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Molecular Characterization on the Anomalous Viscosity Behavior of Cellulose Solutions in *N*,*N*-Dimethyl Acetamide and Lithium Chloride

Zubair Khaliq and Byoung Chul Kim*

*Department of Organic & Nano Engineering, Hanyang University, 222 Wangsimni-ro,
Seongdong-Gu, Seoul 04763, Korea*

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Abstract: The physical properties of dilute cellulose solutions in *N,N*-dimethyl acetamide (DMAc) including 9 wt% lithium chloride (LiCl) were investigated in terms of concentration, temperature and molecular weight of cellulose. Over the concentration range of 0.01 to 2.5 g/dL, the viscosity of the cellulose solutions exhibited a lower critical solution temperature (LCST) behavior which proved thermoreversible between 30 and 60 °C. The LCST behavior was further supported by dynamic light scattering measurement. In the extremely dilute concentration range, 0.01 to 0.08 g/dL, the reduced viscosity (η_{red}) of cellulose solutions was increased with decreasing concentration. The anomalous coil expansion with decreasing concentration could be explained by the increase of the conductivity of cellulose solutions with decreasing concentration, which was also verified by dynamic light scattering experiment. In the concentration range of 0.1 and 2.5 g/dL, both cellulose solutions gave a drastic increase of η_{red} in the vicinity of the critical concentration (C^*), 0.9 g/dL. The slope of the curve of η_{red} *vs*. concentration was higher for the cellulose of higher molecular weight, but it did not change with temperature between 30 and 60 °C.

Keywords: cellulose, *N,N*-dimethylacetamide/LiCl, LCST behavior, thermoreversibility, polyelectrolyte effects.

Introduction

Cellulose is one of the most abundant natural polymers, and its sustainability is believed to offer a solution to the exhaustion of natural resources for oil-based synthetic polymers. In fact, a large volume of cellulose and its derivatives are being consumed for textiles, paper, and membranes.[1-5] In addition, the biodegradability of cellulose has attracted much attention of scientists and engineers to replace synthetic fibers and plastics. Cellulose contains numerous inter- and intramolecular hydrogen bonds together with high crystallinity.[6-8] Consequently, cellulose is dissolved only in the solvents containing acids and alkalis to overcome the intermolecular hydrogen bonds, which frequently brings about the hydrolysis of glucosidic bonds.[9] A limited number of solvents are reported to dissolve cellulose without a significant decomposition. Some examples include *N*-methylmorpholine oxide, aqueous sodium hydroxide, *N*,*N*-dimethyl acetamide (DMAc)/lithium chloride (LiCl) and ionic liquids.[10-19] An intensive study of the cellulose behavior in DMAc/LiCl has been carried out in terms of cellulose activation method,[20-23] metal salt concentration,[24,25] cellulose type,[26,27] water contents[28] and molecule aggregation.[29,30]

In the polar polymer solutions various inter- and intra- physical bonds between polymer and solvent molecules exist, which have a critical effect on the physical properties of the polymer solutions.[31,32] The strength of the physical bonds is not constant but affected by the extent of polarization and bond length. As might be imagined it would be maximum at the van der Waals radius. Thus, the concentration has a profound influence on the physical properties because it determines the distance between functional groups. In addition, temperature also has a paramount effect on the physical properties of the solutions because of the trade-off effects of enthalpy and entropy.

Because of various polar interactions between polymer and solvent molecules, cellulose solutions exhibit some unusual dependence of viscosity on temperature and concentration. Most papers based on thermodynamics deal with a collective molecular behavior.[33-35] Little literature is available to understand the anomalous change of the physical properties in the context of individual cellulose molecules. We tried to explain the effects of concentration and temperature on the physical properties, particularly viscosity behavior, of cellulose solutions in DMAc/LiCl on the basis of physical bonding between hydroxyl groups and the resultant conformation of cellulose molecules.

Experimental

Materials. Two cotton linter-based cellulose samples and LiCl were purchased from Sigma-Aldrich (USA), whose weight

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*Corresponding Author. E-mail: bckim@hanyang.ac.kr

average molecular weight was 99,000 (CL-HMW, high molecular weight cellulose) and 44,000 (CL-LMW, low molecular weight cellulose). The extra-pure grade of DMAc was purchased from Samchun Chemicals Co. (Korea). All reagents were used without further purification. Cellulose and LiCl were vacuum dried at 60 ºC for 48 h prior to use.

Preparation of Cellulose Solutions. Previous studies indicate that cellulose needs activation to dissolve in DMAc/LiCl.[13,14] Cellulose was activated by a solvent exchange method instead of heat activation to avoid degradation.[21,36] The dried cellulose was put in 9 wt% DMAc/LiCl solvent and magnetically stirred at 50 ºC for 3 h to obtain homogeneous solutions. The 1 and 3 g/dL solutions were diluted to the solutions of concentration over 0.9~0.01 and 1.1~2.5 g/dL, respectively. The cellulose solutions were firmly covered to prevent any moisture absorption. To obtain reproducibility of data, the dissolution conditions were strictly controlled to be identical to each cellulose solution.

Viscosity Measurement. The viscosity of cellulose solutions was measured by Ubbelohde viscometer (Schott Co.). Relative viscosity (η_{rel}) was determined by the run time ratio of cellulose solution to solvent. Inherent (η_{inh}) and reduced (η_{red}) viscosities were calculated by Eqs. (1) and (2), respectively. Intrinsic viscosity ([η]) was obtained by extrapolation of η_{inh} to zero concentration.

$$\eta_{inh} = \frac{\ln \eta_{rel}}{c} \tag{1}$$

$$\eta_{red} = \frac{\eta_{sp}}{c} \tag{2}$$

in which, $\eta_{sp}=\eta_{rel}-1$, and c is the concentration of cellulose in g/dL.

The degradability and thermoreversibility of cellulose were checked by measuring the single point intrinsic viscosity ([η]*) using the Solomon-Ciuta equation (Eq. 3).[37] The [η]* was calculated at 0.1 g/dL.

$$[\eta]^* = [2\times(\eta_{sp}-\ln\eta_{rel})]^{1/2}/c \tag{3}$$

Dynamic Light Scattering. Dynamic light scattering (DLS) instrument (Zetasizer Nano ZS; Malvern) was used to measure the hydrodynamic radius (R_h) of cellulose at different concentrations of 0.01~0.1 g/dL. The viscosity and refractive index values of 9 wt% LiCl/DMAc were taken from the reference.[38] The cellulose solution was filtered through 0.45 micrometer PTFE membrane filter under vacuum to make the sample dust free. The cellulose solutions were equilibrated at assigned temperature for 5 min prior to measurement. A 633 nm He-Ne laser was used as a light source. DLS measurement was carried out at an angle of 90º to the incident beam and analyzed by regularized CONTIN method.[39]

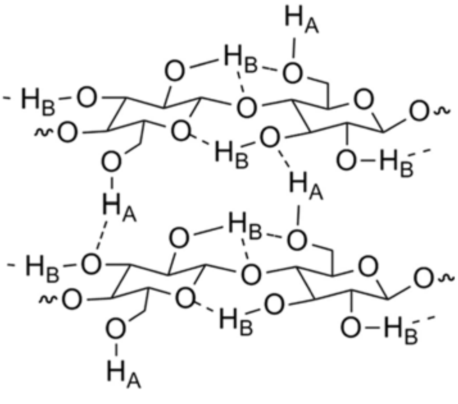
Conductivity Measurement. The conductivity of cellulose solution at different concentrations (0.01~0.09 g/dL) was measured by a conductivity meter (Orion 3 Star Thermo Scientific Co.). The samples were equilibrated for 15 min at 25 ºC before measurement.

Results and Discussion

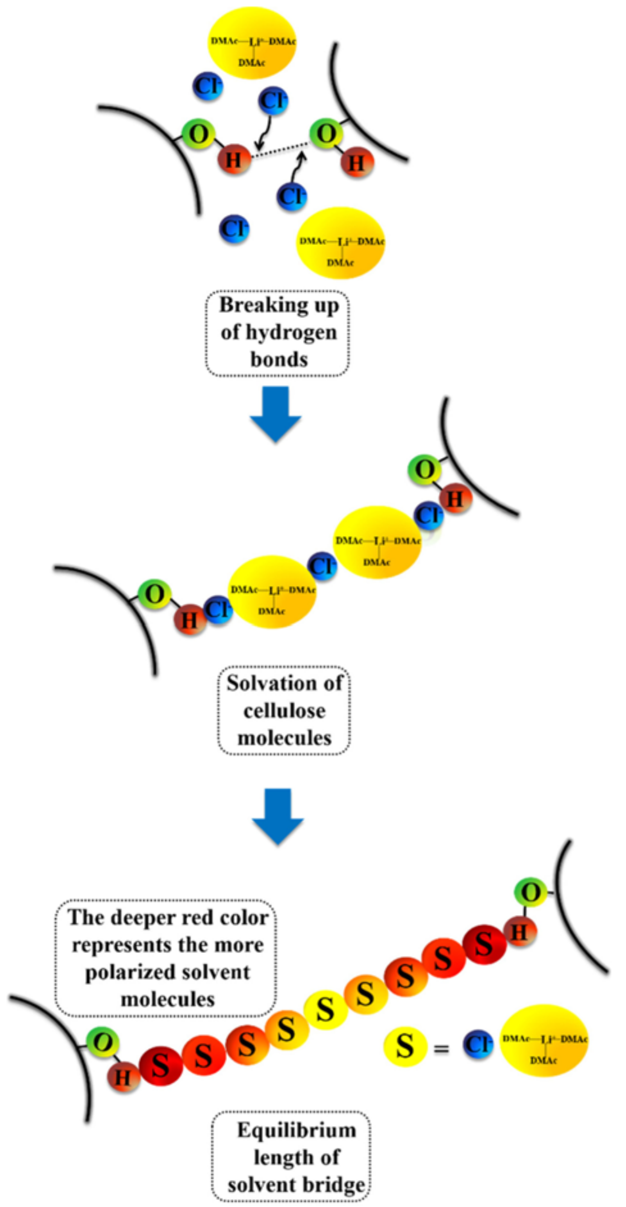
As shown in Scheme I, for every repeating unit of cellulose, the cellobiose, contains 6 hydroxyl groups; 2 hydroxyl groups (-OH$_A$) form intermolecular hydrogen bonds and 4 hydroxyl groups (-OH$_B$), intramolecular hydrogen bonds. DMAc alone cannot dissolve cellulose irrespective of high polarity because cellulose chains possess numerous intra- and intermolecular hydrogen bonds. When LiCl is added to DMAc, however, DMAc molecules surround Li$^+$ and leave Cl$^-$ free.[40-42] The Cl$^-$ ions penetrate between the cellulose chains by breaking up hydrogen bonds between hydroxyl groups because the ionic interaction is greater than hydrogen bonding. In consequence, the cellulose molecules are fully solvated by polar-polar interactions between polymer and solvent molecules. At a given temperature, the cellulose solution reaches a thermodynamic equilibrium, which may be visualized by adopting the concept of solvent bridges.[39] The solvent molecule nearer to the hydroxyl group would be more strongly polarized as illustrated in Scheme II, in which the deeper red color denotes, the more strongly polarized solvent molecule.

Cellulose may degrade in some solvents at the elevated temperature.[36,43] To examine the feasibility of the degradation of cellulose in the solvent system during measurement, the [η]* of cellulose solution in DMAc/LiCl is plotted *vs*. time in Figure 1. Little variation of [η]* with time confirms that the cellulose degradation in DMAc/LiCl is negligible during physical measurement. Two things are notable in Figure 1, CL-HMW gives a higher value of [η]* than CL-LMW, and the [η]* of two cellulose solutions is higher at a lower temperature.

The physical properties of dilute polymer solutions reflect the physicochemical state of individual polymer chains because the intermolecular interactions between polymer chains get negligible.[44,45] Figures 2(a) and (b) show the plots of η_{inh} versus concentration of CL-HMW and CL-LMW solutions in DMAc/LiCl, respectively. The η_{inh} of cellulose solutions decreases with increasing cellulose concentration, which is typical of most polymer solutions. In addition, [η] decreases with raising temperature which indicates that the dimension



Scheme I. Inter-(-OH$_A$) and intramolecular (-OH$_B$) hydrogen bonds between cellulose molecules.



Scheme II. Dissolution mechanism of cellulose in DMAc/LiCl; Breaking up of hydrogen bonds between hydroxyl groups of cellulose, followed by solvation of cellulose molecules by polar-polar interactions between cellulose and solvent molecules to reach an equilibrium state.

of cellulose chains decreases as temperature increases. This implies that both cellulose solutions are lower critical solution temperature (LCST) systems.

When temperature increases, however, the mobility of polymer and solvent molecules increases and finally overcomes the lattice energy of the equilibrium solvent bridges. The equilibrium solvent bridges in Scheme II collapse by escaping the less polarized solvent molecules first. Breaking up the solvent bridges leads to new shorter but stronger equilibrium solvent bridges at higher temperature as illustrated in Scheme III.

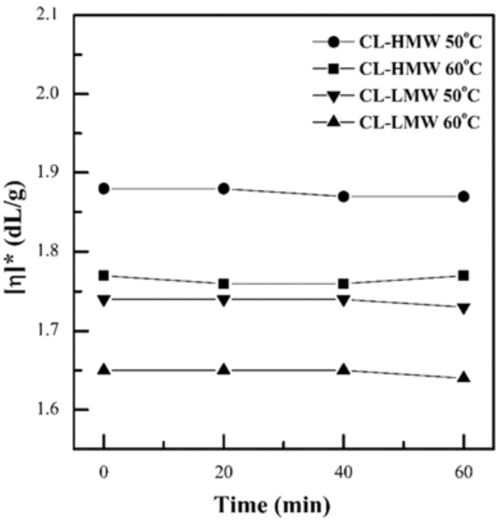
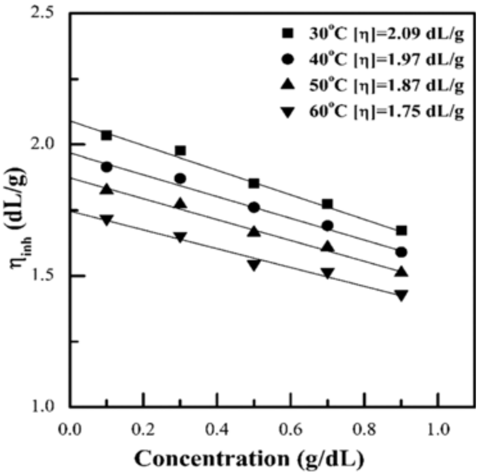
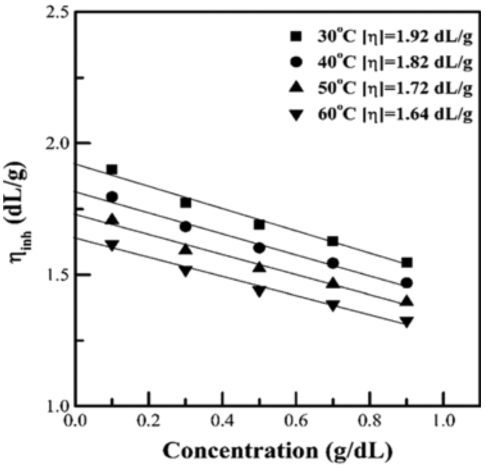


Figure 1. Variation of [η]* at 50 and 60 °C with time for CL-HMW and CL-LMW solutions in DMAc/LiCl at the concentration of 0.1 g/dL.

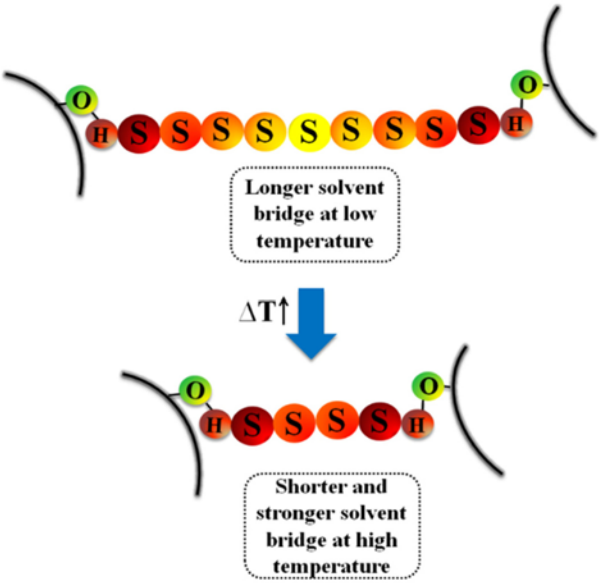


(a) CL-HMW



(b) CL-LMW

Figure 2. Variation of the η_{inh} with concentration of (a) CL-HMW and (b) CL-LMW solutions in DMAc/LiCl at 4 different temperatures. The η_{inh} at zero concentration gives the [η].



Scheme III. LCST mechanism of cellulose solution in DMAc/LiCl with increasing temperature from 30 to 60 °C.

The coil shrinkage with increasing temperature corresponds with the LCST behavior in Figures 1 and 2.

Although the $[\eta]$ is believed to be a measure of the dimension of a polymer molecule, the polymer molecule may have a deformation from the equilibrium dimension because of shear stress exerted during the viscosity measurement. To rule out the possibility of the shear deformation of polymer chains, the variation of the hydrodynamic radius (R_h) of cellulose molecule with temperature was also measured by DLS. Figure 3 further ascertains that R_h decreases with increasing temperature, reconfirming the cellulose solutions in DMAc/LiCl is an LCST system. Similar phase behavior in other polar polymer solutions in polar solvents was also reported by others.[32,39,46]

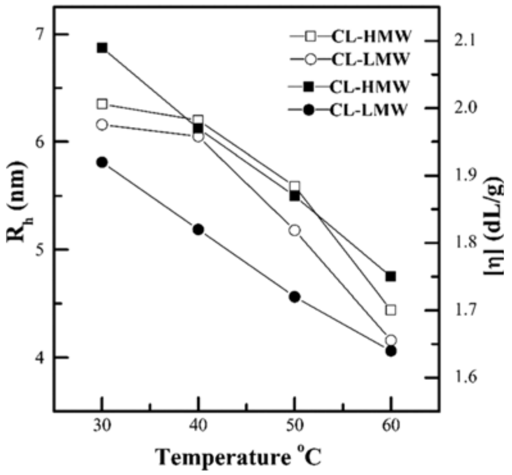


Figure 3. Variation of the $[\eta]$ (filled symbols) and R_h (open symbols) of CL-HMW and CL-LMW solutions in DMAc/LiCl with temperature. R_h is calculated for 0.1 g/dL cellulose solution.

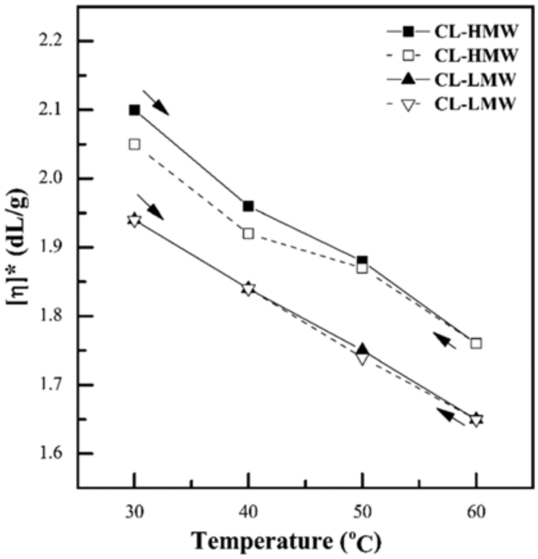
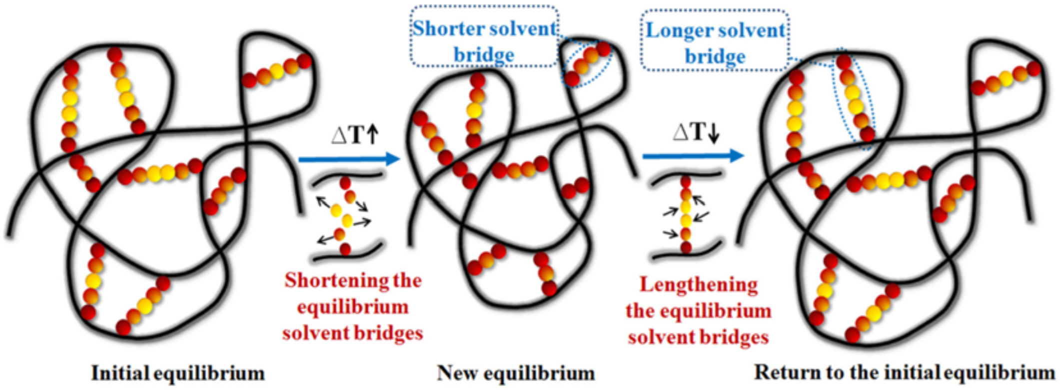


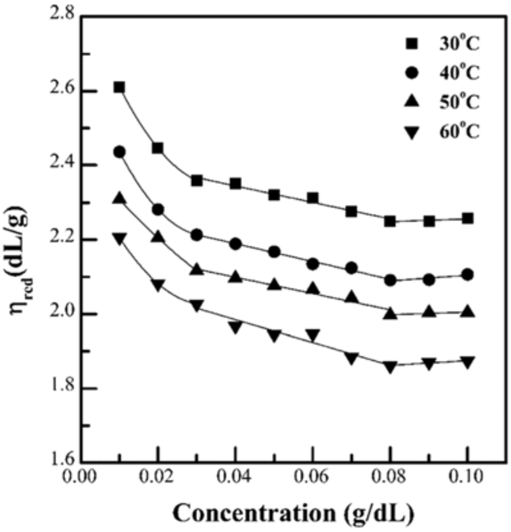
Figure 4. Variation of $[\eta]^*$ with increasing (filled symbols) and decreasing (open symbols) temperature for CL-HMW and CL-LMW solutions in DMAc/LiCl at the concentration of 0.1 g/dL.

Figure 4 presents the variation of the $[\eta]^*$ of cellulose solutions in DMAc/LiCl with temperature between 30 and 60 °C. It is worth mentioning that the variation of the dimension of cellulose molecule with temperature turns out thermoreversible over the temperature range observed. A slight deviation from the thermoreversibility is observed for CL-HMW, which is almost negligible if the scale of the y-axis is taken into consideration. The negative deviation during cooling, however, seems to result from the reminiscence of slower relaxation of the cellulose molecule of higher molecular weight after deformation. The conceptual mechanism of thermoreversibility is illustrated in Scheme IV.

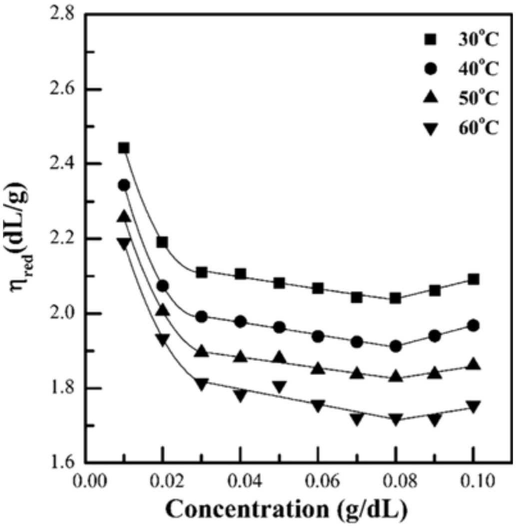
In the extremely dilute concentration range, the η_{red} of polar polymer solutions is reported to vary in an anomalous way because the charge interactions between components have a profound influence on the dimension of polymer molecule.[47,48] The η_{red} of cellulose solutions in DMAc/LiCl also exhibits a very unusual behavior over the concentration range of 0.01 to 0.08 g/dL between 30 and 60 °C with two critical points at 0.03 and 0.08 g/dL as noted in Figure 5. A steep reduction of the η_{red} is observed up to 0.03 g/dL and follows a gradual reduction between 0.03 to 0.08 g/dL for both cellulose solutions. In this concentration range, the intermolecular interactions between polymers are almost negligible in comparison with the interactions between polymer and solvent molecules. Further dilution of the solution increases the ratio of Cl^- ions to $-OH_B$ group, promoting the interactions between Cl^- ions with $-OH_B$ groups of cellulose molecules. The surrounding Cl^- ions bring about repulsion between the hydroxyl groups of cellulose molecule as illustrated in Scheme V. In consequence, the cellulose molecule expands apart from its normal dimension as represented in Scheme VI. In addition, the steep reduction



Scheme IV. The schematic of the thermoreversibility mechanism of cellulose solutions in DMAc/LiCl between 30 and 60 °C.

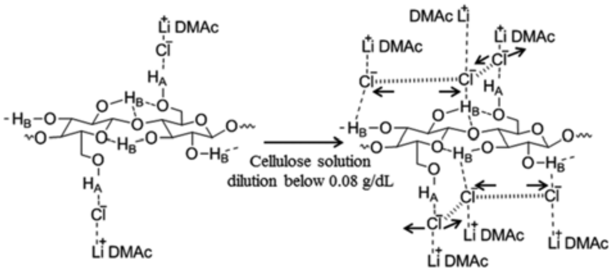


(a) CL-HMW



(b) CL-LMW

Figure 5. Variation of η_{red} with concentration for (a) CL-HMW and (b) CL-LMW solutions in DMAc/LiCl below the concentration 0.1 g/dL at 4 different temperatures.

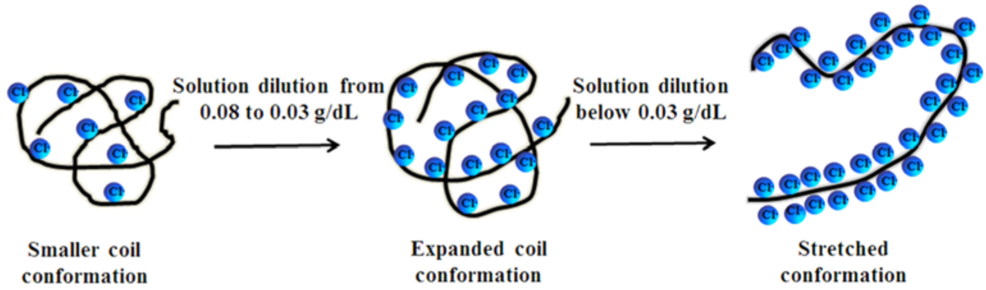


Scheme V. Generation of repulsive forces between hydroxyl groups in the cellulose solution in DMAc/LiCl by increasing the concentration of Cl^- ions with dilution of the solution below 0.08 g/dL.

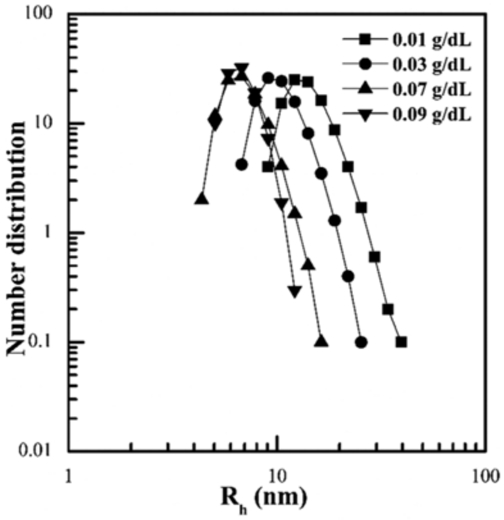
of the η_{red} in Figure 5 is an indication of the conformation transition of cellulose molecules from stretched to coiled ones in the vicinity of 0.03 g/dL as suggested in Scheme VI.

The expansion of polymer chains by decreasing concentration from 0.09 to 0.01 g/dL is also confirmed by the number distribution curves for cellulose solutions in DMAc/LiCl in Figure 6. The number distribution curve shows the distribution of R_h of a polymer in the solution at a given concentration which corresponds to the molecular weight distribution of the polymer. The R_h of cellulose chains generally increases with decreasing concentration from 0.09 to 0.01 g/dL. In addition, CL-HMW of higher molecular weight gives more noticed conformational change than CL-LMW. This result coincides with the theoretical prediction in Figure 5.

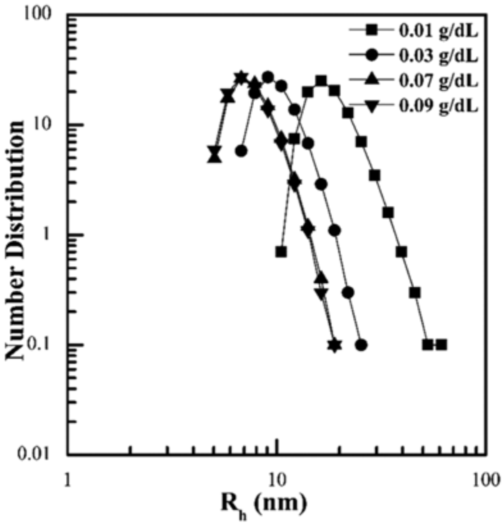
The chain expansion by the repulsive force between Cl^- ions in Scheme V can be evidenced by the conductivity of the cellulose solutions. When cellulose is dissolved in DMAc/LiCl, the free Cl^- ions interact with hydroxyl groups as shown in Scheme V. In consequence, the conductivity of cellulose solution increases with increasing cellulose concentration.[22] In the extremely low concentration, where the intermolecular interactions between cellulose chains become negligible, the Cl^- ions would interact with $-OH_B$ rather than $-OH_A$. Thus, the repulsive force between the same charges of Cl^- ions would be generated as shown in Scheme V. In fact, the conductivity of both solutions decreases with increasing concentration from



Scheme VI. The schematic of the change of the cellulose conformation in DMAc/LiCl solution with dilution below 0.08 g/dL.



(a) CL-HMW



(b) CL-LMW

Figure 6. The number distribution curves of R_h for (a) CL-HMW and (b) CL-LMW chains in DMAc/LiCl at different concentration.

0.01 to 0.09 g/dL as shown in Figure 7. This indicates that the concentration of free Cl$^-$ ions is decreasing in the solution with increasing concentration from 0.01 to 0.09. Such electrolyte effects at the extremely low concentration were also reported by others.[47-49]

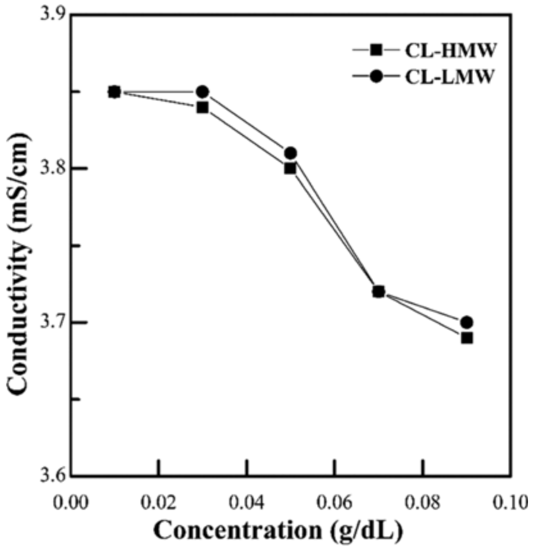
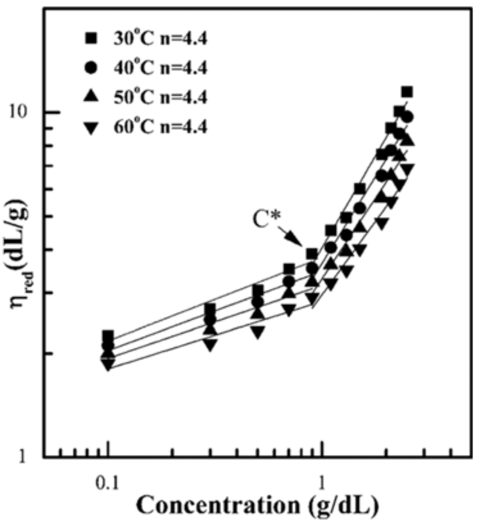
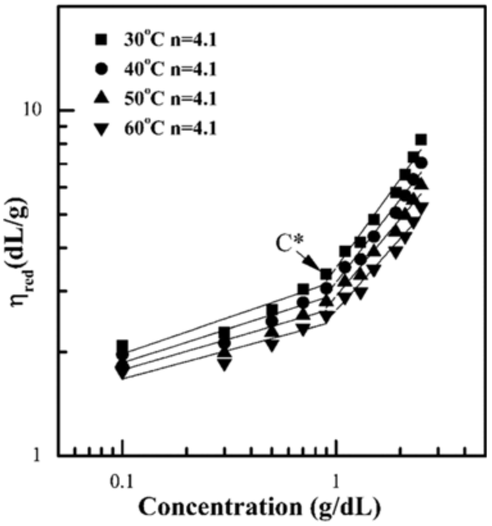


Figure 7. Variation of the conductivity of cellulose solutions with concentration.

Figure 8 shows the plot of η_{red} *vs*. concentration for CL-HMW and CL-LMW solutions in DMAc/LiCl over the concentration range of 0.1 to 2.5 g/dL. The η_{red} of cellulose solutions increases gradually with increasing concentration. However a drastic increase of the η_{red} is observed above 0.9 g/dL, the critical concentration (C^*) for both cellulose solutions over the entire temperature range measured. This implies that intermolecular interactions through crowding effects rather than polyelectrolyte effects get more dominant above C^*. For nonpolar polymers, C^* is generally inversely proportional to molecular weight.[50] In the case of polar cellulose solutions, however, C^* is almost the same for both CL-HMW and CL-LMW solutions because the apparent molecular weight of two cellulose specimens through intermolecular hydrogen bonding would be similar. In addition, slope (n) of the η_{red} curves is 4.4 for CL-HMW and 4.1 for CL-LMW above C^*. It is also worth mentioning in the Figure 8 that the values of C^* and n do not change over the temperature range of 30 to 60 °C. This indicates that intermolecular interactions between cellulose



(a) CL-HMW



(b) CL-LMW

Figure 8. Variation of η_{red} with concentration for (a) CL-HMW and (b) CL-LMW solutions in DMAc/LiCl over the concentration range between 0.1 and 2.5 g/dL at 4 different temperatures.

chains are hardly affected by a temperature between 30 and 60 °C because of thermoreversibility.

Conclusions

The unusual viscosity behavior of cellulose solutions in DMAc/LiCl with concentration and temperature could be accounted for after considering the physical interactions between polar hydroxyl groups of cellulose and solvent molecules. In the concentration range, lower than 0.08 g/dL, the electrolyte effects played a key role in the expansion of cellulose chains with decreasing concentration. In the vicinity of 0.03 g/dL, a rigid to flexible transition of conformation of cellulose molecule seemed to take place with increasing concentration. The LCST behavior of the cellulose solutions over the concentration range of 0.01 to 2.5 g/dL proved thermoreversible between 30 to 60 °C. DLS measurement also endorsed the LCST behavior.

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