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Differences in Rheological Properties of Solutions of Plant and Bacterial Cellulose in LiCl/*N,N*-Dimethylacetamide

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Differences in molecular properties of celluloses from different biological origins were investigated chiefly in terms of the rheological properties of their solutions in 8 wt % LiCl/*N,N*-dimethylacetamide (DMAc). Cotton linter (CC) and dissolving pulp (DP) were used as cellulose samples derived from plant, and a cellulose from *Acetobacter xylinum* was also used as a bacterial cellulose (BC). For the three kinds of cellulose solutions, the values of $\eta_0 - \eta_s$ (η_0 : zero shear rate viscosity of solution, η_s : solvent viscosity) were in proportion to the weight fraction of polymer, ϕ_w , in the dilute region. On the other hand, they were in proportion to ϕ_w^4 for the CC and the DP solutions and ϕ_w^3 for the BC solution in the semidilute or concentrated region. This ϕ_w -dependence of $\eta_0 - \eta_s$ shows that CC and DP, celluloses from plants, behave as a flexible polymer and that BC behaves as a rodlike polymer, according to several molecular theories. Plateau modulus, G_N , was in proportion to ϕ_w^2 for the CC solution, signifying that network structure by entanglement was formed in the CC solution, as is often observed for solutions of flexible synthetic polymers. On the other hand, the concentrated solution of BC showed the typical small-angle X-ray scattering (SAXS) profile of two-phase systems, which can be well approximated by Debye-Bueche equation. This fact indicates that the structure of the BC solution apparently differs from the network structure.

Key Words: Cellulose solution/ LiCl·DMAc/ Rheological properties/ Bacterial cellulose/ Cotton cellulose

1. INTRODUCTION

Recently, many researches have been made to find more effective and innovational ways of utilizing natural polymers in terms of not only industrial application but also scientific interest. Cellulose, which is representative of natural polymers, is a linear polysaccharide consisting of 1,4-linked β -D-anhydroglucopyranose. Great amounts of cellulose are produced chiefly by plants, belonging to the vegetable kingdom. The production of cellulose, however, is not confined to the vegetable kingdom. Bacterial cellulose, produced by a kind of bacteria (e.g., *Acetobacter xylinum*) in the Monera kingdom, has long been known.¹⁾ Tunicin is generally regarded as a form of cellulose^{2),3)} and now called tunicate cellulose (TC) which means a cellulose produced by a kind of marine animal in the *Tunicate* class, ascidians.

To make an effective use of cellulose as a resource of polymer materials, we should have extensive and profound knowledge on the molecular properties of cellulose. For this

purpose, many researchers have investigated on the solution properties of cellulose. Earlier, using cadoxen as a solvent, some researchers made a rigorous investigation in terms of dilute solution properties.⁴⁾ Kamide et al.^{5),6)} have made systematic researches about solubility of cellulose in such alkaline aqueous solutions as NaOH and LiOH systems. However, the advancement of the investigation on the solution properties of cellulose is relatively slower due to the lack of convenient solvent. Around 1980, a new solvent for cellulose, mixture of *N,N*-dimethylacetamide (DMAc) and lithium chloride (LiCl), was discovered by McCormick.⁷⁾ This solvent is a good solvent, colorless and lower toxicity than many other solvents such as cadoxen, which is containing heavy metal ions. In addition, the resulting solution of cellulose is quite stable. McCormick et al. have already made many fundamental studies including the preparation of a number of derivatives⁸⁾ and dilute solution properties.⁹⁾ However, many other solution properties of cellulose in LiCl/DMAc, especially rheological properties in semidilute and concentrated regions, still remain hardly revealed. Moreover, differences in solution properties of celluloses from various biological sources have never been discussed to the best of our

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knowledge. It may be due to the prevalent belief that all celluloses are identical in the molecular properties in a dissolved state, including higher order structures, irrespective of their origins and different biosynthetic pathway.

In the previous paper,¹⁰⁾ we have reported that some differences were observed in the solution properties and the solubility to 8 wt % LiCl/*N,N*-dimethylacetamide (DMAc) among celluloses from plants, bacteria and ascidians. In the present study, we discuss the difference in the solution properties in the semidilute and concentrated region mainly in terms of the rheological properties, using cotton linter (CC) and dissolving pulp (DP) as cellulose samples from plant and bacterial cellulose (BC) and also discuss the molecular conformation of BC in the solution.

2. EXPERIMENTAL SECTION

2.1 Materials and Preparation of Solutions

The cellulose samples used in this study were from several different origins. Softwood dissolving pulp (DP) manufactured by Nippon Paper Industries Co., Ltd. and cotton linter cellulose (CC) were native cellulose samples derived from plant. Bacterial cellulose (BC) provided by Bio-polymer Research Co., Ltd. was from *Acetobacter Xylinum* subsp. *sacrofermentans* BPR2001 strain.¹¹⁾ All the samples were not unfractionated, and no information about the polydispersity of the molecular weight is available.

McCormick et al.⁹⁾ has reported two methods of the dissolution of cellulose in LiCl/DMAc solution. One of these methods requires pretreatment of cellulose samples by solvent-exchange. First, each sample was dispersed in distilled water for 24 hours at room temperature. After filtration, it was immersed into acetone for 48 hours and subsequently into DMAc for 24 hours at room temperature. The sample was vacuum-dried for ca. 48 hours at 60°C after the solvent-exchange procedure. The dried sample was dissolved in 8 wt % LiCl/DMAc at room temperature. The homogeneous solution was obtained in a few days for DP, in a few weeks for BC and in a month for CC.

2.2 Scattering Measurements

Low-angle laser light scattering photometer KMX-6 (Chromatix Co., USA) and light scattering photometer SLS-5000HM (Otsuka Electronics Co., Ltd., Osaka) were used for static light scattering measurements. Each photometer has a He-Ne laser source with a wavelength of 633 nm. The sample solutions were filtrated by membrane filters with a pore size of

0.2 μm several times before the measurement. The value of specific refractive index increment, dn/dc , used is 0.0575 ml/g, which is given by McCormick and coworkers.⁹⁾

Small angle X-ray scattering (SAXS) measurement was carried out using a 6 m point-focusing SAXS camera at High Intensity X-ray Laboratory in Kyoto University.¹²⁾ The CuK α line, $\lambda = 0.154$ nm and two-dimensional position sensitive proportional counter were used for SAXS measurements. The length from the sample to the detector is 1.61 m. Isotropic two dimensional scattering intensity was circular averaged and the scattering intensity of sample solution was corrected by subtracting the intensity of background.

2.3 Measurements for Viscoelastic Properties and Limiting Viscosity Number

A cone-plate type rheometer Rheosol-G2000 (UBM Co., Ltd., Kyoto) was used for dynamic viscoelasticity and steady flow measurements. Radii of the cone and plate were 50 mm and the angle of the cone was 2°. A reservoir was equipped for the rheometer to prevent the sample drying during the measurements. The dynamic viscoelasticity measurements were performed at various temperatures ranging from -15 to 80°C. All the data were reduced to the data at a reference temperature of 30°C by the time-temperature superposition principle.¹³⁾

Limiting viscosity number was determined with an Ubbelohde type capillary viscometer. All measurements were made in a constant-temperature bath regulated at 30°C.

3. RESULTS AND DISCUSSION

3.1 Characterization of Cellulose Molecules

Before the rheological measurements, we first performed simple characterization of cellulose molecules by limiting viscosity number and static light scattering (SLS) measurements. When polymer concentration in g/ml, c , is sufficiently small, η_{sp}/c and $(\ln \eta_r)/c$ are in proportion to c , where $\eta_r (= \eta_0/\eta_s$; η_0 : zero shear rate viscosity of solution, η_s : solvent viscosity) and $\eta_{sp} (= \eta_r - 1)$ denote the relative viscosity and the specific viscosity, respectively. Both plots of η_{sp}/c and $(\ln \eta_r)/c$ versus c give two straight lines with an identical intercept at $c = 0$, which corresponds to the limiting viscosity number, $[\eta]$. The Huggins constant, k' , can also be estimated independently from the slopes of the straight lines. Fig.1 shows the c -dependence of η_{sp}/c and $(\ln \eta_r)/c$ for the CC, the BC, and the DP solutions in 8 wt % LiCl/DMAc. For each cellulose solution, the extrapolated intercepts at $c = 0$ of both

Fig. 1 Concentration dependence of η_{sp}/c (open symbols) and $(\ln \eta_t)/c$ (filled symbols) for the CC (circle and triangle), BC (square) and DP (diamond) solutions in 8 wt % LiCl/DMAc at 30°C. For CC solution, the circle symbols are the results from the first measurement; and the triangles are the results from the second measurements performed 30 days after the first measurement. Intercept of each line at $c = 0$ corresponds to $[\eta]$.

plots were agreed within the experimental error. This agreement shows the accuracy of the measurements. The figure also shows the results obtained from the second measurement (triangles, dotted lines) carried out for the CC solution again 30 days after the first measurement (circles, solid lines). The value of $[\eta]$ obtained from the second measurement was exactly equal to that from the first. This indicates that CC molecules do not degrade in the solution at least for a month; that is, the solutions of cellulose in 8 wt % LiCl/DMAc are quite stable, as is generally accepted.

Other dilute solution properties were investigated with the static light scattering measurements. For a dilute solution, the reciprocal reduced scattered intensity, Kc/R_θ , at the scattering angle, θ , can be approximately expressed as follows:

$$\frac{Kc}{R_\theta} = \frac{1}{M_w} \left[1 + \frac{1}{3} \langle R_g^2 \rangle_z q^2 \right] + 2A_2c \quad \left(q = \frac{4\pi}{\lambda_0/n} \sin \frac{\theta}{2} \right) \quad (1)$$

where K , R_θ , M_w , $\langle R_g^2 \rangle_z$, λ_0 , n , and A_2 denote an optical constant, the excess Rayleigh ratio of the solution at θ , the weight average molecular weight, the z -average mean square radius of gyration, the wavelength of incident beam, the refractive index of the solvent, and the second virial coefficient, respectively. A plot of $(Kc/R_\theta)_{\theta \rightarrow 0}$ versus c , called the Debye plot, gives a straight line of intercept $1/M_w$ at $c = 0$ and slope $2A_2$. Fig. 2-a shows the relationship between $(Kc/R_\theta)_{\theta \rightarrow 0}$ and c

Fig. 2 (a) Debye plot, $(Kc/R_\theta)_{\theta \rightarrow 0}$ vs. c ; (b) Berry plot, $[(Kc/R_\theta)_{\theta \rightarrow 0}]^{1/2}$ vs. c ; (c) Zimm plot, Kc/R_θ vs. $\sin^2(\theta/2) + Pc$, for CC solution in 8 wt % LiCl/DMAc at 25°C. K , c , R_θ , and P represent optical constant, concentration, excess Rayleigh ratio at scattering angle θ and a constant (here, $P = 20$).

Table I Molecular characteristics of CC, BC and DP molecules in 8 wt % LiCl/DMAc solution.

Sample	$10^{-4} M_w$	$10^3 A_2$ / g ² ·ml·mol	$\langle R_g^2 \rangle_z^{1/2}$ / nm	$[\eta]$ / ml·g ⁻¹	k'	Chain stiffness
CC	170	1.33	109	1504	0.43	
DP	98.2	2.16	—	704	0.48	
BC	192	1.12	98.1	935	0.31	
PC-9 ^{a)}	70	3.69	144.9	1164	0.52	persistence length = 25.2 nm
Lin 3 ^{b)}	229	1.25	145	1573	—	Kuhn segment length = 15.3 ± 0.3 nm

a) Cellulose from buckeye cotton; properties of PC-9 were obtained from the solution in 9% LiCl/DMAc by McCormick et al. (ref. 9).

b) Cellulose from cotton linter; properties of Lin 3 were obtained from the solution in Cd-tren by Saalwächter et al. (refs. 13, 14).

at 25°C for the CC solution. The values of $(Kc/R_\theta)_{\theta \rightarrow 0}$ were in proportion to c in the region of c less than ca. 0.4 mg/ml. Above the concentration of 0.4 mg/ml, however, the deviation of $(Kc/R_\theta)_{\theta \rightarrow 0}$ from the straight line was observed and became gradually larger with increasing concentration. This signifies that the CC solution cannot be regarded as a dilute solution for the scattering measurement at the concentration above 0.4 mg/ml. This concentration corresponds to the overlap concentration, c^* , at which the polymer molecules start to overlap each other and more definitely determined as $1/M_w A_2$ (= 0.442 mg/ml). Interestingly, this is close to the concentration of 0.352 mg/ml, which was determined for a cotton linter cellulose ($M_w = 2.22 \times 10^6$, $R_g = 145$ nm) solution in Cd-tren (tren=tris (2-aminoethyl)amine) by Saalwächter et al.¹⁴⁾ In the case of lower c^* systems, it is quite useful to apply the Berry plot, which shows the relationships between the square root of $(Kc/R_\theta)_{\theta \rightarrow 0}$ and c , for more accurate calculation of M_w and A_2 . This plot allows the linear approximation in the wider region of c . As shown in Fig.2-b, the square root of $(Kc/R_\theta)_{\theta \rightarrow 0}$ was proportional to c for the CC solution in the whole c -region where the measurements were carried out. The values of M_w and A_2 evaluated from the Debye plot were in agreement with those from the Berry plot within the experimental error. As is clear from the Eq. (1), the value of $\langle R_g^2 \rangle_z$ can be estimated from the θ -dependence of $(Kc/R_\theta)_{c \rightarrow 0}$. For the CC solutions at $c < c^*$, the θ -dependence of Kc/R_θ was shown in the form of a Zimm plot in Fig.2-c. The value of $\langle R_g^2 \rangle_z$ of a CC molecule in the 8 wt % LiCl/DMAc solution was evaluated from the slope of the straight line representing the linear relationship between $(Kc/R_\theta)_{c \rightarrow 0}$ and q^2 .

The characteristic values, M_w , A_2 , $\langle R_g^2 \rangle_z^{1/2}$, $[\eta]$, and k' , are

listed in Table I for the three kinds of cellulose samples in 8 wt % LiCl/DMAc dilute solution. The data obtained by McCormick et al.⁹⁾ (in 9 wt % LiCl/DMAc) and Saalwächter et al.^{14),15)} (in Cd-tren) are also listed as a comparison. The values of k' were ranging from 0.3 to 0.5 for all of the three kinds of cellulose solutions. These values are similar to those obtained by McCormick et al.⁹⁾ In general, the value of k' is insensitive to the molecular weight of a solute polymer and the kind of a solvent, and the experimental value ranges roughly from 0.3 to 0.6 for many systems of synthetic polymer solutions except for those of polyelectrolyte aqueous solution.¹⁶⁾ Although it is quite difficult to give a theoretical explanation for these values on the basis of the thermodynamics,¹⁷⁾ it is empirically known that the value is tend to be larger as solvent power decreases, and that it is about 0.5–0.6 for Θ systems. Moreover, if it is over 1, association among polymer molecules can take place.^{18),19)} Therefore, cellulose molecules are probably dispersed molecularly in the dilute solution without forming some intricate association.

As to the value of $\langle R_g^2 \rangle_z^{1/2}$, only simple comparison is made here with several existing data because it is prone to vary considerably with the molecular weight distribution and wide distribution will hamper a precise and strict analysis of the chain structure. McCormick et al.⁹⁾ determined the persistence length $q_p = 25.2$ nm and characteristic ratio $C_\infty = 91.9$ for a cotton cellulose in 9% LiCl/DMAc solution. In contrast, our results apparently signify a much more compact or coiled conformation for the CC and BC molecule in 8 wt % LiCl/DMAc solution. Recently, Potthast et al.²⁰⁾ revealed that the existence of trace of water in the solution promotes the

association of cellulose molecules one another. It was also reported that the limiting solubility of LiCl in absolutely dry DMAc is 8.46 wt % at 25°C, and that it increases with increasing water content. In addition, Schult et al.²¹⁾ clarified that a cellulose molecule tends to take a less extended conformation at low LiCl concentration using size exclusion chromatography with multi-angle laser light scattering: $R_g \propto M^{0.55 \pm 0.01}$ for the cellulose solution in 0.5% LiCl/DMAc. Thus, some delicate differences of the conditions of the solution can markedly affect dilute solution properties, or the conformation of the cellulose molecule in the solution. It is very interesting that our results of M_w and $\langle R_g^2 \rangle_z^{1/2}$ for the CC molecule are roughly in agreement with those obtained for a cotton linter cellulose by Saalwächter et al.^{14),15)} in terms of the chain dimension, although the absolutely different solvent was used for the molecular characterization.

The most remarkable feature in Table I is that the value of $[\eta]$ for the BC solution is much smaller than that for the CC solution though the value of M_w of BC is larger than that of CC. This relationship can hardly be explained if CC and BC have the same molecular architecture. As widely accepted, no experimental evidence for the difference in the chemical composition of these cellulose samples can be found through our simple investigation, including elemental analysis, sugar unit analysis and IR measurements. Consequently, the difference between CC and BC molecules seems to be related to some difference in higher order structure in the solution. We roughly assume that CC and BC molecules have a random coil and a rodlike molecule made up by a helical structure in 8 wt % LiCl/DMAc solution, respectively. This assumption is based on (i) the fact that only the BC solution can form lyotropic liquid crystal¹⁰⁾ and (ii) the viscoelastic data on the semidilute and concentrated solution described later. Several workers have theoretically calculated $[\eta]$ of a flexible polymer using appropriate models. In many cases, $[\eta]$ can be given in a simple expression:

$$[\eta] = \frac{\Phi_v}{M} (6R_g^2)^{3/2} \quad (2)$$

where M and R_g^2 represent the molecular weight and the mean square radius of gyration. The constant Φ_v is called the Flory-Fox parameter. Various theories give Φ_v values ranging from 2.2×10^{23} to 2.87×10^{23} .²²⁾ With $R_g = 109$ nm and $M = 1.70 \times 10^6$, Eq. (2) gives $[\eta]$ for the CC solution as $2.44 \times 10^3 - 3.19 \times 10^3$ ml/g. These values appear much higher than the experimental value (1504 ml/g). Considering that the R_g value is z -average quantity, however, such numerical disagreement

can be within the difference caused by the polydispersity of the molecular weight. On the other hand, $[\eta]$ of a rodlike particle can be expressed as follows:

$$[\eta] = \frac{N_A}{M} \cdot \frac{2\pi L^3}{45(\ln(L/d) - \gamma)} \quad (3)$$

where L , d , and N_A denote the length of the cylinder along the axis, the diameter of its cross-section, and Avogadro's number, respectively. Various theoretical calculations give different values of a correction factor, γ , ranging from 0.697 to 1.72.²³⁻²⁵⁾ For the BC solution, L can be evaluated to be 340 nm from the relationship of $L^2 = 12R_g^2$ and the experimental result of $\langle R_g^2 \rangle_z = 98.1$ nm. The value of d can also be estimated to be 4.73 nm from the SAXS measurements discussed later. As a result, $[\eta]$ is calculated to be $4.81 \times 10^3 - 6.75 \times 10^3$ ml/g. This is rather small compared to the value listed in Table I (935 cm³/g). Again, the numerical disagreement between the theoretical calculation and the experimental results is not so important, taking the polydispersity into account. What is important here is the result that the discrepant relationship between $[\eta]$ and M_w can be explained by assuming the difference in the shape of the molecule in the solution.

3.2 Dynamic Viscoelastic Measurements and Activation Energy

The dependence of storage moduli, G' , and loss moduli, G'' , on the reduced angular frequency, $\omega \cdot a_T$, is shown in Fig.3 for the CC solution at various weight fraction of polymer, ϕ_w , ranging from 0.007 to 0.05. The reference temperature is 30°C. Each pair of the master curves of G' and G'' is shifted upward by a factor B except for the curves for the CC solution at $\phi_w = 0.007$. The solid lines represent the calculation curves reproduced by appropriate relaxation spectra. These are discussed later. The solutions at $\phi_w \leq 0.03$ showed typical viscoelastic behavior observed in the plateau zone and the terminal zone for many synthetic polymer solutions. At lower frequencies the flow region was clearly observed; that is, G' and G'' were proportional to ω^2 and ω^1 , respectively, and the plateau region appeared at higher frequencies. As ϕ_w increased, the flow region shifted towards lower frequencies and the plateau region became longer. Moreover, the flow region cannot be observed for the solution at $\phi_w = 0.05$. Under cross-polarizers, a small amount of minute undissolved fibers were observed to be suspended in the solution, signifying that the weight fraction of 0.05 seems to be around the solubility limit for the CC solution.

Fig.4 shows the ω -dependence of the dynamic moduli for

Fig.3 Dependence of dynamic storage moduli, G' (open symbols), and loss moduli, G'' (filled symbols), on reduced angular frequency, $\omega \cdot a_T$, for CC solutions at various weight fraction of polymer, ϕ_w , ranging from 0.007 to 0.05. Reference temperature is 30°C. The curves are shifted vertically by a factor B except for those at $\phi_w = 0.007$. Solid lines represent the curves reproduced by calculation using Eq. (5) with appropriate combinations of τ_p and G_p , which denote relaxation time and relaxation intensity of p -th mode, respectively.

the BC solutions at ϕ_w ranging from 0.01 to 0.07. All the curves except for those for the solutions at $\phi_w = 0.01$ and 0.02 are shifted vertically by a factor B in the same manner as in Fig.3. The BC solutions at $\phi_w \leq 0.04$ showed typical viscoelastic behavior for the isotropic polymer solution, which is similar to the CC solutions. At $\phi_w = 0.05$, however, the tendency that the ω -dependence of G' became weaker was observed in the low frequency region. At $\phi_w = 0.07$, this weaker ω -dependence was clearly observed in lower frequency region. In the previous paper¹⁰⁾, we have already reported that the viscoelastic behavior of the critical gel was observed for the BC solution at $\phi_w = 0.085$, and also reported that anisotropic phase was clearly observed under cross-polarizers above this critical concentration. The appearance of the weaker ω -dependence of G' at long time scale region with

Fig.4 Dependence of dynamic storage moduli, G' (open symbols), and loss moduli, G'' (filled symbols), on reduced angular frequency, $\omega \cdot a_T$, for BC solutions at various weight fraction of polymer, ϕ_w , ranging from 0.01 to 0.07. Reference temperature is 30°C. The curves are shifted vertically by factor B except for those at $\phi_w = 0.01$ and 0.02.

increasing concentration indicates that anisotropic phase begin to form partially in the solution below the critical concentration and that it grows with increasing concentration. As shown in Fig.5, G' became almost flat against ω axis for the BC solution at $\phi_w = 0.1$; that is, flow behavior was not observed. This means that a certain heterogeneous structure (i.e., a liquid crystalline structure) was constructed throughout the system. These changes in viscoelastic behavior with increasing concentration are popular to lyotropic liquid crystalline systems.²⁶⁾

In comparison with the data of Figs. 3 and 4, it is most interesting that the longest relaxation time, τ_1 , of the CC solutions seems to be longer than those of the BC solutions although M_w of CC are smaller than that of BC. This indicates some difference between the CC and the BC solutions in the relaxation mechanism. It can be inferred that this difference is related to the differences in the structure of the solution and

Fig.5 Dependence of dynamic storage modulus, G' (open symbols), and loss modulus, G'' (filled symbols), on angular frequency, ω , at 30°C for BC solutions at $\phi_w = 0.1$, which is anisotropic solution.

Fig.6 Dependence of activation energy for an elementary flow, ΔE_a , on weight fraction of polymer, ϕ_w , for CC, BC and DP solution in 8 wt % LiCl/DMAc.

also related basically to the difference in the molecular properties as discussed in the previous section.

For the CC, the BC, and the DP solutions, ϕ_w -dependence of the activation energy for an elementary flow, ΔE_a , are shown in Fig.6. The values are calculated with the data of shift factor, a_T , from the dynamic viscoelastic measurements, using WLF equation for the CC and BC solutions and Arrhenius equation for the DP solution. The values of ΔE_a can be regarded as almost constant (ca. 40 kJ/mol) independent of the sort and concentration of the cellulose solutions. It is expected that no complicated polymer-polymer interactions, such as an electrostatic interaction, other than the topological constraint act in the flow process. Similar behavior has been clearly observed for the curdlan (1,3- β -D-glucan) in DMSO and 0.1 N NaOH aqueous solution.²⁷⁾

3.3 Concentration Dependence of Zero-Shear Viscosity

For the CC, the BC, and the DP solutions, Fig.7 shows concentration (ϕ_w) dependence of $\eta_0 - \eta_s$ in the form of double logarithmic plot. In this figure, not only the data from the dynamic viscoelastic measurements but also the results from

Fig.7 Dependence of $\eta_0 - \eta_s$ on ϕ_w at 30°C for CC, BC and DP solutions in 8 wt % LiCl/DMAc. Here, η_0 , η_s and ϕ_w represent zero shear rate viscosity of solution, viscosity of solvent and weight fraction of polymer, respectively. Overlap concentration, c^* , which was determined from static light scattering measurements, is also shown by arrow. For each solution, the dependence can be approximately represented by two straight lines with a slope of 1 in dilute region, and a slope of 4 (CC and DP) or 3 (BC) in semi-dilute and concentrated region.

the measurements of the limiting viscosity number and the steady flow¹⁰⁾ are simultaneously plotted. For all of the three kinds of cellulose solutions, ϕ_w -dependence of $\eta_0 - \eta_s$ can be represented approximately by two straight lines in the double logarithmic plot. The concentration at the point where the change of the slope of the straight line occurs is a kind of critical concentration, $\phi_{w,cr}$, at which the intermolecular interactions in the flow process changes drastically. A solution sufficiently below $\phi_{w,cr}$ can be roughly regarded as a dilute solution, where polymer molecules are dispersed separately. Strictly speaking, a dilute solution must be defined as a solution below the overlap concentration, c^* , as already seen in the section of the characterization. In this figure, c^* ($= 4.42 \times 10^{-4}$ g/ml for the CC solution) determined by the static light scattering measurements corresponds to the concentration at which the viscosity data start to deviate from the straight line with a slope of unity. In this concentration

regime, therefore, many of physical properties of the solution are expected to be proportional to the concentration. As shown in Fig.7, the slopes of the lines in the dilute regime are unity for all kinds of cellulose solutions, signifying that this speculation can apply to the ϕ_w -dependence of $\eta_0 - \eta_s$ of all these cellulose solutions.

As the concentration increases above $\phi_{w,cr}$, the polymer molecules are strongly overlapped and intermolecular interactions become predominant. Such a solution is called a semidilute or moderately concentrated solution in general. According to this speculation, various types of interactions can be reflected in the ϕ_w -dependence of $\eta_0 - \eta_s$. Actually, various values of the exponent α in $\eta_0 \propto c^\alpha$, ranging approximately from 4 to 6, has been experimentally observed in the semidilute region for many solutions of flexible polymers including biopolymers.²⁸⁻³¹⁾ In many cases, thus, it is extremely difficult to estimate only the effect of the interaction purely by physical entanglement (i.e., universal nature for flexible polymers) from the actual concentration dependence of η_0 . It

probably involves various contributions of additional interpolymer interactions. However, the discussion on the activation energy as described above can simplify the situation; that is, it can be hypothesized that no complicated intermolecular interaction other than topological constraints needs to be taken into account for these cellulose solutions in the flow process. Consequently, it is expected that only topological constraint is reflected in the ϕ_w -dependence of $\eta_0 - \eta_s$. For the CC and the DP solutions, the relation of $\eta_0 - \eta_s \propto \phi_w^4$ was observed as shown in Fig.7. Theoretically, several values of the exponent α are given. For example, according to the scaling theory, it is calculated to be 3.75 by de Gennes.³²⁾ The theory of Doi and Edwards³³⁾ gives about 4 for flexible polymers. Compared to these theoretical results, it can be inferred from the ϕ_w -dependence of $\eta_0 - \eta_s$ for the CC and the DP solutions that these cellulose molecules behave as a flexible polymer in 8 wt % LiCl/DMAc solution. On the other hand, the relation of $\eta_0 - \eta_s \propto \phi_w^3$ was observed for the BC solution in the semidilute and concentrated regime, as shown in Fig.7. This value of the exponent is evidently smaller than that for flexible polymers. According to Doi and Edwards' theory,³⁴⁾ the exponent α is predicted to be 3 for rodlike polymers. It can be inferred that BC behave as a rodlike polymer in this solution. These presumptions are rather reasonable considering the fact that the CC and the DP solutions form the isotropic phase and the BC solution form an anisotropic phase above a certain concentration.¹⁰⁾

Fig.8 Dependence of $\eta_0 - \eta_s$ on $\phi_w \cdot [\eta]$ at 30°C for CC, BC and DP solutions in 8 wt % LiCl/DMAc. Parameter of $\phi_w \cdot [\eta]$ is not dimensionless but almost equal to overlapping parameter, $c \cdot [\eta]$, which is generally used as a reduced concentration.

Fig.8 shows the double logarithmic plot of $\eta_0 - \eta_s$ versus the overlap parameter $\phi_w [\eta]$. Strictly speaking, the overlap parameter must be the product of the concentration c in g/ml and $[\eta]$, which is dimensionless. The difference between $\phi_w [\eta]$ and $c [\eta]$ is derived from the density of the solution. If the concentration of the solution is not so high, the density of the solution can be regarded as constant and roughly equal to that of the solvent. Considering that the density of 8 wt % LiCl/DMAc is 0.99978 g/ml at 30°C, the difference is negligible. By using this parameter, all the data are superimposed excellently in the dilute region, where the intermolecular interactions can be neglected. For the CC and the DP solutions, the data can also be superimposed well in the semidilute region, where the intermolecular interactions become predominant. This suggests that cellulose molecules of CC and DP, which are derived from plant sources, are different only in hydrodynamic volume of polymer but otherwise identical in terms of the flow behavior or hydrodynamic properties. In addition, this good superposition also enables us to develop the further discussion on the chain

stiffness of the plant cellulose. For many synthetic polymer solutions, it has confirmed that the following equation holds: $\alpha\nu' = 3.4$, where ν' represents the exponent in the well-known Mark-Houwink-Sakurada relationship: $[\eta] = K_{\eta} M^{\nu'}$.^{28),30)} Interestingly, the excellent research by Saalwächter et al.¹⁴⁾ has revealed that the equation holds also for cellulose solutions in Cd-tren: $\alpha = 4.75 \pm 0.09$, $\nu' = 0.72 \pm 0.03$ and $\alpha\nu' = 3.42 \pm 0.16$. These facts suggest that the equation can also hold in the case of the CC and the DP solutions in 8 wt % LiCl/DMAc. That is to say, MHS exponent ν' can be estimate from the ϕ_w -dependence of $\eta_0 - \eta_s$. As a result, the value of ν' is 0.85. This is somewhat larger than 0.8, which is expected for a flexible polymer in a good solvent, but surprisingly lower than 1.19, determined for cellulose solutions in 9% LiCl/DMAc by McCormick et al.⁹⁾ This difference between their and our results is consistent with the difference of the dilute solution properties which have been already discussed in the section of the molecular characterization.

3.4 Concentration Dependence of Plateau Modulus

In the case that the maximum can be observed in the curve of $G''(\omega)$ at $\omega = \omega_{\max}$, the plateau modulus, G_N , can be determined generally by the following equation.³⁵⁾

$$G_N = \frac{4}{\pi} \int_{-\infty}^{\omega_{\max}} G''(\omega) d \ln \omega \quad (4)$$

However, this equation is not facile to be applied to the experimental data because the experimental data of dynamic moduli, $G'(\omega)$ and $G''(\omega)$, are usually obtained against the discrete ω . Moreover, this equation cannot be used in the case that no maximum can be observed in the G'' curve. Instead of using Eq. (4), the expressions with discrete variables are more available for the calculation of G_N .

$$G'(\omega) = \sum_p G_p \frac{\omega^2 \tau_p^2}{1 + \omega^2 \tau_p^2} \quad G''(\omega) = \sum_p G_p \frac{\omega \tau_p}{1 + \omega^2 \tau_p^2} \quad (5)$$

$$G_N = \lim_{\omega \rightarrow \infty} G'(\omega) = \sum_p G_p \quad (6)$$

It is necessary to determine the combination of τ_p and G_p , which can reproduce simultaneously both of the frequency dependence curves of $G'(\omega)$ and $G''(\omega)$ using Eq. (5). The sum of all G_p can be determined, which corresponds to G_N , as expressed in Eq. (6). Experimental data of $G'(\omega)$ and $G''(\omega)$ over wide range of ω where the plateau region is clearly observed are required for the accurate estimation of G_N .

Fig.3 shows also the reproducibility of the master curves of $G'(\omega)$ and $G''(\omega)$ with appropriate combinations of τ_p and G_p for the CC solution. These curves of $G'(\omega)$ and $G''(\omega)$ reproduced by the calculation are in good agreement with the experimental data. For the CC solutions at ϕ_w ranging from 0.007 to 0.03 in Fig.3, the values of G_N were estimated in the manner described above. As for the solution at $\phi_w = 0.05$, G_N was estimated from a lateral shift factor by which the calculated curve at $\phi_w = 0.03$ was shifted to superpose onto the experimental data at $\phi_w = 0.05$ in the higher frequency region.

Fig.9 shows the ϕ_w -dependence of G_N for the CC solution. G_N is in proportion to $\phi_w^{2.14}$. This exponent of 2.14 seems slightly smaller than the values of exponent experimentally and theoretically obtained for semidilute solutions of flexible polymers. For example, the relation of $G_N \propto c^{2.3}$ was observed for polystyrene and poly(α -methylstyrene) in chlorinated biphenyl solution.³⁶⁾ According to the scaling theory,³⁷⁾ the exponent β in the relation of $G_N \propto c^\beta$ is expected to be 2.25 for flexible polymer solutions. Doi and Edwards³⁸⁾ have theoretically predicted $\beta \approx 2.5$. However, it has also been found experimentally that G_N is proportional to c^2 for the concentrated polymer solution of flexible polymer.³⁹⁾ Thus, the ϕ_w -dependence of G_N of the CC solution indicates that the typical network structure is formed by the entanglement of the CC molecules in the semidilute solutions; that is, the CC

Fig.9 Dependence of plateau modulus, G_N , on weight fraction of polymer, ϕ_w , for CC solutions in 8 wt % LiCl/DMAc at 30°C.

molecules behave as a flexible polymer in the semidilute solution.

3.5 Molecular conformation of BC

Fig.10 shows the SAXS profile for 13.6 wt % BC solution ($\phi_w = 0.136$), in which the liquid crystalline structure was observed. The scattering intensity, $I(q)$, is well fitted by the calculated curve with the Debye-Bueche equation as shown in the solid line. The D-B equation is:

$$I(q) = \frac{K_s}{(1 + a^2 q^2)^2} \quad (a \cdot q < 1) \quad (7)$$

where q , a and K_s denote the magnitude of the scattering vector, the correlation length and a constant, respectively. With $a = 4.5$ nm, the best fitting curves can be obtained. Such a profile is often observed for many two-phase systems including heterogeneous gels.^{40),41)} In the large q -region, $I(q)$ is approximately in proportion to q^{-4} . This indicates that the system has a sharp transition in the electron density at the interface between two phases according to the Porod's law.⁴²⁾ These results suggest that the structure in the BC solution apparently differs from the typical network structure from the viewpoint of the entanglement.

The specific inner surface, O_s , for the two-phase system can be calculated by

$$O_s = \pi w_1 K_1 / Q_q. \quad (8)$$

Fig.10 SAXS profile, $\log I(q)$ vs $\log q$, for BC solution in 8 wt % LiCl/DMAc at $\phi_w = 0.136$. Here, $I(q)$ and q represent scattering intensity and magnitude of scattering vector. Solid line represents theoretical curve expressed by Debye-Bueche equation, Eq. (7). Best fit gives correlation length a of 4.5 nm.

Here w_1 and K_1 represent the volume fraction of the medium and a constant in the relation of $I(q) = K_1 q^{-4}$ in the large q -region, respectively. Q_q is the Porod invariant defined by

$$Q_q = \int_0^\infty I(q) q^2 dq. \quad (9)$$

For the disperse systems of particles⁴³⁾ which has negligibly small fluctuation of the electron density inside, O_s means

$$O_s = \frac{\text{surface area of the particle}}{\text{volume of the particle}}. \quad (10)$$

If the shape of the dispersed particles is given, some quantities in length characteristic of the shape can be estimated from the O_s value.⁴⁴⁾ If both the shape and the size are definitely given, some properties of a fine structure such as the surface roughness can be estimated.^{43),45)} Fig.11 shows a plot of $I(q) \cdot q^2$ versus q for the BC solution, where the values of $I(q) \cdot q^2$ tend to reach to zero in the small and large q -regions. Thus, the plot allows to calculate the invariant Q_q in Eq. (9) as the area disclosed by the abscissa and the smooth curve representing the experimental data. As a result, we obtained 17.1 nm^{-3} as the value of the invariant Q_q . With $K_1 = 0.532 \text{ nm}^{-4}$, estimated from a plot of $I(q) \cdot q^4$ versus q^4 , and $w_1 = 0.864$, assuming that the volume fraction equals to the weight fraction, Eq. (8) gives O_s value of 0.846 nm^{-1} . It must be noted that we regarded the scattering intensity as the dimensionless quantity. For the thin rodlike particle ($L \gg d$) with a smooth surface, O_s can be estimated from the following equation:

Fig.11 Kratcky plot, $I(q) \cdot q^2$ vs q , for BC solution in 8 wt % LiCl/DMAc at $\phi_w = 0.136$. Here, scattering intensity, $I(q)$, is regarded as dimensionless quantity.

$$O_s = \frac{\pi d L + 2\pi (d/2)^2}{\pi (d/2)^2 L} = \frac{4}{d} + \frac{2}{L} \approx \frac{4}{d} \quad (11)$$

No decisive experimental evidence about the structure of the BC molecule in the solution has not been available to us so far, which confine the discussion on the O_s value. Assuming that the BC molecule has rodlike structure, d can be estimated to be 4.73 nm. This value gives the axial ratio $p (= L/d)$ of 71.9 in connection with $L = 340$ nm. According to the theory of Onsager,⁴⁶⁾ the critical volume fraction at which anisotropic phase begin to appear in the isotropic phase is given by $3.34/p$, and is found to be 0.046 for the BC solution. Provided that the volume fraction is equal to the weight fraction, ϕ_w , it is interesting that this value is in good correspondence with the results of the dynamic viscoelastic measurements; that is, the weak ω -dependence of G' in the low frequency region was observed for the BC solutions above $\phi_w = 0.05$.

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