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Aggregate Structure and Rheological Properties of Mercerized Cellulose / LiCl·DMAc Solution

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The effect of mercerization on the cellulose solution was investigated in terms of rheological and dilute solution properties in 8 wt % LiCl/*N,N*-dimethylacetamide (DMAc). Cotton lint, cotton linter, and dissolving pulp were used for native cellulose samples. Static light scattering (SLS) measurements show that the second virial coefficient, A_2 , of the cellulose solutions decreased by the mercerization, indicating that the affinity between cellulose and the solvent molecules decreased by the mercerization. A long time relaxation was found only for the mercerized cellulose solution by viscoelastic measurements for semidilute solutions. This indicates that some heterogeneous structures were formed in the mercerized cellulose solution. Some aggregate structures, which have slow decay time, were observed in the 0.5 wt % mercerized cellulose solution by dynamic light scattering (DLS) measurements. According to these results, the low affinity between cellulose and the solvent makes some aggregate structures in the mercerized cellulose solutions in 8 wt % LiCl·DMAc above the overlap concentration.

Key Words: Cellulose solution / Mercerization / LiCl·DMAc / Rheological properties / Long time relaxation

1. INTRODUCTION

Cellulose, most abundant natural polymer on the earth, has various morphologies depending on its biological sources and artificial treatments. For example, the crystalline structure of cellulose can be changed by physical or chemical treatments.¹⁾ In these treatments, “mercerization”, immersing cellulose in an alkaline solution such as NaOH aq, is well known. The crystalline structure of native cellulose is changed from cellulose I to cellulose II by mercerization.

There have been numerous investigations to clarify the mechanism of mercerization, however, it has not been completely understood. Therefore, the study on mercerization still attracts many researchers on the cellulose chemistry. Fengel *et al.*²⁾ observed the changes by mercerization in the hydrogen bonds of OH groups of cellulose using deconvoluted FT-IR spectra. Kim *et al.*³⁾ examined the structure of alkali swollen cellulose by means of X-ray and electron diffraction analysis, and discussed the mechanism of mercerization. However, most of these investigations focus on the solid-state structure of

cellulose such as crystalline structures, and there are no studies discussed the molecular and the solution properties of cellulose.

Not only about mercerization, in the past, but also investigations on the diversity of cellulose have been limited in the study of the solid-state structure. It may be based on the “common knowledge” that cellulose with various morphologies have the same molecular properties except molecular weight. Therefore, the solution properties of cellulose with different crystalline structures have hardly been compared. Yasuda *et al.*⁴⁾ studied the flow birefringence and viscosity of cellulose/NaOH aq and cellulose/cadoxen using hardwood pulp (cellulose I) and regenerated cellulose (cellulose II). They found differences in the flowing behavior between cellulose I solution and cellulose II solution. However, they concluded that some incomplete dissolution of cellulose caused these differences.

To make an effective use of various celluloses as a resource of polymer materials, we should have extensive and profound knowledge on the molecular properties of cellulose. In the previous papers^{5), 6), 7)}, we have reported some differences in the molecular and rheological properties of the cellulose solutions derived from different biological sources (plants, bacteria, and ascidians) in 8 wt % LiCl/*N,N*-dimethylacetamide (DMAc) or 8 wt % LiCl/1,3-dimethyl-2-imidazolidinone

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(DMI). These researches suggest that cellulose from different biological sources have different conformations in the solutions.

In this study, we focus on the mercerization of cellulose, and discuss the effect of mercerization of cellulose on the solution properties in 8 wt % LiCl-DMAc in terms of rheological and dilute solution properties. The relationship between a long time relaxation found by the viscoelastic measurements in the flow region for the mercerized cellulose solution and some aggregate structures, which have slow decay time, observed by the dynamic light scattering measurements in the solution were also discussed.

2. EXPERIMENTAL

2.1 Materials and Preparation of Solutions

Cotton lint (CC1), Cotton linter (CC2), and dissolving pulp (DP; Nippon Paper Industries Co., Ltd., 92 % α -cellulose) were used for native cellulose samples. These cellulose samples were derived from plant.

Mercerized cellulose samples (CC1m, CC2m, and DPM) were prepared from the native cellulose samples using the following procedure: the native cellulose samples were soaked in each of 17.5 wt % sodium hydroxide solutions (bath ratio: 1 g cellulose/100 g NaOHaq) at room temperature for 1 hour. NaOHaq was subsequently removed by filtering through 1G2 glass filter, and the swollen cellulose samples were washed in 10 wt % acetic acid followed by enough washing with distilled water. Water was then removed by soaking in methanol and filtering through a Buchner funnel.

The dissolution of cellulose in LiCl-DMAc requires a pretreatment of cellulose.^{8), 9), 10)} In this study, the solvent exchange method consisting of the sequential soaking cellulose in water, acetone and DMAc was employed. The procedure was performed as described in the previous paper.⁶⁾ To obtain completely dissolved state, the solutions prepared were allowed to stand at room temperature for 1 month for the samples under 0.2 wt %, and for 2 ~ 3 month for 0.3 ~ 5 wt % before the measurement.

2.2 Methods

Wide-angle X-ray diffraction (WAXD) measurements were performed with a RINT 2200V (Rigaku Co., Ltd.). The diffracted intensity of CuK α radiation (wavelength of 0.1542 nm, under a condition of 40 kV and 30 mA) was measured in a 2θ range between 5° and 40°.

Limiting viscosity number was determined with an Ubbelohde type capillary viscometer in a constant-temperature

bath regulated at 30°C.

Static light scattering (SLS) measurements were performed with a light scattering photometer SLS-5000HM (Otsuka Electronics Co., Ltd.) under the following conditions: wavelength, $\lambda_0 = 632.8$ nm (He-Ne laser); scattering angle, $30^\circ \leq \theta \leq 150^\circ$; temperature, 25°C. The sample solutions were filtered by PTFE membrane filters (Toyo Roshi Kaisha Ltd.) with a pore size of 0.2 μ m several times before the measurement. The value of specific refractive index increment, dn/dc , used was 0.0575 ml/g which is given by McCormick *et al.*⁹⁾ For a dilute solution, the reciprocal reduced scattered intensity, Kc/R_θ , at a scattering angle, θ , can be approximately expressed as follows:

$$\frac{Kc}{R_\theta} = \frac{1}{M_w P(\theta)} + 2A_2c + \dots \quad (1-a)$$

$$P(\theta) = 1 - \frac{1}{3}q^2 \langle R_g^2 \rangle_z + \dots \quad (1-b)$$

where K , c , R_θ , M_w , $P(\theta)$, A_2 , q , and $\langle R_g^2 \rangle_z$ represent the optical constant, the polymer concentration, the excess Rayleigh ratio of the solution at θ , the weight average molecular weight, the particle scattering factor, the second virial coefficient, the magnitude of scattering vector ($q = (4\pi/\lambda)\sin(\theta/2)$; λ is the wavelength of incident beam in the solution), and z -average mean square radius of gyration. According to Eqs.(1-a) and (1-b), A_2 , $\langle R_g^2 \rangle_z$, and M_w were estimated from the initial slope in the concentration dependence of the extrapolated value of Kc/R_θ for $\theta \rightarrow 0$, the initial slope in the angular dependence of the extrapolated value for $c \rightarrow 0$, and extrapolated value for $c \rightarrow 0$ and $\theta \rightarrow 0$ (Zimm plot).

Dynamic light scattering (DLS) measurements were performed with the same light scattering photometer as SLS measurements equipped with an ALV-5000/E correlator (ALV Co.) at 25°C. By DLS measurements, the relationship between the second-order time auto-correlation function of the electric field of the scattered light, $g^{(2)}(q, \tau)$, and τ was obtained. Here τ is correlation time. The function, $g^{(2)}(q, \tau)$, is related to the first-order auto-correlation function $g^{(1)}(q, \tau)$ in a homodyne experiment by Eq.(2):

$$g^{(2)}(q, \tau) = 1 + |g^{(1)}(q, \tau)|^2 \quad (2)$$

For a polydisperse system or a system with some relaxation modes, $g^{(1)}(q, \tau)$ can be expressed as superposition of exponential functions as follows:

$$g^{(1)}(q, \tau) = \int_0^\infty G(\Gamma) \exp(-\Gamma \tau) d\Gamma \quad (3)$$

where Γ and $G(\Gamma)$ represent the decay rate, and probability density function of Γ . Γ is related to the translational diffusion coefficient, D_T , with $\Gamma = q^2 D_T$, which is related to hydrodynamic radius, R_H , with Stokes-Einstein relationship, Eq.(4):

$$R_H = \frac{k_B T}{6\pi\eta_s D_T} \quad (4)$$

where k_B , T , and η_s represent Boltzmann constant, absolute temperature, and viscosity of the solvent. Equation (3) represents Laplace transformation of the $G(\Gamma)$ of the Γ , so that, by inverse Laplace transformation of Eq.(3), the intensity-weighted distribution of the R_H of the particles in the solution can be estimated. In this study, $G(\Gamma)$ was estimated by the regularized fitting with CONTIN method¹¹⁾ from $g^{(2)}(q, \tau)$.

Dynamic viscoelasticity and steady flow measurements were performed with a cone-plate type rheometer Rheosol-G2000 (UBM Co., Ltd.). 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.¹²⁾

3. RESULTS

3.1 X-ray Diffraction

Figure 1 shows the wide angle X-ray diffraction profile of the CC1 and the CC1m. The peak of (1 $\bar{1}$ 0) plane of cellulose I at $2\theta = 14.8^\circ$ disappeared and that of cellulose II appeared at $2\theta = 12.1^\circ$ by the mercerization. This confirmed that the crystalline structure of the CC1 was completely transformed from cellulose I to cellulose II. The cellulose samples requires the solvent-exchange pretreatment^{8),9)} to be dissolved in LiCl-DMAc. The solvent-exchange has no effects on the crystalline structure of cellulose.¹⁰⁾ The CC2 and the DP also showed the same tendency as the CC1.

3.2 Dilute Solution Properties

The data obtained from SLS measurements were evaluated by Zimm plots. Figure 2 shows Zimm plot for the CC2m solutions, in which only the data expressed by the filled circle ($30^\circ \leq \theta \leq 90^\circ$) were used for the determination of the molecular properties because the plots at higher angles were deviated from the extrapolated straight line. The same

tendency was also observed in the CC1, the CC2, and the CC1m solutions. The deviation from the extrapolated straight line is discussed later.

Figure 3 shows the relationship between Kc/R_θ versus c (Debye plot) for the CC1, the CC2, the CC1m, and the CC2m solutions. Here, Kc/R_θ is the extrapolated value of Kc/R_θ at $\theta = 0$. The intercept of the extrapolated straight line for the CC1 was equal to that for the CC1m, indicating that the CC1 was not depolymerized by the mercerization. In constant, the intercept for the CC2m was larger than that for the CC2, indicating that M_w of the CC2m was decreased to a half of the CC2. Furthermore, the slope of Debye plot became smaller by the mercerization for the CC1 and the CC2, indicating that the second virial coefficient, A_2 , decreased by the mercerization.

Fig.1 Wide-angle X-ray diffraction profile of CC1 and CC1m.

Fig.2 Zimm plot for CC2m solution in 8 wt % LiCl-DMAc. K , c , and R_θ represent optical constant, concentration of polymer, and excess Rayleigh ratio at scattering angle, θ . For the determination of the molecular properties only the data expressed by the filled circle ($30^\circ \leq \theta \leq 90^\circ$) were used. The squares represent extrapolated value from the experimental data at scattering angle $\theta = 0$ and a concentration $c = 0$.

Figure 4 shows the concentration dependence of η_{sp}/c and $(\ln \eta_r)/c$ for the CC1, and the CC1m solutions. Here $\eta_{sp} (= (\eta - \eta_s)/\eta_s)$; η : viscosity of solution, η_s : solvent viscosity, and $\eta_r (= \eta/\eta_s)$ denote the specific viscosity and relative viscosity. The limiting viscosity number, $[\eta]$, was estimated from the intercepts at $c = 0$, and the Huggins constant, k' , was estimated from the slopes of the straight line. The molecular characteristics of the native and the mercerized cellulose molecules in 8 wt % LiCl-DMAc solution estimated from the SLS and the limiting viscosity number measurements are summarized in Table I.

3.3 Rheological Properties

Figure 5-a shows the dependence of storage moduli, G' , and loss moduli, G'' , on the reduced angular frequency, ωa_T for the CC1 solution at various weight fraction of the polymer, ϕ_w , ranging from 0.01 to 0.05. The reference temperature is 30°C. As ϕ_w increased, a plateau region became longer in the higher frequency region. In the lower frequency region, the flow region was clearly observed; that is, G' and G'' were proportional to ω^2 and ω^1 , respectively. These data are very similar to those obtained for cotton linter cellulose solutions.⁶⁾

Figure 5-b shows ωa_T -dependence of G' and G'' for CC1m solutions at ϕ_w ranging from 0.01 to 0.05. For the CC1m solutions, ω -dependence of G' became weaker with cellulose concentration in the lower frequency region, indicating that there are some long-time relaxations. For the CC2 samples, the long-time relaxation was also observed only for the mercerized samples as well as the CC1 (Fig.5-c).

Activation energy for an elementary flow, ΔE , at 30°C were calculated from the data of shift factor, a_T , from the dynamic viscoelastic measurements using WLF-equation.¹²⁾ As a result, the values of ΔE were almost constant (ca. 40 kJ/mol) independent of the source, the mercerization, and the concentration of the cellulose samples. The value of 40 kJ/mol is equal to the value of any cellulose samples estimated before.⁶⁾

Figure 6 shows flow curves for the CC1m solutions at various concentrations. The solid line represents the data for the solvent. The solutions at $\phi_w \leq 0.013$ reveal Newtonian flow in the lower shear rate region. On the other hand, the solution at $\phi_w = 0.02$ shows weaker $\dot{\gamma}$ -dependence in the lower shear rate region.

Figure 7 shows double logarithmical plot between $\eta - \eta_s$ versus $\phi_w \cdot [\eta]$ for the native and the mercerized cellulose solutions. Here $\phi_w \cdot [\eta]$ represents reduced concentration which

Table I Molecular characteristics of native and mercerized cellulose molecules in 8 wt % LiCl-DMAc solution.

sample	$10^{-4} M_w$	$10^3 A_2$ / $\text{g}^{-2} \cdot \text{ml} \cdot \text{mol}$	$\langle R_g^2 \rangle_z^{1/2}$ /nm	$[\eta]$ / $\text{ml} \cdot \text{g}^{-1}$	k'
CC1	157	1.14	106	1050	0.36
CC2	205	1.28	128	1504	0.43
DP	53.9	1.04	62.6	704	0.48
CC1m	151	0.614	119	1114	0.38
CC2m	105	0.617	83.1	852	0.31
DPm	45.2	1.22	51.6	490	0.33

Fig.3 Debye plot, $(Kc/R\theta)_{\theta \rightarrow 0}$ versus polymer concentration, c , for cellulose solutions in 8 wt % LiCl-DMAc. Filled marks represent data for mercerized celluloses.

Fig.4 Huggins plot (circle) and Mead-Fuoss plot (square) for CC1 (filled symbols) and CC1m (open symbols) solutions in 8 wt % LiCl-DMAc.

Fig.5 Dependence of dynamic storage moduli, G' (open symbols), and loss moduli, G'' (filled symbols), on reduced angular frequency, ωa_T ; (a) for CC1 solutions ($\phi_w = 0.01, 0.013, 0.02, 0.03$, and 0.05); (b) for CC1m solutions ($\phi_w = 0.01, 0.013, 0.02, 0.03$, and 0.05); (c) for CC2 and CC2m solutions at $\phi_w = 0.03$. Reference temperature is 30°C. The curves in Figure (a) and (b) are shifted vertically by factor A except for those at $\phi_w = 0.01$.

Fig.6 Shear stress, σ , is double-logarithmically plotted versus shear rate, $\dot{\gamma}$, for CC1m solutions in 8 wt % LiCl/DMAc.

Fig.7 Dependence of $\eta_0 - \eta_s$ on $\phi_w \cdot [\eta]$ native and mercerized cellulose solutions in 8 wt % LiCl/DMAc at 30°C. Here, η_0 , η_s , $[\eta]$, and ϕ_w represent zero shear rate viscosity of solution, viscosity of solvent, intrinsic viscosity number, and weight fraction of polymer, respectively. 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.

is not dimensionless but almost equal to $c \cdot [\eta]$ generally used as a reduced concentration.^{5,6)} By using this parameter, all the data are superimposed in the whole concentration region, and $\eta - \eta_s$ were proportional to $\phi_w \cdot [\eta]$ in the dilute region and to $(\phi_w \cdot [\eta])^4$ in the semidilute region.

3.4 Dynamic Light Scattering

Figure 8 shows the second-order time auto-correlation function, $g^{(2)}(\tau)$, for 0.5 wt % CC1 and CC1m solutions at 90°. Only one mode of motion was observed for the CC1 solution, however, a second slower mode was observed for the CC1m solution. Figure 9 shows the decay rate distribution, $G(\Gamma)$, for 0.5 wt % CC1 and CC1m solutions calculated from $g^{(2)}(\tau)$ by Eqs.(2) and (3). In Fig.9, hydrodynamic radius, R_H , calculated with Einstein-Stokes relation, Eq.(4), is also shown in the top axis. In the CC1 solution, only a single maximum (Fast mode: $R_H \approx 10$ nm) was found in $G(\Gamma)$. In constant, in the CC1m solution, the same maximum as in the CC1 solution (Fast mode) and some other maxima corresponding to larger particles (Slow mode: $R_H \approx 100 \sim 1000$ nm) were found. For the fast mode, the mean value of Γ was proportional to q^2 . For the slow mode, however, q^2 -dependence of Γ cannot be confirmed because the reproducibility of Γ was not so good.

4. DISCUSSION

4.1 Molecular Characteristics in Dilute Solution

The values of M_w and $[\eta]$ were not changed by the mercerization for the CC1, however, those for the CC2 were decreased by half after the mercerization (Table I). This depolymerization of the CC2 should have been caused by an oxidative degradation by oxygen in the air in the process of the suction filtration¹³⁾. The CC1 was filtered after neutralization so that it was not depolymerized. The second virial coefficient, A_2 , is a parameter of an affinity between a polymer and a solvent. The values of A_2 for the CC1 and the CC2 tend to

decrease by the mercerization, indicating that an affinity between the cellulose and the solvent molecules decreased by the mercerization. The values of Huggins constant, k' , were ranging from 0.3 to 0.5 for all the cellulose solutions. 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 if the polymer is dispersed molecularly. It is empirically known that the value tends to be larger as solvent power decreases, and if it is over 1, association among polymer molecules can take place.¹⁴⁾ Therefore, these cellulose molecules are provably dispersed molecularly in the dilute solution. The decrease in A_2 by the mercerization took no effect on k' . The value of $\langle R_g^2 \rangle^{1/2}$ for the CC1 is far from that of R_H obtained by the DLS measurement for the 0.5 wt % CC1 solution. The concentration of 0.5 wt % (≈ 5 mg/ml) is higher than the overlap concentration c^* determined as $1/A_2 M_w c$ ($= 0.559$ mg/ml), or $1/[\eta]$ ($= 0.952$ mg/ml), for CC1 solution. Therefore, the value of R_H obtained by the DLS measurement does not correspond to the size of a single cellulose molecule in the solution but to the size of the blob of concentration fluctuation corresponding to the size of the mesh in the network structure.

The value of A_2 for the DP solution did not decrease after the mercerization, which is different from the case of the CC1 and the CC2. This should be caused by lower purity of the cellulose: first, DP is denatured in the process of digestion or bleaching; and second, DP contains hemicelluloses derived from wood. Therefore, the data from the CC1 and the CC2 are discussed mainly in this paper.

Fig.8 Time correlation functions at 90° for CC1 and CC1m solutions in 8 wt % LiCl-DMAc.

Fig.9 Decay rate distribution, $G(\Gamma)$, plotted versus the reciprocal of decay rate, Γ^{-1} , for CC1 and CC1m solutions in 8 wt % LiCl-DMAc. Hydrodynamic radius, R_H , calculated with Einstein-Stokes relation $D_T = k_B T / 6\pi\eta_s R_H$ is shown in top axis. Here k_B , T , and η_s are Boltzmann's constant, absolute temperature, and viscosity of the solvent. D_T is translational diffusion coefficients with $\Gamma = q^2 D_T$.

For the solutions of the native (CC: the CC1 and the CC2) and the mercerized (CCm: the CC1m and the CC2m) cotton cellulose, $\sin^2(\theta/2)$ -dependence of Kc/R_θ was deviated from the extrapolated straight line to $c \rightarrow 0$ at higher angles (Fig.2). This deviation was caused by the effect of the particle scattering factor, $P(\theta)$; the effect of $P(\theta)$ cannot be ignored at higher angles ($q \cdot \langle R_g^2 \rangle_z \gg 1$). $P(\theta)$ for a Gaussian chain is expressed as a function of $X_z = q \cdot \langle R_g^2 \rangle_z$:

$$P(\theta) = \left(\frac{2}{X_z^2} \right) [e^{-X_z} - 1 + X_z]. \quad (5)^{(15)}$$

On the assumption that the molecular weight distribution of a polymer is expressed by Schulz-Zimm distribution¹⁶⁾ (Eq.(6)), $P(\theta)$ of the polydisperse Gaussian chain is calculated as Eq.(7)¹⁷⁾.

$$f(M_i) = \frac{y^{h+1}}{\Gamma(h+1)} M_i^h \exp(-yM_i) \quad (6)$$

$$P_z(\theta) = \frac{2}{X_w} - \frac{2(h+1)}{hX_w^2} \left[1 - \frac{(h+1)^h}{(h+1+X_w)^h} \right] \quad (7)$$

where, $\Gamma(h+1)$ is gamma function of $h+1$; h and y are polydispersity parameter ($h^{-1} = (M_w/M_n) - 1$; $y = h/M_n = (h+1)/M_w$); $X_w = q^2 \cdot \langle R_g^2 \rangle_w = (M_w/M_n) \cdot X_z$. M_w/M_n can be obtained from the extrapolated value at $\theta = 0$ for the initial part and the asymptote at higher angles of the $(Kc/R_\theta)_{c=0}$ versus $\sin^2(\theta/2)$ plot.¹⁸⁾ X_z -dependence of $P(\theta)$ for the CC and the CCm solutions were well reproduced by Eq.(7). Figure 10 shows X_z -dependence of $P(\theta)$ for the CC2m solution as an example. This result suggests that each conformation of the native and

the mercerized cellulose molecule in 8 wt % LiCl-DMAc is almost regarded as a Gaussian chain in the scale observed by the light scattering measurement. It is reported that Eq.(5) agrees with experimental values better than $P(\theta)$ function assumed the excluded volume effect even in good solvent systems except electrolyte polymer solutions.¹⁹⁾

Consequently, it is considered that an affinity between the cellulose and the solvent molecules is decrease by the mercerization but the conformation and the dispersibility of cellulose molecule are essentially constant.

4.2 Rheological Properties of Semidilute Solution

The CC solutions showed typical viscoelastic behavior for homogeneous polymer solutions, but the CCm solutions showed long-time relaxations in the lower frequency region (Fig.5-a ~ 5-c). The long-time relaxation is observed in heterogeneous systems such as molten state multi-arm star polymers²⁰⁾ and heterogeneous suspensions^{21),22)}, and is considered to be related with translational and rotational diffusion of aggregate particles²¹⁾ or transformation and surface tension of heterogeneous structures.^{22),23)} The long-time relaxation observed in the CCm solutions indicates that some heterogeneous structure was formed in the CCm solutions. In the previous paper^{5),6)}, we have reported that a weaker ω -dependence was observed for the bacterial cellulose (BC) solution of higher concentration ($\phi_w \geq 0.05$) accompanied with the appearance of an optically anisotropic phase. In contrast, the CCm solution was optically isotropic even in the concentration region in which the long-time relaxation was observed. This difference indicates that the CCm and the BC form different heterogeneous structure in 8 wt % LiCl-DMAc.

Figure 11 shows ϕ_w -dependence on plateau modulus, G_N , estimated from the experimental data of the dynamic viscoelastic measurements. The value of G_N was estimated as described in the previous paper⁶⁾. Regardless of whether the cellulose sample is mercerized or not, ϕ_w -dependence on G_N can be represented by an identical straight line with a slope of 2 in a double logarithmic plot for all the cellulose samples. This indicates that the effect of the mercerization on the network structure by the polymer entanglement can be almost negligible. However, the long time relaxation at the CCm solutions suggests that there were some heterogeneous structure such as an aggregate structure in the CCm solution. If there were isolate aggregations in the CCm solutions, the density of the polymer entanglement in the system would be smaller. Therefore, some tight entanglements of the CCm molecules having longer relaxation time than normal

Fig.10 Plots of particle scattering factor, $P(\theta)$, versus $\langle R_g^2 \rangle_z q^2$ for CC2m solution; Solid curves remarks theoretical ones¹⁷⁾ of monodisperse sphere, rod, and Gaussian chain. Dotted curve remarks theoretical one for polydisperse Gaussian chain¹⁷⁾ calculated on the assumption of Schultz-Zimm distribution.¹⁶⁾

entanglements produce the long time relaxation. Combined with the result of DLS measurements (Fig.9), there are some aggregate structures in the CCm semidilute solutions in which the CCm molecules are associated by the “tight entanglement”.

Although the results of the dynamic viscoelastic and the DLS measurements indicates the existence of some aggregate structure in the CCm solution, $\phi_w[\eta]$ -dependence of $\eta - \eta_s$ were identical for the CC and the CCm solutions (Fig.7). This leads to the following two assumptions: first, there is no effect of the mercerization on the conformation of cellulose molecule; second, the aggregate structure in the CCm solution effects on the elasticity of the solution in the long time region but hardly effects on the viscosity of the solution. The former is supported by the result of the SLS measurements that $P(\theta)$ of the CC and the CCm was approximated by the one of a polydisperse Gaussian chain. The latter corresponds to the fact that the effect of the long-time relaxation appear mainly on G' and little on G'' as seen in Fig.5-b and 5-c. However, the effect of the long-time relaxation was observed on G'' as well as on G' at 2 wt % CC1m solution (Fig.5-b), and $\dot{\gamma}$ -dependence of σ became weaker in the lower shear rate region (Fig.6). Therefore, the effect of the aggregate structure on the viscous behavior of the CCm solution cannot be neglected at higher concentration.

4.3 Aggregate Structure in Mercerized Cellulose Solution

The aggregate structure observed in the DLS measurements (Fig.9) has no detectable effect on the rheological behavior at

Fig.11 Dependence of plateau modulus, G_N , on weight fraction of polymer, ϕ_w , for CC1, CC2, CC1m, and CC2m solutions in 8 wt % LiCl/DMAc at 30°C.

$\phi_w < 0.01$ (Fig.5-b). The difference in sensitivity for large aggregates may be caused by the fact that the z -average of particle sizes is observed in light scattering measurements. Therefore, the light scattering measurement is very sensitive to large particles. Saalwächter *et al.*²⁴⁾ investigated semidilute solutions of a cotton linter in Cd-tren (tren = tris(2-aminoethyl) amine), and reported that the onset of association was observed from the static and the dynamic light scattering measurements in spite of no detectable effect on the rheological behavior when the concentration was increased beyond the overlap concentration. The long-time relaxation observed in the CCm solutions became more clearly as cellulose concentration became higher in the viscoelastic measurements. This indicates that the number of aggregate structure in the CCm solutions become larger as cellulose concentration become higher.

The driving force for aggregation of the CCm in 8 wt % LiCl-DMAc is still unclear. Changes in the chemical structure of cellulose by the mercerization were not detected with FT-IR and ^{13}C NMR measurements. However, it cannot be denied completely that undetectable slight chemical changes were occurred in the process of the mercerization. Potthast *et al.*²⁵⁾ reported that water in cellulose/LiCl-DMAc induces aggregation which can be removed by filtration through 0.45 μm filters. In our study, however, the aggregate structures in the CC1m solution were observed in the DLS measurements after filtration through 0.45 μm filters. Therefore, the aggregate structure in the CCm solution is not caused by water in the solution. It is confirmed with deconvoluted FT-IR spectra²⁾ that the crystalline structure changed by mercerization is accompanied by splitting and new formation of inter- and intra-molecular H-bonds. The aggregation of the CCm in 8 wt % LiCl-DMAc may be caused by a manner of H-bonds unique to the mercerized cellulose.

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