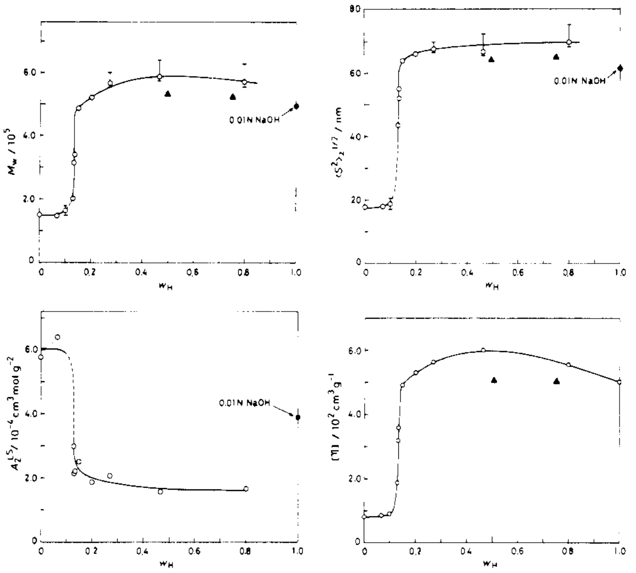

Figure 6. Composition dependence of M_w, $\langle S^2\rangle_z^{1/2}$, A_2^{LS}, and $[\eta]$ for the schizophyllan sample in water + Me_2SO mixtures at 25 °C. Filled triangles, values in water + Me_2SO mixtures containing 0.005 N NaOH.

mixtures of w_H between 0.2 and 0.8 were significantly higher than that in pure water. A more recent study in our laboratory revealed that scleroglucan solutions in the range of w_H between 0.5 and 0.8 were slightly turbid below 20 °C, whereas pure water solutions were transparent in the comparable temperature region. This fact indicates that solubility of scleroglucan is lower in mixtures of w_H from 0.5 to 0.8 than in pure water. Since scleroglucan and schizophyllan are essentially identical in chemical structure, the same should be true for schizophyllan.

(3) Kashiwagi et al.[7] reported that addition of a small amount of NaOH to an aqueous solution of schizophyllan prevents association of the triple helix. We therefore tried light scattering and viscosity measurements, with NaOH added to water + Me_2SO mixtures in such a way that the NaOH concentration was held at 0.005 N. The results are indicated by filled triangles in Figure 6, which come close to the values expected for the molecularly dispersed triple helix of schizophyllan.

(4) We extended viscosity measurements in mixtures containing 0.005 N NaOH to lower w_H. Though not shown here, the result was off the expectation in that $(\ln \eta_r)/c$ (η_r is the relative viscosity) for solutions of w_H = 0.3–0.4 decreased with decreasing c and appeared to approach the value in pure Me_2SO. This behavior indicates that the presence of a small amount of NaOH in water + Me_2SO mixtures not only prevents association of schizophyllan triple helices but even decomposes them when w_H is lowered below 0.4.

In Figure 6, we see that the values of M_w, $\langle S^2\rangle_z^{1/2}$, and $[\eta]$ in the range of w_H between 0.20 and 0.15 are close to those in 0.01 N NaOH or pure water. Thus, in this w_H region, the schizophyllan triple helix should be free from association and molecularly dispersed. What is more important in Figure 6 is the fact that in a very narrow w_H range around 0.13, M_w, $\langle S^2\rangle_z^{1/2}$, and $[\eta]$ all decrease to the values in pure Me_2SO. These decreases in M_w and $\langle S^2\rangle_z^{1/2}$ most directly demonstrate that the schizophyllan triple helix dissociates abruptly to single chains at $w_H \sim 0.13$ and confirm the previous deduction[3] from $[\eta]$ data. It is to be noted that this dissociation is accompanied by an almost discontinuous increase in A_2^{LS}.

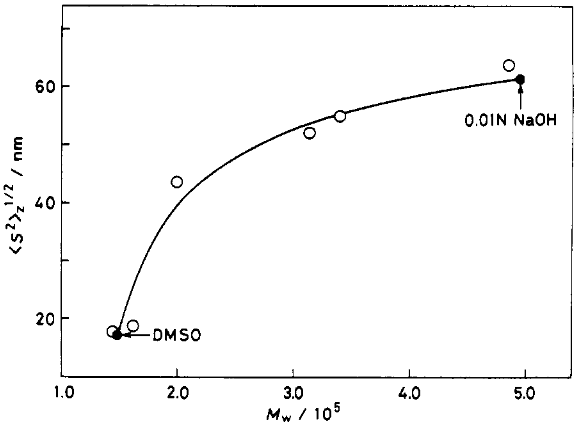

Figure 7. Comparison of the experimental relation (circles) between $\langle S^2\rangle_z^{1/2}$ and M_w with the theoretical one (solid line) predicted by eq 3.

Dissociation Behavior. The observed sharp decreases in M_w and $\langle S^2\rangle_z^{1/2}$ suggest that the schizophyllan triple helix dissociates not through intermediate steps such as partial breaking of helical portions but directly to single chains. If only intact triple helices and single chains coexist in a solution, it can be shown that $\langle S^2\rangle_z$ of the polymer mixture is expressed by

$$\langle S^2\rangle_z = \frac{1}{M_w(M_3 - M_1)}[M_1(M_3 - M_w)\langle S^2\rangle_1 + M_3(M_w - M_1)\langle S^2\rangle_3] \tag{3}$$

where M_3 and M_1 are the molecular weights of the triple helix and the single chain, respectively, and $\langle S^2\rangle_3$ and $\langle S^2\rangle_1$ are the mean-square radii of gyration of the corresponding species. We note that eq 3 holds for a polydisperse sample if M_i (i = 1, 3) and $\langle S^2\rangle_i$ are replaced, respectively, by the weight-average molecular weight and z-average mean-square radius of gyration of the species i.

In Figure 7, the experimental relation between $\langle S^2\rangle_z^{1/2}$ and M_w in mixtures of w_H below 0.2 is compared with the theoretical one calculated from eq 3, with the measured M_w in 0.01 N NaOH and pure Me_2SO as M_3 and M_1 and the corresponding $\langle S^2\rangle_z$ as $\langle S^2\rangle_3$ and $\langle S^2\rangle_1$. The close fit of the curve to the data points substantiates the assumptions underlying the theory and allows us to conclude that the schizophyllan triple helix in isothermal aqueous Me_2SO dissociates directly, i.e., in all-or-none fashion, to single chains as w_H is lowered below about 0.15.

Concluding Remarks

Our light scattering measurements have made it clear that aqueous Me_2SO solutions of schizophyllan at 25 °C comprise only triple helices at w_H above 0.15, only single chains at w_H below 0.1, and these two species in the intermediate region of w_H. The fraction of the trimer species varied sharply from unity to zero as w_H is lowered from 0.15 to 0.10. For the convenience of presentation the region in which this change in trimer fraction occurs is called the transition region. All the present measurements were performed after freshly prepared solutions were left standing at 25 °C until no substantial changes occurred in scattering intensity and viscosity. Hence, one might consider that our experimental data were concerned with equilibrium states of the system at given w_H. We are confident that this was true for the solutions that comprised only triple helices or separated single chains. In other words, it seems certain that the thermodynamically stable form of schizophyllan in aqueous Me_2SO is triple helices at w_H above 0.15 and single chains at w_H below 0.10. However, we have reason to say that the system was not

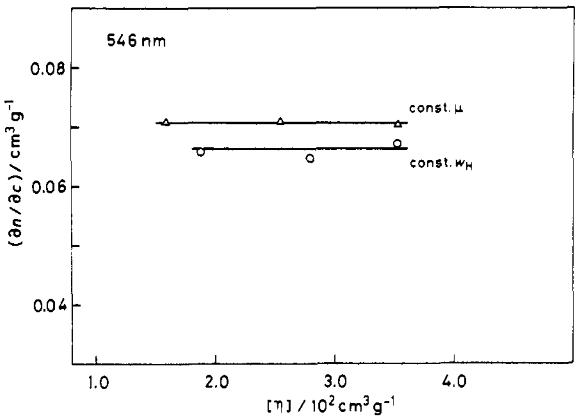

Figure 8. Dependence of $(\partial n/\partial c)_\mu$ and $(\partial n/\partial c)_{w_H}$ on $[\eta]$ determined at 25 °C for heat-treated and untreated schizophyllan solutions of $w_H = 0.1350$.

at equilibrium in the transition region where these two species were found to coexist.

When a solution containing a monomer and its trimer is at thermodynamic equilibrium, the two species must be in the state of association equilibrium, and their relative amounts should vary as the solution is diluted with the solvent. However, this dilution effect was not seen in our light scattering envelopes and viscosity plots.[4] Hence, we can say that coexisting triple helices and single chains in the transition region were not in the state of association equilibrium but an irreversible conversion of one species to the other was occurring in the solution. The probability that three separated chains of schizophyllan happen to bind themselves together in the form of an intact triple helix seems to be very low. In fact, as shown in our previous papers,[3,4] the schizophyllan triple helix is no longer restored once decomposed to single chains either by heating or by changing the solvent composition. Thus, in the transition region, there is virtually no chance that the backward reaction from monomers to trimers takes place, so that what actually occurs should be a continuous and irreversible dissociation of triple helices to single chains. This process will continue until all helices disappear from the solution. The final state represents the equilibrium state of the system at w_H between 0.1 and 0.15.

There arises a question of why, despite the occurring of a continuous decomposition of trimers, stable, reproducible light scattering measurements could be made on solutions in the transition region. Our tentative answer is that this process was proceeding very slowly in these solutions, so that the relative amounts of triple helices and single chains stayed almost unchanged during the time scale of each measurement. The dissociation kinetics of the schizophyllan triple helix is a problem worthy of detailed investigation.

Acknowledgment. We acknowledge with thanks a grant from Taito Co.

Appendix

Irreversible melting of the schizophyllan triple helix in aqueous Me_2SO in the transition region was found by the following observation: $(\ln \eta_r)/c$ of a solution underwent a gradual decrease to a constant value upon heating, but the leveling-off value remained unchanged when the solution was cooled to the initial temperature.[4] This irreversibility implies that cooling brings about no change in the composition of the solution. We know from our previous study[4] that the relative amounts of triple helices and single chains coexisting in the transition region can be varied by heating the solution to different temperatures. Thus, it is possible to prepare a series of isothermal solutions in which w_H is fixed but the relative amounts of triple helices and single chains are different by heating a solution of given w_H to various temperatures and cooling it back to the initial temperature. By taking advantage of this fact, we determined the refractive index increments of the schizophyllan triple helix and single chain in a given water + Me_2SO mixture at 25 °C.

A schizophyllan solution of $w_H = 0.1350$ was "equilibrated" at 25 °C, heated at 50 °C for 1 h or at 70 °C for 10 min, and then cooled to 25 °C. The heat-treated solution and the original untreated solution were dialyzed against the mixed solvent of $w_H = 0.1350$ at 25 °C and subjected to viscosity and differential refractive index measurements. These solutions were also examined without dialysis.

The results are illustrated in Figure 8. Both $(\partial n/\partial c)_\mu$ and $(\partial n/\partial c)_{w_H}$ are seen to be independent of $[\eta]$, a quantity related closely to the amount of triple helices relative to that of single chains present in a given solution. Thus, we can conclude that the specific refractive index increments of the triple helix and the single chain in the mixed solvent of $w_H = 0.1350$ at 25 °C are equal.

Registry No. Dimethyl sulfoxide, 67-68-5; schizophyllan, 9050-67-3.

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