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Interfacial Tension between Coexisting Isotropic and Cholesteric Phases for Aqueous Solutions of Schizophyllan

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ABSTRACT: The interfacial tension γ between the coexisting isotropic and cholesteric phases of aqueous solutions of a rigid triple-helical polysaccharide, schizophyllan, was determined by the sessile drop method, as a function of the polymer molecular weight. The values of γ are almost inversely proportional to the molecular weight of schizophyllan in accordance with theories for solutions of hard rods, but the experimental absolute values are much larger than the theoretical ones. This disagreement may be ascribed to the polydispersity in the molecular weight of schizophyllan samples used and also the attractive interaction among schizophyllan triple helices. Schizophyllan triple helices align parallel to the isotropic−cholesteric interface in the cholesteric phase near the interface, and this alignment direction agrees with the theoretical prediction for hard-rod systems.

Interfacial properties are essential to determine the morphology and properties of phase-separating systems.[1] For lyotropic polymer liquid crystal systems, the understanding of interfacial properties is less advanced than that of bulk properties,[2] and thus we are recently undertaking a series of studies on interfacial properties of such systems.

In the previous studies, we[3,4] investigated the interfacial tension γ between the coexisting isotropic and nematic phases in toluene solutions of a semiflexible polymer, poly(*n*-hexyl isocyanate) (PHIC), and found that γ of this system is almost independent of the polymer molecular weight. This molecular weight independence differs from the theoretical prediction of the inversely proportional molecular weight dependence of γ for solutions of hard rods,[5−7] indicating a strong effect of the polymer chain flexibility on γ.

In the previous studies, we also found that PHIC molecules tend to align parallel to the isotropic−nematic interface in the nematic phase near the interface, in accordance with the theoretical prediction for hard-rod systems.[5−7] This tendency determines the molecular alignment in phase-separating systems of liquid-crystalline polymers.[8−10]

In the present study, we have extended the study of the interfacial tension and molecular alignment to a more stiff polymer, a triple-helical polysaccharide schizophyllan. Aqueous solutions of this polymer undergoes a phase separation into isotropic and cholesteric phases within a narrow polymer concentration range, and the phase behavior has already been studied extensively by Itou et al.[11−13] Their interfacial properties are compared with the previous results for the isotropic−nematic interface in PHIC solutions and use to test the theoretical predictions.[5,7]

Experimental Section

Samples. A sonicated schizophyllan sample was kindly supplied by Taito Co. This original sample was divided into four fractions by fractional precipitation with water as the solvent and acetone as the precipitant,[14] and the second fraction was further divided into three fractions. Then, the middle fraction of the second generation was further divided into three fractions by using the isotropic−cholesteric phase separation,[12] and the middle one, named T222, was chosen for the phase separation experiment and the interfacial tension measurement. In addition to this fraction, three fractionated schizophyllan samples, JA162, JB162, and JB122, were selected from our stock to use for the same experiments. Those three samples were also fractionated ones by fractional precipitation and isotropic−cholesteric phase separation just like sample T222. The weight-average molecular weight M_w and the ratio of the *z*-average molecular weight M_z to M_w of each sample were determined by sedimentation equilibrium following the established procedure.[14] The results obtained are listed in Table 1, along with the contour length L and the numbers of Kuhn's statistical segments N calculated from M_w. The values of N indicate that the conformations of the present schizophyllan samples range from nearly rodlike to a weakly bending one. The values of M_z/M_w indicate that the molecular weight distributions of the schizophyllan samples used are not as narrow as those of poly(*n*-hexyl isocyanate) (PHIC) samples used in the previous interfacial tension study ($M_w/M_n \leq 1.06$).[4]

Phase Separation Experiments. A biphasic test solution was prepared by mixing a schizophyllan sample with water in a test tube and stirring the mixture by a magnetic chip for 1−2 days in a 25 °C air bath. Each solution was centrifuged at 4000 rpm at 25 °C in a Sorval RC centrifuge to achieve a complete phase separation, and the coexisting isotropic and cholesteric phases were separately taken using pipets. An aliquot of each separated solution was freeze-dried to determine the binodal polymer concentration, and then each dried sample was redissolved in water to determine the intrinsic viscosity at 25 °C. In the following, the binodal concentration and intrinsic viscosity determined for the isotropic (cholesteric) phase will be denoted as c_I (c_A) and $[\eta]_I$ ($[\eta]_A$), respectively. The remaining isotropic and cholesteric solutions were used for interfacial tension measurements.

Interfacial Tension Measurements. The interfacial tension between coexisting isotropic and cholesteric phases for aqueous solutions of schizophyllan was determined at 25 °C by the sessile drop method. The sessile drop of the cholesteric

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Table 1. Characteristics of Schizophyllan Samples Used

sample	$M_w/10^4$ [a]	M_z/M_w [a]	L/nm [b]	N [b]
JB162	8.47	1.3	39	0.099
T222	15.6	1.3	73	0.18
JA162	22.2	1.3	103	0.26
JB122	26.0	1.2	121	0.30

[a] Determined by sedimentation equilibrium for aqueous solutions. [b] Calculated from M_w using the wormlike chain parameters, $M_L = 2150$ nm^{-1} and $q = 200$ nm, for schizophyllan in 25 °C water.[17]

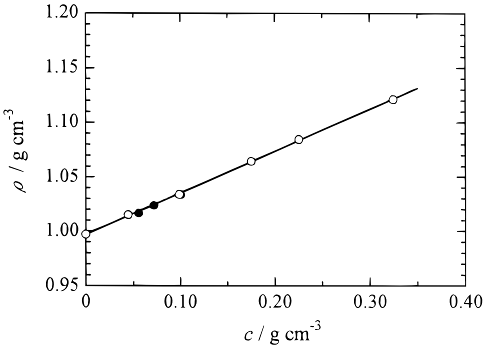

Figure 1. Concentration dependence of the density of aqueous schizophyllan solutions at 25 °C: (○) data of the present work; (●) data of Van.[16]

phase was formed on the bottom of a glass cuvette containing the coexisting isotropic phase using a microsyringe. The detailed procedure was just similar to that of the pendant drop method[15] previously applied to measure the isotropic−nematic interfacial tension for toluene solutions of poly(n-hexyl isocyanate) (PHIC), which was described in the previous paper.[3]

Density Measurements. Densities ρ of aqueous solutions of schizophyllan were measured at 25 °C as a function of the schizophyllan concentration using a Lipkin-Davison-type pycnometer with a 5 cm^3 capacity. Figure 1 shows the plot of ρ against c over a wide concentration range from isotropic through cholesteric phase region, where c was calculated from the polymer weight fraction w multiplied by ρ. The unfilled and filled circles represent the data obtained in the present study and by Van,[16] respectively. Both data points follow a straight line and exhibit no discontinuity at the isotropic−cholesteric phase boundaries.

Polarizing Microscopic Observation of the Interface. A biphasic schizophyllan solution was placed into a drum-shaped cell with a 10 mm diameter and 2 mm thickness and centrifuged at 3000 rpm for 2−4 h to achieve complete phase separation. The interfacial region in the cell was observed by a polarizing microscope (Olympus BHS-P) under the crossed polar condition with or without a compensator with the retardation of 530 nm to determine the direction of the director in the cholesteric phase near the interface.

Results and Discussion

Isotropic−Cholesteric Binodal Concentrations. Table 2 summarizes the results of the phase separation experiments for aqueous solutions of four schizophyllan samples. Figure 2a compares our results of the isotropic−cholesteric binodal concentrations c_I and c_A with Itou et al.'s results[11] for the same system. Both the present and Itou et al.'s data of c_I and c_A are fairly close to the corresponding theoretical solid curve calculated by the scaled particle theory for solutions of wormlike hard-spherocylinders.[2] Here the theory uses the molecular parameters determined previously for schizophyllan in 25 °C water:[2,17] the persistence length $q = 200$ nm, the molar mass per unit contour length $M_L = 2150$ nm^{-1}, and the hard-core diameter $d = 1.68$ nm.[18] However, the agreement between the theory and experiment is worse in c_A than in c_I.

The broken curves in Figure 2a show the theoretical values for c_I and c_A calculated by the scaled particle theory for solutions of *straight* hard-spherocylinders with $M_L = 2150$ nm^{-1}, $d = 1.68$ nm, and $q = \infty$. The disagreement of this theory with the experimental results is gradually enhanced with increasing the schizophyllan molecular weight, which demonstrates the importance of the chain flexibility on the isotropic−cholesteric binodal concentrations even for such a rigid polymer as schizophyllan.

Figure 2b compares the experimental phase gap $c_A - c_I$ with the theoretical results. The experimental data points of the present study and Itou et al.[11] deviate upward from the solid curve of the scaled particle theory for wormlike hard-spherocylinders. This deviation may come from the polydispersity in the molecular weight of the schizophyllan samples used; it is known that the polydispersity enlarges the biphasic region.[2] As demonstrated in the previous paper,[4] the same theory can accurately predict the phase gap for toluene solutions of poly(n-hexyl isocyanate) (PHIC) where the sample polydispersity was much narrower than for the present schizophyllan samples (cf. Experimental Section). The phase gap calculated from the scaled particle theory for straight hard-spherocylinders (the broken curve in Figure 2b) looks closer to the experimental results. However, this apparent improvement does not necessarily justify the neglect of the chain-flexibility effect, because the polydispersity of the samples also enlarges the phase gap.

Table 2 lists the intrinsic viscosities $[\eta]_I$ and $[\eta]_A$ in water for the schizophyllan samples recovered from the coexisting isotropic and cholesteric phases, respectively, and the viscosity-average molecular weights $M_{v,I}$ and $M_{v,A}$ estimated from $[\eta]_I$ and $[\eta]_A$, respectively, using the $[\eta]$−molecular weight relation of Yanaki et al.[17] For all the schizophyllan samples examined, $M_{v,A}$ is larger than $M_{v,I}$. This demonstrates the molecular weight fractionation taking place in the schizophyllan samples at the phase separation, where higher molecular weight components tend to distribute in the coexisting cholesteric phase in excess of lower molecular weight components.[2]

Molecular Alignment at the Interface. The isotropic−cholesteric interfacial region was observed by inserting a compensator with the retardation of 530 nm oriented at 45° to the direction of crossed polarizers. When the interfacial plane was parallel to the azimuth of vibration of the fast ray in the compensator, a subtraction color was observed at the cholesteric phase near the interface. This indicates that the refractive index of the cholesteric phase parallel to the interface is larger than that normal to the interface.[19] From the birefringence of the cholesteric layer[20] and also electric birefringence measurements,[21] the schizophyllan triple helix is known to be positively birefringent, so that the above observation indicates that schizophyllan triple helices should be parallel to the interface in the cholesteric phase near the interface.

Figure 3 shows a polarizing micrograph of a biphasic aqueous schizophyllan solution equilibrated at 4 °C for a long time,[22] under the crossed polar condition with the compensator. The upper part with the interference color of the retardation 530 nm is the isotropic phase, and the lower part with a fingerprint pattern is the cholesteric phase. In the vicinity of the interface, the

Table 2. Results of Phase Separation Experiments and Interfacial Tension Measurements for Aqueous Schizophyllan

	original solution		isotropic phase			cholesteric phase			
sample	c/g cm^{-3}	$[\eta]$/cm^3 g^{-1}	c_I/g cm^{-3}	$[\eta]_I$/cm^3 g^{-1}	$M_{v,I}/10^4$	c_A/g cm^{-3}	$[\eta]_A$/cm^3 g^{-1}	$M_{v,A}/10^4$	$\gamma/10^{-3}$ N m^{-1}
JB162	0.339	43.0	0.245	31.5	8.4	0.342	51.0	11.4	0.1025
T222	0.202	101	0.187	91.6	15.4	0.223	115	18.1	0.0387
JA162	0.161	170	0.153	161	21.5	0.182	240	28.0	0.0276
JB122	0.152	190	0.139	165	22.0	0.164	212	26.5	0.0239

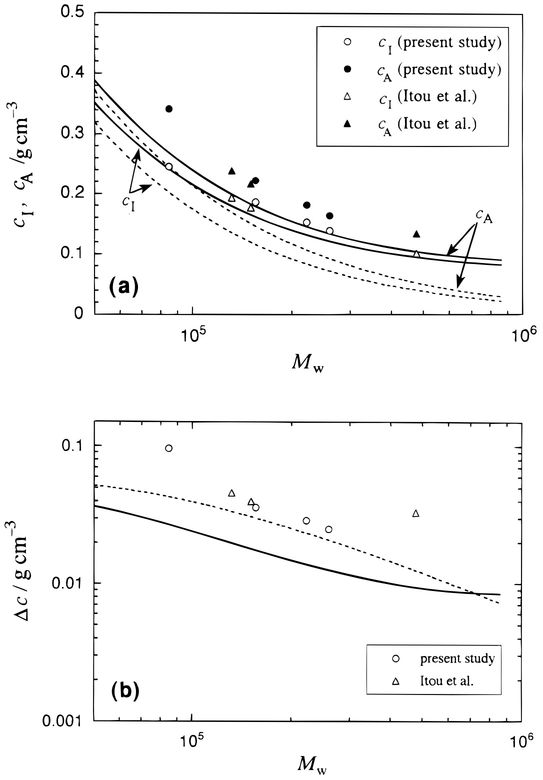

Figure 2. Molecular weight dependencies of (a) the isotropic−cholesteric binodal concentrations c_I and c_A and of (b) the phase gap $\Delta c \equiv c_A - c_I$ for aqueous schizophyllan solutions at 25 °C: (○, ●) data of the present work; (△, ▲) data of Itou et al.;[11] solid curves, calculated by the scaled particle theory (SPT) for hard wormlike spherocylinders with the persistence length q = 200 nm, the molar mass per unit contour length M_L = 2150 nm^{-1}, and the hard-core diameter d = 1.68 nm;[2] broken curves, calculated by the SPT for straight hard-spherocylinders with M_L = 2150 nm^{-1} and d = 1.68 nm.

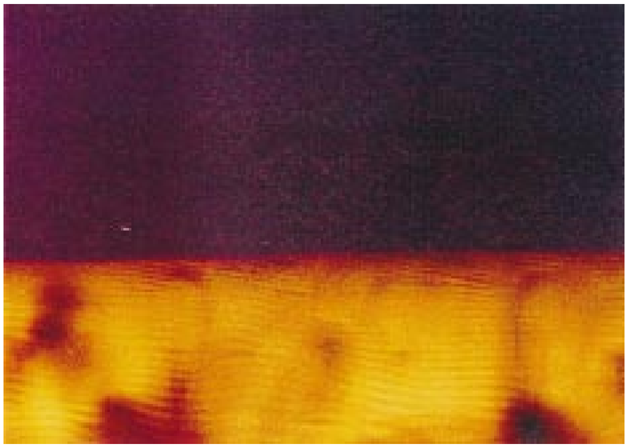

Figure 3. Polarizing micrograph of a biphasic aqueous solution of a schizophyllan sample with a viscosity-average molecular weight of 13.1 × 10^4, near the isotropic−cholesteric interface; the average polymer concentration = 0.243 g/cm^3, temperature = 4 °C.

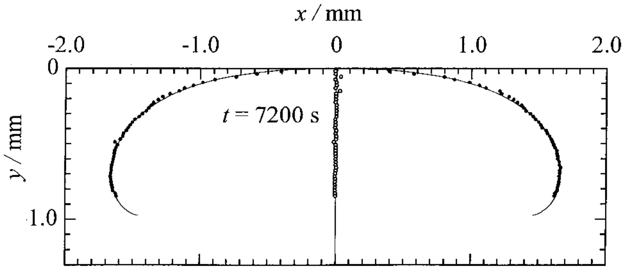

Figure 4. Meridian curve for a sessile drop of the cholesteric phase formed in the coexisting isotropic phase for an aqueous solution of schizophyllan sample JB162 at 25 °C: filled circles, experimental data; curve, theoretical result obtained by least-squares regression; unfilled circles, midpoints of horizontal segments cut by the experimental meridian curve.

bright and dark lines in the cholesteric phase align almost parallel to the interface, indicating that the cholesteric axis is perpendicular to the interface. This is consistent with the conclusion from the above retardation measurements that the schizophyllan molecules align parallel to the interface.

The parallel alignment of polymer molecules was also observed in nematic solutions of PHIC near the isotropic−nematic interface[3] and agrees with the prediction of theories for the isotropic−nematic interface of rodlike polymer solutions.[7,23]

Interfacial Tension. Figure 4 shows an example of the meridian curve measured for a sessile drop of a cholesteric phase of aqueous schizophyllan formed in the coexisting isotropic phase. Here, the x and y axes are chosen to coincide with the tangent and normal lines at the apex of the drop, respectively. The midpoints of horizontal segments cut by the meridian curve, indicated by the small unfilled circles in Figure 4, are on the y axis, which guarantee the proper choice of the x and y axes. By fitting the theoretical meridian curve calculated by the Young−Laplace equation to the experimental points,[3] we determined the radius of the curvature r_0 at the drop apex and the dimensionless shape factor β, both included in the Young−Laplace equation.

From the results of r_0 and β, the interfacial tension γ was calculated by the equation[24,25]

$$\gamma = (r_0^2/\beta)g\Delta\rho \tag{1}$$

where g is the gravitational acceleration and $\Delta\rho$ is the density difference between the coexisting two phases. For each solution, $\Delta\rho$ was estimated from the binodal concentrations c_I and c_A determined by the phase separation experiments (cf. Table 2) using the density−concentration relation shown in Figure 1.[3]

The picture of the sessile drop of the cholesteric phase was taken at different times t elapsed after forming the drop into the coexisting isotropic solution, and r_0, β, and then γ were determined at different t. As shown in Figure 5, γ is almost constant in the examined t range, demonstrating that the sessile drop of each schizophyllan cholesteric phase reaches its equilibrium shape. The

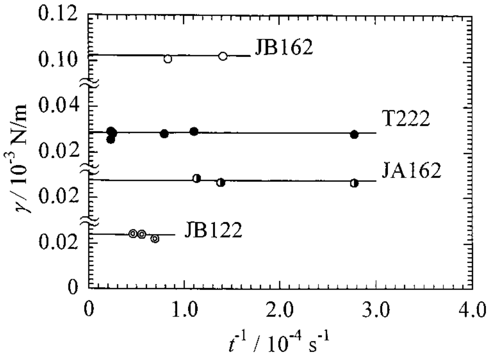

Figure 5. Plots of γ against t^{-1} for aqueous solutions of four schizophyllan samples.

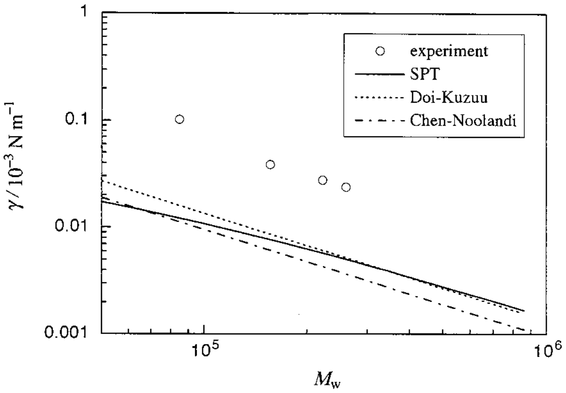

Figure 6. Molecular weight dependence of γ for aqueous solutions of schizophyllan: circles, experimental data; solid curve, the scaled particle theory;[4] dotted curve, Doi−Kuzuu theory;[5] dash−dotted curve, Chen−Noolandi theory.[7]

equilibrium γ for each schizophyllan sample was evaluated by averaging the results at different t, shown in Figure 5.

Figure 6 plots the equilibrium γ against the weight-average molecular weight M_w of the schizophyllan samples, double logarithmically. The data points seem to follow a line with the slope of ca. −1, though the molecular weight range examined is not wide enough. This molecular weight dependence of γ is in contrast with the previous results[4] of isotropic−nematic interfacial tension for solutions of a more flexible polymer poly(*n*-hexyl isocyanate) (PHIC), which are almost independent of the PHIC molecular weight.

In the previous study,[4] we have improved the theory of Doi and Kuzuu[5] for the isotropic−nematic interface in solutions of hard rods by incorporating the third and higher virial terms as well as the contribution of the non-crossed configuration among rods to the free energy, using the scaled particle theory for straight hard-spherocylinders. Now, we compare this improved theory with experimental γ for schizophyllan solutions. When the molecular parameters M_L and d are chosen to be 2150 nm^{-1} and 1.68 nm, respectively, as in the case of the binodal concentration calculations (cf. Figure 2), the theory provides the solid curve in Figure 6. Although the theory predicts a molecular weight dependence similar to the experimental, the theoretical curve is far below the experimental data points in the same figure. The dash−dotted curve in the figure represents the theory of Chen and Noolandi[7] for the isotropic−nematic interfacial tension for hard rodlike polymer solutions, which is superior to the Doi−Kuzuu theory by calculating γ without any specific assumptions on the interfacial profiles (but does not consider the effects of the higher virial terms or of the non-crossed configuration). This curve is also far below the data points.

In the calculation of γ, the scaled particle theory for straight hard-spherocylinders neglects the effects of (1) the chain flexibility, (2) the polydispersity in molecular weight, and (3) soft attractive interactions. As shown in Figure 2b, the chain flexibility decreases the phase gap $c_A - c_I$ and thus makes the change in the polymer concentration within the interfacial region less drastic. Therefore, it is expected that this effect diminishes the interfacial energy or γ, and the disagreement between the theory and experiment is further enhanced. Moreover, since the schizophyllan samples used in this study take a nearly rodlike conformation (cf. the N values in Table 1), the chain flexibility effect may not be responsible for the disagreement in γ between the theory and experiment for the aqueous schizophyllan system.

As mentioned above, the polydispersity enlarges the phase gap $c_A - c_I$ (cf. Figure 2b) and may increase γ. In fact, we have recently found that toluene solutions containing two PHIC samples with different molecular weights have larger interfacial tensions, corresponding to larger phase gaps, than toluene solutions with a single PHIC sample.[26] Therefore, the inclusion of the polydispersity effect in the theoretical calculation of γ is expected to improve the disagreement between theory and experiment. Such a theoretical improvement will be attempted along with the comparison with the experimental data in the forthcoming paper.[26]

Previously, Sato et al.[27] analyzed data of the second virial coefficient and osmotic compressibility for some stiff-chain polymer solutions [aqueous solutions of schizophyllan, hexane and dichloromethane solutions of PHIC, and dimethylformamide solutions of poly(γ-benzyl L-glutamate)] to estimate the strength of the soft attractive interaction among stiff-chain polymers. The results indicated that the attractive interaction of schizophyllan in water is appreciably stronger than other stiff-chain polymers examined (especially the interaction of the chain-end portion). We can show that the isotropic attractive interaction between polymer chains enlarges the phase gap $c_A - c_I$,[28] so that we may regard it as another factor inducing the disagreements between theory and experiment both in Figure 2b and in Figure 6.

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References and Notes

(1) *Physics of Polymer Surfaces and Interfaces*; Sanchez, I. C., Ed.; Butterworth-Neinemann: Boston, 1992.
(2) Sato, T.; Teramoto, A. *Adv. Polym. Sci.* **1996**, *126*, 85.
(3) Chen, W.-L.; Sato, T.; Teramoto, A. *Macromolecules* **1996**, *29*, 4283.
(4) Chen, W.-L.; Sato, T.; Teramoto, A. *Macromolecules* **1998**, *31*, 6506.
(5) Doi, M.; Kuzuu, N. *J. Appl. Polym. Sci., Appl. Polym. Symp.* **1984**, *41*, 65.
(6) McMullen, W. E. *Phys. Rev. A* **1988**, *38*, 6384.
(7) Chen, Z. Y.; Noolandi, J. *Phys. Rev. A* **1992**, *45*, 2389.
(8) Meyer, R. B. In *Polymer Liquid Crystals*; Ciferri, A., Krigbaum, W. R., Meyer, R. B., Eds.; Academic Press: New York, 1982; Chapter 6.
(9) Donald, A. M.; Windle, A. H. *Liquid Crystalline Polymers*; Cambridge University Press: Cambridge, 1992.

(10) Ogawa, E.; Sato, T.; Teramoto, A. *Polym. Prepr., Jpn.* **1992**, *41*, 1409.

(11) Itou, T.; Van, K.; Teramoto, A. *J. Appl. Polym. Sci., Appl. Polym. Symp.* **1985**, *41*, 35.

(12) Itou, T.; Teramoto, A. *Polym. J.* **1984**, *16*, 779.

(13) Itou, T.; Teramoto, A. *Macromolecules* **1984**, *17*, 1419.

(14) Norisuye, T.; Yanaki, T.; Fujita, H. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 547.

(15) For aqueous schizophyllan, the pendant drop of the cholesteric phase formed in the coexisting isotropic phase was not stable and easily fell down from the outlet of a microsyringe. Therefore, we did not adopt the pendant drop method for this system.

(16) Van, K. Ph.D. Thesis Thesis, Osaka University, 1984.

(17) Yanaki, T.; Norisuye, T.; Fujita, H. *Macromolecules* **1980**, *13*, 1462.

(18) The value of *d*, which was previously estimated from the second virial coefficient and osmotic compressibility data for aqueous schizophyllan (=1.75 nm),[27] is slightly larger than the *d* value of 1.68 nm, estimated from the specific volume. If we use the former value of *d*, the agreement between the theory and experiment for the binodal concentrations becomes slightly worse.

(19) Slayter, E. M.; Slayter, H. S. *Light and Electron Microscopy*; Cambridge University Press: Cambridge, 1992.

(20) Van, K.; Asakawa, T.; Teramoto, A. *Polym. J.* **1984**, *16*, 61.

(21) Jinbo, Y.; Varichon, L.; Sato, T.; Teramoto, A. *J. Chem. Phys.*, in press.

(22) It is known that the cholesteric pitch of aqueous schizophyllan abruptly enlarges below ca. 5 °C,[29] so that the fingerprint pattern observation becomes easy under such a condition.

(23) Doi, M.; Kuzuu, N. *J. Appl. Polym. Sci., Polym. Symp.* **1985**, *41*, 65.

(24) Andreas, J. M.; Hauser, E. A.; Tucker, W. B. *J. Phys. Chem.* **1938**, *42*, 1001.

(25) Rotenberg, Y.; Boruvka, L.; Neumann, A. W. *J. Colloid Interface Sci.* **1983**, *93*, 169.

(26) Chen, W.-L.; Sato, T.; Teramoto, A., to be submitted.

(27) Sato, T.; Jinbo, Y.; Teramoto, A. *Macromolecules* **1997**, *30*, 590.

(28) Kasabo, F.; Sato, T.; Teramoto, A., unpublished work.

(29) Asakawa, T.; Van, K.; Teramoto, A. *Mol. Cryst. Liq. Cryst.* **1984**, *116*, 129.

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