Physical state of cellulose in BmimCl: dependence of molar mass on viscoelasticity and sol-gel transition†

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In this work, we investigated the correlation between the molar mass and the rheological properties of cellulose/1-butyl-3-methylimidazolium chloride (BmimCl) solutions, and provided the depolymerization kinetics of cellulose in BmimCl. Gel permeation chromatography was used to track the change in molar mass and kinetics as a function of the dissolution time. The molar mass of cellulose in BmimCl decreased significantly as the dissolution time increased, following a zeroth order rate law. The decrease of inter-chain friction induced by depolymerization resulted in a lower viscosity, shorter relaxation time, and lower activation energy. The activation energies for flow were distinctly different above and below the critical molar mass, which indicates that the relaxation mechanisms were not identical above and below the critical molar mass. The transition behavior of liquid crystalline phase also changed at the critical molar mass, which strongly demonstrated the effect of chain length on the formation of cholesteric phase. The exponents of Mark–Houwink–Sakurada and the radius of gyration showed that cellulose in BmimCl existed as a Gaussian chain in a theta solvent.

1. Introduction

Global environmental concerns have triggered researchers’ interest in replacing energy consuming processes and eco-hazardous materials with sustainable energy processes and eco-friendly materials.1–4 Cellulose is a promising eco-friendly material for replacing synthetic polymers. Cellulose is the most abundant natural organic material with ∼1.5 trillion tons on Earth at any given time.5,6 For thousands of years, natural cellulose (e.g., wood, cotton, and hemp) has been used in textiles, furniture, and housing. The applications of cellulose have now extended to high-technology areas such as biomedical products, bio-energy sources, and engineered structural reinforcement materials.7,8

Dissolution of cellulose is of fundamental importance for its processing and chemical derivatization. However, solvent systems for cellulose dissolution are quite limited because of its high crystallinity associated with extensive hydrogen bonding networks. In addition, most of the solvent systems9 for cellulose, such as N-methylmorpholine-N-oxide monohydrate, LiCl/N,N-dimethylacetamide, ammonium fluoride/dimethylsulfoxide, and NaOH/water with urea, have serious drawbacks, including high toxicity, volatility, oxidative side reactions, thermal instability, and high energy consumption during the dissolution process. As an alternative to these solvents, ionic liquids have received considerable attention for cellulose processing in a homogeneous solution.10 Since Swatloski et al.11 reported cellulose dissolution using ionic liquids, many ionic liquids have been synthesized, such as 1-butyl-3-methylimidazolium chloride (BmimCl), 1-ethyl-3-methylimidazolium acetate (EmimOAc) and 1-allyl-3-methylimidazolium chloride (AmimCl). Ionic liquids have many advantages compared with traditional organic solvents, namely, excellent dissolving capability, negligible vapor pressure, ease of recycling, and high thermal stability.12–14

To design or improve a dissolution process, it is critical to understand the impact of ionic liquids on the properties of cellulose and its solutions. Of particular importance is our understanding of the rheological behavior of cellulose in ionic liquids. Rheological behaviors of polymer solutions play a significant role in processes for fibers, films, and nonwoven materials. Most studies on the rheological properties of cellulose-ionic liquid solutions have focused on the influences of source, concentration and temperature on the rheological behavior of cellulose solutions.15–17 Although linear viscoelastic properties were comprehensively investigated for the cellulose/ionic liquids, there are few studies on the influence of dissolution conditions on the changes in molecular properties and structure, such as molar mass and distribution. Recently, it has been reported that...
cellulose dissolved in some ionic liquids was fairly depolymerized along the dissolution time.\textsuperscript{18} It is expected that there is some degree of molar mass reduction during the dissolution process, which strongly influences the rheological properties.

This study focused on the change in cellulose molar mass during dissolution, and the effect of this change on the rheological behaviors of the solution and the physical state of cellulose in BmimCl. We observed a reduction of the molar mass during dissolution of cellulose in BmimCl. The depolymerization mechanism of cellulose in ionic liquid BmimCl was investigated using reducing ends analysis. According to the change in molecular structure, the molar mass dependence on viscoelasticity was investigated using the time–temperature superposition. The relaxation behaviors of the solutions for different molar masses were interpreted using the generalized Maxwell model. Based on the physical state, Mark–Houwink–Sakurada exponents and observation of the phase transition behavior were employed to assess the relationship between the molar mass and the rheological properties, and the conformation of the dissolved cellulose. An understanding of the relationship between depolymerization and rheological properties would provide important information to help industries to optimally use cellulose-ionic liquid processing.

2. Experimental

2.1. Materials and preparation of solutions

Cellulose from poplar was kindly provided by Hyosung Co. (Korea). Its molar mass and composition were determined by GPC and composition analysis (see Table S1, ESI\textsuperscript{+}). Cellulose was dried overnight at 60 °C in a vacuum oven before use. BmimCl (>99%, water content: 0.22 wt%) and N,N-dimethylacetamide (DMAc, >99%) were purchased from BASF and Daejung Chemical & Metal Co. Cellulose and BmimCl were mixed in a sealed reaction vessel and stirred at 85 °C for 24–240 h. The cellulose concentration used in this study was fixed at 7 wt%.

2.2. Rheological properties

Rheological measurements were performed on a stress-controlled rheometer (RS-1, ThermoFisher Scientific, Germany) equipped with a 35 mm parallel plate geometry. Steady state viscosity measurements were carried out at 30 °C within the shear rate range 10\textsuperscript{-3}–10\textsuperscript{3} s\textsuperscript{-1}. Dynamic viscoelasticity was measured in the temperature range 30–110 °C. The range of the oscillatory frequency was 10\textsuperscript{-2}–10\textsuperscript{2} Hz at each temperature. The data were reduced to the reference temperature (70 °C) data using the time–temperature superposition principle.\textsuperscript{19} The open edge of the specimen sandwiched between the plates was covered with a thin layer of silicone oil (Shin-Etsu Chemical Co.) to prevent water uptake by the sample.

The intrinsic viscosity was determined from the viscosities of dilute cellulose/BmimCl solutions calculated using eqn (1) and (2) proposed by Huggins and Kraemer.\textsuperscript{6,20–22}

\[
\frac{\eta_p}{c} = [n] + K_h [n]^2 c
\]  
\[
\frac{\ln \eta_s}{c} = [n] - K_k [n]^2 c
\]

where \(K_h\) is the Huggins coefficient, \(K_k\) is the Kraemer coefficient, and \(\eta_p = \eta_0/\eta_s\) (\(\eta_0\) = zero shear rate viscosity; \(\eta_s\) = solvent viscosity) is the relative viscosity.

The plots of \(\eta_p/c\) and \(\ln \eta_s/c\) versus \(c\) gave two straight lines with an identical intercept with the y-axis (\(c = 0\)). The intercept corresponds to the intrinsic viscosity, \([n]\). The graphically determined intrinsic viscosities are summarized in Table 1.

2.3. Molar mass measurement

The prepared solution was poured into deionized water at room temperature, for cellulose precipitation. The precipitate was washed several times with deionized water until all residual BmimCl was removed. The precipitated cellulose samples were dried in a vacuum oven for 1 day. For size-exclusion chromatography, the precipitated cellulose was dissolved in 9% LiCl/DMAc using the method reported by McCormick et al.\textsuperscript{23} This dissolution method involved the following solvent exchange process. First, each cellulose sample was suspended in deionized water for 24 h. After filtration, the sample was immersed in anhydrous methanol for 30 min and filtered again. This process was repeated three times. After solvent exchange with methanol, the same process was repeated five times with DMAc. These solvent exchanges were carried out at room temperature. The cellulose samples were dissolved in 9 wt% LiCl/DMAc after being completely dried in a vacuum below 60 °C. GPC was performed on a YL9100 (Young Lin Instruments, Republic of Korea), equipped with a refractive index concentration detector (RI), and two angle light scattering detectors at 90° and 45°. A mobile phase consisting of 0.5 wt% LiCl in DMAc was used at a flow rate of 1 mL min\textsuperscript{-1}. The temperature was set at 40 °C. Light scattering (LS) constants were calibrated using standard polysaccharides with molar masses of 34.4, 19.4, 10.7, 4.7, 3.3 and 1.1 × 10\textsuperscript{4} g mol\textsuperscript{-1} (see Fig. S1, ESI\textsuperscript{+}). The injection volume was 100 µL, and the run time was 30 min. The refractive index increment constant, \(dn/dc\), representing cellulose in 9 wt% LiCl/DMAc was 0.055 cm\textsuperscript{3} g\textsuperscript{-1}, based on a value reported in the literature.\textsuperscript{23}

2.4. Reducing ends measurement

In order to determine the degree of cellulose depolymerization, the number of cellulose reducing ends was measured via a colorimetric assay using 2,2′-bicinchoninate (BCA). The assay solutions were prepared by mixing two solutions. For assay

<table>
<thead>
<tr>
<th>(t) (h)</th>
<th>(M_n) (10\textsuperscript{3} g mol\textsuperscript{-1})</th>
<th>(M_w) (10\textsuperscript{3} g mol\textsuperscript{-1})</th>
<th>No. of reducing ends</th>
<th>Intrinsic viscosity (cm\textsuperscript{3} g\textsuperscript{-1})</th>
</tr>
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<tbody>
<tr>
<td>Raw</td>
<td>229</td>
<td>283</td>
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<td>24</td>
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<td>72</td>
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<td>165</td>
<td>1.7</td>
<td>219</td>
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<tr>
<td>96</td>
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<td>1.9</td>
<td>179</td>
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<td>152</td>
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<td>192</td>
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</tr>
<tr>
<td>216</td>
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<td>63</td>
<td>3.7</td>
<td>121</td>
</tr>
<tr>
<td>240</td>
<td>29</td>
<td>55</td>
<td>3.9</td>
<td>110</td>
</tr>
</tbody>
</table>
solution A, Na₂CO₃ (5.4230 g), NaHCO₃ (2.4198 g), and bicinechoninic acid disodium salt hydrate (Sigma-Aldrich, > 98%, 0.1944 g) were dissolved in milli-Q-purified water, and the volume of solution was adjusted to 100 mL. In assay solution B, CuSO₄·5H₂O (Sigma-Aldrich, > 98%, 0.1242 g) and l-serine (Sigma-Aldrich, 0.1260 g) were dissolved in milli-Q-purified water, and the volume was adjusted to 100 mL. BCA reagent solution was prepared by combining solutions A and B in a 1:1 v/v ratio just prior to use. The BCA reagent solution was added to an aqueous slurry of cellulose solution at 80 °C for 1 h. Assay tubes were quenched in an ice bath and the absorbance at 560 nm was recorded using an Optizen 3220UV UV/Vis spectrophotometer (Mecasys).

2.5. Optical microscope observation

The phase transition of cellulose/BmimCl solutions with different molar masses and concentrations was observed from optical micrographs taken using a BX41 Olympus polarized optical microscope. 1-Methylimidazole (5 wt%) was added to prevent further hydrolysis during dissolution.¹⁸ A 530 nm sensitive tint plate (U-TP530, Olympus) was used as a test plate compensator, which resulted in a magenta background in the micrographs.

3. Results

3.1 Molecular characterization of cellulose dissolved in BmimCl for different dissolution times

Fig. 1 shows the calculated molar mass distribution of cellulose with various dissolution times. The molar mass distribution was fitted to a Zimm–Schultz (Z–S) distribution using eqn (3).

\[
w(P_i) = \frac{b^{b+1}}{b!} M_i^b \exp(-aM_i)
\]

where \(a\) and \(b\) in the Z–S distribution are related to the weight- and number-average molar masses according to eqn (4) and (5).

\[
a = \frac{1}{M_w - M_n}
\]

\[
b = \frac{M_w}{M_w - M_n}
\]

The number-average \(M_n\) and weight-average \(M_w\) molar masses were calculated using eqn (4) and (5), respectively, and summarized in Table 1. The polydispersity index, \(Q\), is given by eqn (6).

\[
Q = \frac{M_w}{M_n}
\]

As shown in Fig. 1, the peak of the GPC curves shifted to lower molar masses as the dissolution time increased. The shift to lower molar masses without peak splitting suggests that cellulose was homogeneously depolymerized during dissolution. Based on a model of homogeneous depolymerization for cellulose, the plot of molar mass as a function of time can be fitted by the zeroth order rate law proposed by Matthes,²⁵ as shown in eqn (8).

\[
dS/dt = k
\]

\[
S = S_0 + kt
\]

where, \(S\), \(k\), and \(t\) are degrees of splitting (1/\(M_w\)), depolymerization rate, and depolymerization time, respectively.

Fig. 2 shows the degrees of splitting and the polydispersity index (PDI) of the regenerated cellulose with various dissolution times. The degree of splitting linearly increased as the dissolution time increased. From a regression analysis using the zeroth-order rate law, the depolymerization rate \(k\) was obtained as 0.057 µmol h⁻¹, indicating that the degree of splitting can be nicely described by eqn (7). This value is consistent with the results obtained under the same conditions reported by Gazit and Katz.¹⁸ According to eqn (7), the molar mass of cellulose can be estimated based on the dissolution time at 85 °C. On the other hand, the PDI increased continuously from 1.2 to 1.9 as the dissolution time increased. This trend is often observed for depolymerization of cellulosic polymers.²⁶,²⁷ The data seem to indicate that cellulose randomly depolymerized during dissolution, which led to the wide range of molecular sizes. This point

![Fig. 1](image1)

Fig. 1 Changes in molar mass distribution during the dissolution of cellulose in BmimCl at 85 °C. The solid lines are fits to the Zimm–Schultz distribution function.

![Fig. 2](image2)

Fig. 2 Changes in reciprocal molar mass, 1/\(M_w\), and PDI during the dissolution of cellulose in BmimCl. The slope of the solid line (blue) represents the hydrolysis rate calculated by the zeroth order rate law.
is discussed later in this paper based on the rheological properties of the cellulose solutions.

### 3.2 Steady shear viscosity of cellulose/BmimCl solutions

Steady shear viscosities were recorded over a range of different shear rates. Fig. 3(a) shows the shear rate dependence of the steady shear viscosity for 7 wt% cellulose/BmimCl solutions on the dissolution times at 30°C. Shear thinning behavior was observed for the solutions dissolved for 24–168 h, which indicates that entanglement regions exist. However, the onset of shear-thinning shifted to higher shear rates as the dissolution time increased. For the solutions dissolved for longer times (192–240 h), all the solutions show Newtonian behavior without shear-thinning behaviors.

To quantitatively evaluate this shear thinning behavior, non-Newtonian flow (Fig. 3[a]) under steady shear conditions was studied using the quantitative Cross model (eqn (9)), which is known to describe well the dependence of viscosity on the shear rate:

$$\eta(\dot{\gamma}) = \frac{\eta_0}{1 + (\tau \dot{\gamma})^n}$$  \hspace{1cm} (9)

where $\eta_0$, $\tau$, $n$, and $\dot{\gamma}$ represent the zero shear viscosity, characteristic relaxation time, power-law exponent and shear rate, respectively.

The values of $\eta_0$ and $\tau$ for each solution are listed in Table 2. For uncrosslinked polymer solutions, the changes in shear-thinning behavior and viscosity can be ascribed to intermolecular interactions. Shear flow contorts the polymer chain structure and changes conformation with certain relaxation times. To confirm the change in relaxation mechanism, the steady shear viscosity was normalized by the zero-shear viscosity, $\eta_0$ (see Fig. 3[b]). This normalization yielded good superposition of the viscosity curves, which implies universality in the viscoelastic properties of cellulose/BmimCl solutions at different dissolution times.

In addition, the characteristic relaxation time $\tau$ is closely related to the zero-shear viscosity. The definition of zero shear viscosity for entangled polymer solutions is shown in eqn (10):

$$\eta_0 = G_N(\phi)\tau(\phi)$$  \hspace{1cm} (10)

where $G_N$ and $\phi$ are the plateau modulus and volume fraction of the polymer, respectively.

As shown in Fig. 3(c), zero-shear viscosity had a logarithmical linear relationship with relaxation time and the slope was found to be 1 without regard to the dissolution times. These plots indicate that the plateau modulus is independent of zero-shear viscosity and suggests that the inter-chain frictional coefficient was the only change. In the calculations, the weight fraction of cellulose was fixed as 0.07. This result can be explained in terms of the relationship between friction and the molecular size. Based on the relationship $\zeta = \eta_s R$ ($\zeta =$ frictional coefficient, $\eta_s =$ solvent viscosity, $R =$ molecular size), the frictional coefficient varies linearly with the molecular size. The decrease of molecular size resulted in a lower frictional force between neighboring chains, which led to the viscosity decrease.

<table>
<thead>
<tr>
<th>$t$ (h)</th>
<th>$\eta_0$ ($10^2$ Pa s)</th>
<th>$\tau$ ($10^{-2}$ s)</th>
<th>$\tau$ ($10^{-2}$ s)</th>
<th>$G_N^0$ ($10^3$ Pa)</th>
<th>$M_e$ ($10^3$ g mol$^{-1}$)</th>
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<tr>
<td>24</td>
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<td>27.75</td>
<td>21.04</td>
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<tr>
<td>192$^a$</td>
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<td>0.21</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>216$^a$</td>
<td>0.21</td>
<td>0.19</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>240$^a$</td>
<td>0.19</td>
<td>0.17</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

$^a$ The generalized Maxwell model cannot be adopted for these data.
3.3. Dynamic frequency sweeps test of cellulose/BmimCl solutions at varying temperatures

Fig. 4 shows the master curves of 7 wt% cellulose/BmimCl solutions with various dissolution times, obtained by the time–temperature superposition principle. All of the curves shifted upward by a factor $B$ except for the curves at 144 h. Over the range of dissolution times (24–168 h), a plateau region between $G’$ and $G''$ was observed when the relationships of $G’ \propto \omega^2$ and $G'' \propto \omega^4$ were held. Two crossover points can be clearly seen, which is a typical behavior of entangled polymer solutions. The first cross-over corresponds to the macromolecular reputation, and the second crossover corresponds to entanglement relaxation. With the increasing dissolution time, the first cross-over point shifts to a higher frequency, indicating the faster relaxation of the cellulose chains by low interaction time, the first cross-over point shifts to a higher frequency, indicating the faster relaxation of the cellulose chains by low interaction (entanglement or hydrogen bonding) with its neighboring chains. For dissolution times above 192 h, the curve of $G''$ was larger than that of $G’$ over the entire $\omega$-region where the measurements were carried out. This behavior is usually observed for dilute solutions, for which the dynamic viscoelastic behavior is similar to that of the terminal region in the Rouse model.\(^{30,31}\) Accordingly, the development of the network structure by entanglement was immature when cellulose was dissolved for longer times.

The dependence of the viscoelastic behavior on temperature provides useful information on the qualitative aspects of the relaxation process in polymer chains. The dynamic moduli of cellulose/BmimCl solutions were measured at a series of temperatures, taken at every 20 °C interval from 30 to 110 °C. The time–temperature superposition principle was used to shift all the rheological data to a reference temperature of 70 °C.

Fig. 5 Relationship between (a) log $\alpha_T$ and $1/T$ and (b) activation energy, $\Delta E_a$, and dissolution time, where $\alpha_T$ and $T$ represent the horizontal shift factor and absolute temperature, respectively. The solid lines show the results of curve fitting using the WLF equation.

As shown in Fig. 5(a), the time–temperature superposition principle applied well to the viscoelastic curves of the cellulose/BmimCl solutions. These results suggest that the relaxation mechanism does not change over the temperature range 30–110 °C. The apparent activation energy for viscoelastic relaxation, $\Delta E_a$, can be evaluated from the temperature dependence of the shift factor, $\alpha_T$. The shift factor is defined as $\eta(T)T/m(T)/\eta(T_r)T_r$, where $\rho$ is the density and the subscript $r$ refers to the properties of a reference state.\(^{19}\) Since the change in density versus temperature is negligible, the definition of $\alpha_T$ can be simplified to $\eta(T)/\eta(T_r)$. Near the glass transition temperature, $T_g$, the polymer flow is restricted to the free volume required to allow the necessary rotation of chain segments. Thus, the viscosity can be described by the Williams–Landel–Ferry (WLF) equation shown in eqn (11).

$$\log \alpha_T = \frac{-C_1(T - T_g)}{C_2 + (T - T_g)} \quad (11)$$

where $C_1$ and $C_2$ denote experimental constants and $T_g$ is the reference temperature.

Then, activation energy at the reference temperature can be estimated from eqn (12).

$$\Delta E_a(T = T_r) = R \left. \frac{d \ln \alpha_T}{d(1/T)} \right|_{T = T_r} = 2.303 R(C_1/C_2)T_r^2 \quad (12)$$
The apparent activation energy of flow $\Delta E_a$ is plotted against the dissolution time as shown in Fig. 5(b). As the dissolution time increased, the activation energy decreased and then leveled off when the time was longer than 196 h. Similar to the reason for the viscosity change, the decrease can be explained in terms of the reduction of the molecular size and its effect on flow. However, the molecular size did not contribute to the change of the activation energy further more when the size reached a certain value, i.e. when the dissolution time exceeded 196 h. The discussion on this topic will be continued in Section 4.3.

4. Discussion

4.1. Cellulose depolymerization in BmimCl

Table 1 gives the characteristic values of the number average molar mass, $M_n$, weight average molar mass, $M_w$, polydispersity, number of reducing ends and intrinsic viscosity for 7 wt% cellulose/BmimCl solution with different dissolution times. The molar mass and the intrinsic viscosity of the cellulose/ BmimCl solution rapidly decreased with the increase of dissolution time meaning that the viscoelastic properties are sensitive to the molar mass and polydispersity, respectively. Similarly, the molar mass of cellulose was reduced as its distribution increased during dissolution. The number of reducing ends in cellulose was measured using a 2,2'-bicinchoninate (BCA) colorimetric assay in order to verify the type of hydrolysis. The number of reducing ends in the solution strongly suggests that the cellulose is depolymerized by the acid hydrolysis mechanism.

4.2. Relaxation behavior of cellulose chain

The calculated $G_i$ and $\tau_i$ allow the evaluation of overall viscoelastic characteristics of cellulose/BmimCl solutions. These parameters were calculated using eqn (15)–(17).

$$G_N^0 = \sum G_i$$

$$M_c = \frac{\rho RT}{G_N^0}$$

$$\bar{\tau} = \frac{\sum \tau_i^2 G_i}{\sum \tau_i G_i}$$

where $G_N^0$, $M_c$, $\rho$, $R$, $T$, and $\bar{\tau}$ are the plateau modulus, entanglement molar mass, density, ideal gas constant, absolute temperature and mean relaxation time, respectively.

The calculated values of $\eta_0$, $\tau$, $\bar{\tau}$, $G_N^0$, and $M_c$ for cellulose/ BmimCl solutions with various dissolution times are listed in Table 2. The difference between $\tau$ and $\bar{\tau}$ originating from the Cross model became larger for longer dissolution times. This difference, a result of the polydispersity of cellulose molecules, means that the viscoelastic properties are sensitive to the molar mass distribution.34 The large polydispersity resulted from random hydrolysis of cellulose. This tendency was also observed in the van Gurp and Palmen plot of the phase angle (Fig. 6).35 The vGP plot is a useful method to study the molar mass distribution, tacticity, and chemical composition (i.e. existence of copolymers).36 As the dissolution time increased, the minimum value of the phase angle increased, and the curves became wider. It was previously found that shifting the vertical position and broadness of the minimum phase angle correlated with the change in molar mass and polydispersity, respectively. Similarly, the molar mass of cellulose was reduced as its distribution increased during dissolution, which corresponds perfectly with the measured GPC data.

The solid lines in Fig. 4 represent the curves calculated using the generalized Maxwell model with an appropriate combination of $G_i$ and $\tau_i$ values for the solutions. These curves, represented by eqn (13) and (14), are in good agreement with the experimental data. The well-fitted curves indicate the similarity and the universality in the shape of their viscoelastic curves.37,38 The storage modulus $G_i$ shows a frequency-independent plateau over a

![Fig. 6 Reduced van Gurp–Palmen plots of cellulose/BmimCl solutions having different dissolution times.](image-url)
certain frequency range, which is the plateau modulus $G'_0$ of the solution. The estimated $G'_0$ was insensitive to the molar mass, indicating that the entangled molar mass was almost constant as calculated by eqn (16) and shown in Table 2.

### 4.3 Relationship between rheological behavior and molar mass

Fig. 7 shows the double logarithmic plot of viscosity versus the molar mass. The point at which the slope changes in the plot of viscosity versus molar mass can be assigned to the critical point for the transition between unentangled and entangled chains. The molar mass dependence on viscosity ($\eta \propto M_w^{1.1}$ and $\eta \propto M_w^{1.7}$) can be found for cellulose/BmimCl solutions, which mutually intersect at the point corresponding to the critical molar mass, $M_{\text{cr}} = 76\,000 \text{ g mol}^{-1}$. For the solutions consisting of molar masses below the critical point, the cellulose chains were isolated and interacted with their neighbor chains only during short times of encounter, thus viscosity increased slowly with an increase of the molar mass. Above the critical point, cellulose chains became more entangled with each other and viscosity increased rapidly as the molar mass increased with a slope of 3.7. The relationship of viscosity and molar mass in poly(cis-isoprene) was fitted by two straight lines with slopes of 1.0 and 3.7, in good agreement with previous studies.

Based on the critical molar mass, the activation energy independence of molar mass can be explained by the change in the relaxation mechanism. Although the chain conformation did not dramatically change as the molar mass changed, the relaxation behaviors were different above and below the critical molar mass. Above the critical molar mass, the change in the molar mass greatly influenced the polymer–polymer interactions due to significant differences in the degree of entanglement. As a result, it required more time to be relaxed and more energy to flow. The entanglement in the network above the critical molar mass became dense as the molar mass increased. Thus, the value of the activation energy strongly depended on the molar mass. On the other hand, the cellulose molecules below the critical point had a finite size and less chance to interact with their neighbor chains, which was not entangled sufficiently. The unentangled molecules are easy to flow with freely translational and rotational motion. It makes no significant contribution to the relaxation process as indicated by the fact that the relaxation times were almost constant below the critical molar mass. The molar mass independence of the activation energy was similarly found in a polysaccharide, curdlan, dissolved in 0.1 N NaOH aqueous solution.40

The Mark–Houwink–Sakurada (MHS) equation is efficient to describe the molecular properties of a polymer, which correlate with the intrinsic viscosity and the molar mass. Fig. 8 shows a double logarithmic plot of the calculated intrinsic viscosity against the molar mass for cellulose in BmimCl at 30 °C. The figure contains the data published by other researchers.15,23,42 From the experimental data, the parameters of the MHS equation (eqn (18)) were obtained using eqn (19).

$$[\eta] = KM_w^{\alpha}$$

$$[\eta] = (0.64 \pm 0.3)M_w^{0.47 \pm 0.06}/\text{cm}^3 \text{ g}^{-1}$$

Using eqn (19), the parameters $K$ and $\alpha$ for the cellulose samples were obtained. The exponent $\alpha$ and coefficient $K$ were determined to be 0.47 and 0.64, respectively, suggesting that BmimCl may be a theta solvent for cellulose.15 Compared to other results (cellulose/DMAc/LiCl solution), $\alpha$ in the study was much lower.23 It indicates that the intermolecular interactions were significantly lowered by the ionic liquid used in the study. The inter-/intra-molecular hydrogen bonds should be broken because the chloride anions released from the ionic liquid were associated with the backbone.

From the obtained intrinsic viscosity and molar mass, the radius of gyration $R_g$ was estimated using the Flory approach for flexible polymer chains as shown in eqn (20).

$$R_g^2 = \frac{1}{6} \frac{[\eta]}{\Phi} \frac{M}{\Phi}^{2/3}$$

where $\Phi$ is Flory constant $2.8 \times 10^{-23} \text{ mol}^{-1}$. The radius of gyration ranged from 11.3 to 25.1 nm for the molecules with molar masses from 55 to 283 kg mol$^{-1}$ respectively. Fig. 9 shows the change in the radius of gyration along the molar mass.
Fig. 9 also includes the data reported previously by other researchers. All the data showed a good linear relationship. This relationship can be expressed based on the assumption that \( R_g = bN^n/\sqrt{6} \). An exponent of \( n \) was calculated to be 0.54, which suggests that the conformation of the cellulose molecules in BmimCl can be considered as a Gaussian chain in a theta solvent.

4.4 Phase transition behavior of cellulose/BmimCl solutions

Cellulose solutions are, in principle, able to form a cholesteric phase in suitable solvents at certain concentrations. It is also known that the formation of the liquid crystalline phase strongly depends on molecular conformation and topological constraints. To further clarify the influence of different physical states, above and below the critical molar mass, on the phase transition, the birefringence observation and the rheological behavior were compared. Fig. 10 shows the polarized optical micrographs of the cellulose/BmimCl solutions at 30 °C. For 55 kg mol\(^{-1}\) molar mass solution, the changes in visible color and phase transition are clearly distinguished. Below 10 wt% concentration, the solution is completely isotropic, and then the anisotropic texture gradually became more obvious upon further increasing the concentration. At 13 wt% concentration, fingerprint-like textures of the cholesteric phase appeared. As the cellulose concentration was further increased, apparent optical textures appeared. For 252 kg mol\(^{-1}\) molar mass solution, the overall tendency for change from isotropic to anisotropic phases is similar to high molar mass solutions, but the cholesteric phase could not be observed distinguishingly. The reason for the absence of a fingerprint-like pattern and appearance of a non-aligned cholesteric phase in the higher molar mass solutions may lie in their large domain size which accelerates aggregation of liquid crystalline phase.

The distinguishable behaviors of phase transition also can be observed in rheological behaviors as shown in Fig. 11. For the solutions with low molar masses, the viscosities of low molar mass solutions steeply increased up to a maximum value at a concentration by 10 wt%, a slightly decreased by 14 wt%, and increased again. This trend indicates the typical behavior of lyotropic liquid crystalline solutions. Compared to the low molar mass solutions, zero shear viscosity exponentially increased with increasing concentration, suggesting a sol–gel transition of cellulose/BmimCl solution. The different behavior of phase transition can be explained in terms of the absence of an interconnected structure by reduction below the critical molar mass. As shown in Fig. 12, each anisotropic domain forms a self-organization network chain by entanglement above the critical molar mass. The solution of united clusters makes a gel state with a drastic increase of viscosity. Below the critical molar mass, the cellulose chains can also have opportunities to form liquid crystalline domains but do not have an inter-connection.
of each domain due to the insufficient chain length for entanglement. As a result, the cellulose/BmimCl solution passes through viscosity drop (cholesteric phase) between sol–gel transitions.

On the basis of this speculation, it would be possible to explain the formation of the cholesteric phase of cellulose above and below the critical molar mass. The quantitative analysis of the characteristic time provides the physical state of cellulose chains. This time constant $\tau$ can be approximated as follows:

$$\tau = \frac{12\eta_0}{\pi^2 k_B T}$$

where $\nu$, $k_B$ and $T$ are the number of molecules per unit volume, Boltzmann constant and the absolute temperature, respectively. Based on values of $\eta_0$ and $\tau$ obtained above, we estimated the $\nu$ values, above and below the critical molar mass, to be $4.85 \times 10^{-6}$ mol cm$^{-3}$ and $5.39 \times 10^{-6}$ mol cm$^{-3}$, respectively. It implies that cellulose chains were more packed closely and the states changed from entangled to unentangled regions. The dense structure has more chance to interact each chain, which may help to transit from the isotropic state to the cholesteric phase.

5. Conclusions

The dissolution time significantly changed the molar mass and rheological behavior of cellulose dissolved in 1-butyl-3-methylimidazolium chloride. The GPC and van Gurp–Palman plot confirmed that the dissolution time increased as the molar mass decreased, which occurred at a rate of 0.057 $\mu$mol h$^{-1}$. Depolymerization decreased the inter-molecular entanglement and friction, and, in turn, showed a decrease in the viscosity and terminal region in the dynamic test, as well. The activation energy decreased as cellulose was depolymerized. However, chain isolation by severe depolymerization resulted in leveled-off activation energy. In the same way, the increasing rate of viscosity versus molar mass changed at the critical point of 76 000 g mol$^{-1}$. The dependence of molar mass on phase transition suggested a correlation between the physical state and the cholesteric phase, which showed different behaviors above and below the critical molar mass. The exponents for Mark–Houwink–Sakurada and the result of the radius of gyration suggest that cellulose in BmimCl existed as a Gaussian chain in a theta solvent.

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