Intrinsic Viscosity of Pullulan in Ionic Liquid Solutions Studied by Rheometry

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Intrinsic viscosity $[\eta]$ of nine pullulan samples with different molecular weights and narrow molecular weight distributions are obtained in 1-butyl-3-methylimidazolium chloride (BmimCl) and 1-ethyl-3-methylimidazolium acetate (EmimAc) from the Newtonian viscosities measured by oscillatory and steady shear flow in conventional rheometer for dilute solutions. For low molecular weight $M_w$ samples, $[\eta]$ in BmimCl and EmimAc almost coincide with that in aqueous solutions compared at the same $M_w$. The data at $M_w < 30 \text{ kg/mol}$ can be represented by $M_w^{0.5}$ dependence. The excluded volume effects observed in BmimCl and EmimAc at higher $M_w$ are somewhat stronger than in aqueous solutions. Mark-Houwink-Sakurada equations for pullulan in BmimCl and EmimAc are determined in 20 $\text{kg/mol} < M_w < 100 \text{ kg/mol}$. It is conclude that measurement of $[\eta]$ by rheometer is a promising method for characterization of polymers in ionic liquids.

Key Words: 1-butyl-3-methylimidazolium chloride / 1-ethyl-3-methylimidazolium acetate / Pullulan / Intrinsic viscosity / Mark-Houwink-Sakurada equation

1. INTRODUCTION

Ionic liquid (IL) is a kind of organic salts existing as liquid at around room temperature thereof the low melting temperature. Because of its unique characteristics such as extremely low vapor pressure, thermal stability, and high ionic conductivity, ILs are widely used in many fields of science and engineering. Among them, imidazolium-based ILs have been tested as solvent for the so-called insoluble natural polymers such as cellulose and silk fibroin. 1-butyl-3-methylimidazolium chloride (BmimCl), 1-allyl-3-methylimidazolium chloride (AmimCl) and 1-ethyl-3-methylimidazolium acetate (EmimAc) have been focused on as new green solvents for cellulose. Several rheological studies of polymers using ILs as solvents have been also reported.

The basic understanding of dilute solution properties of standard synthetic polymers, such as polystyrene with narrow molecular weight distributions (MWD), well contributed to the progress of polymer science and industry of synthetic polymers. Therefore, it is also preferable to have standard polymer samples for IL solutions for the progress in the studies of insoluble natural polymers.

Pullulan is a linear polysaccharide consist of $\alpha$-1,6 linked maltotriose units. Since it is a water soluble polymer and whose properties in aqueous solution are clarified, the fractionated pullulan has been used as standard polymer for water soluble polymers. As reported in a previous study, pullulan can be dissolved into ILs without chain degradation, so that it is a candidate of a standard sample for IL soluble polymers. However, most of conventional experimental methods such as GPC and light scattering widely used for dilute solutions in ordinary solvents are inadequate for the IL solutions because of the character of ILs. Even capillary viscometry is difficult for IL solutions due to the high solvent viscosity.

In this study, therefore, intrinsic viscosity $[\eta]$ of pullulan in ILs is determined from the data obtained by conventional rheometry. Nine pullulan samples with different molecular weights and narrow MWD are dissolved into BmimCl and EmimAc. Oscillatory and steady shear flow measurements are carried out for dilute solutions. By using zero shear viscosities of solutions and solvent, intrinsic viscosity of pullulan in BmimCl and EmimAc are determined by the ordinary method. The Mark-Houwink-Sakurada equations are determined from the data and compared with that in aqueous solution.

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2. EXPERIMENTAL

2.1 Materials

EmimAc (purity: 97%, water content: ≤0.5%) was purchased from Sigma-Aldrich Co and used as received. BmimCl was synthesized in toluene following the method in literatures\(^1,\)\(^2,\)\(^4\) with slight modifications and purified by activated carbon. Pullulan Samples with different molecular weights and narrow MWDs are purchased from Showa Denko K. K. and used without further purification. Weight averaged molecular weight, where \(M_n\) is number averaged molecular weight, are tabulated in Table I. Before the preparation of the solutions, all the pullulan samples and ILs were dried at 60 °C for 12 hrs.

2.2 Preparation of Sample Solutions

As reported in a previous study\(^3\), homogeneous pullulan/BmimCl solutions are prepared by the following methods since pullulan is degraded when the solution is prepared at higher temperatures, say 80 °C. First, dilute aqueous solution of pullulan was prepared and then the prescribed amounts of aqueous pullulan solution and BmimCl are gently mixed without mechanical agitation. Finally, the sample solution was dried at 60 °C in vacuo to remove the water for 72 hrs. The water content of BmimCl solutions and the sameley treated BmimCl was measured by Karl-Fischer titration method and confirmed that it is always less than 2 wt%. EmimAc solutions of pullulan were prepared by direct dissolution of pullulan into EmimAc at 60 °C in vacuo for 72 hrs without mechanical agitation. The water content of solutions and EmimAc obtained by Karl-Fisher titration method was always less than 1 wt%.

Concentration of the solutions are converted from \(c\) (wt%) to \(C\) (g/cm\(^3\)) by using the following empirical relationships obtained by the density measurements in a DMA 4500 density meter (Anton Paar GmbH) at different temperatures from 10 °C to 80 °C under atmospheric pressure.\(^2\)

\[
\rho = \rho_c + \rho_0 \left( \frac{g}{cm^3} \right)
\]

\[
C = \rho c/100 \left( \frac{g}{cm^3} \right)
\]

Here, \(\rho_0\) is the density of pure IL and \(\rho\) is the density of pullulan/IL solution. It was confirmed that residual water in the solutions (< 2 wt%) does not affect the above relations. Some representative results are shown in Figure 1.

2.3 Rheological Measurements

Rheological measurements are carried out in an MCR-300 rheometer (Anton Paar GmbH) equipped with peltier temperature control system with 50 mmϕ and 1° cone-plate geometry under N\(_2\) atmosphere. To prevent moisture adsorption during sample loading and to reduce the contamination of air during measurements, a homemade plastic chamber surrounding the original sample chamber filled with N\(_2\) gas was used. Both oscillatory and steady shear measurements are carried out for solutions and solvents in a temperature \((T)\) range from 10 to 40 °C, mainly at 25 °C. Dynamic oscillatory shear measurement are carried out in a frequency \((\omega)\) range from 0.1 to 100 rad/s with varying strain from 5% to 10% to maintain linear region measurement.

After the rheological measurements, pullulan samples are recovered from BmimCl and EmimAc solutions by

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Table I. Molecular characteristics of pullulan samples and their intrinsic viscosities in ILs.

<table>
<thead>
<tr>
<th>Molecular characteristics of pullulan samples</th>
<th>Intrinsic viscosities of pullulan in ILs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample codes (M_n)/(M_w) (\eta_0) (\eta_4)</td>
<td>(\eta_0) [25°C] (\eta_4) [40°C] (\eta_0) [10°C] (\eta_4) [25°C] (\eta_0) [40°C]</td>
</tr>
<tr>
<td>P-1300 1.33 \times 10^3 1.37</td>
<td>---- ---- 440 450 ----</td>
</tr>
<tr>
<td>P-800 7.88 \times 10^2 1.23</td>
<td>268 ---- 265 280 ----</td>
</tr>
<tr>
<td>P-400 3.93 \times 10^2 1.10</td>
<td>147 150 206 203 ----</td>
</tr>
<tr>
<td>P-200 2.12 \times 10^2 1.13</td>
<td>119 ---- 128 130 ----</td>
</tr>
<tr>
<td>P-100 1.13 \times 10^2 1.13</td>
<td>63 65 84 85 83</td>
</tr>
<tr>
<td>P-50 4.88 \times 10^1 1.07</td>
<td>45 ---- 46 46 44</td>
</tr>
<tr>
<td>P-20 2.28 \times 10^1 1.07</td>
<td>22 ---- ---- 25 ----</td>
</tr>
<tr>
<td>P-10 1.18 \times 10^1 1.10</td>
<td>17 ---- ---- 18 ----</td>
</tr>
<tr>
<td>P-5 0.59 \times 10^1 1.09</td>
<td>12 ---- ---- ---- ----</td>
</tr>
</tbody>
</table>

(a): \(M_w\) determined by ultra-centrifugal sedimentation equilibrium, reported by manufacture.
(b): \(M_n/M_w\) determined by size exclusion chromatography, reported by manufacture.

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Fig. 1. Concentration dependence of the density \(\rho\) for pullulan/ILs solution at different temperatures. The open symbols denote data for EmimAc solutions (left axis) and the filled symbols denote data for BmimCl solutions (right axis).

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precipitation method. Intrinsic viscosities of recovered pullulan in aqueous solution was always practically the same with a value for the fresh sample, confirming that no sample degradation occurred by the experiments.

3. RESULTS AND DISCUSSION

3.1 Viscoelastic Measurements

It is known that BmimCl and EmimAc strongly adsors moisture resulting in decrease of solvent viscosity. The effect of moisture adsorption was examined for both ILs by repeating viscosity measurements for a certain time interval combined with Karl-Fisher titration before and after the measurement. In the most significant case, about 10% decrease of viscosity was observed for BmimCl after 2 hours duration time even treated in the N2 box mentioned in Experiment part. The initial water content 1.8 wt% was increased to 2.2 wt% in this case. However, the decrease of viscosity for BmimCl became less than 5% when the measurement time is kept within 30 min. For EmimAc, the effect was much less than for BmimCl. The effect of moisture adsorption become almost negligible when the measurement time is kept within 30 min.

Since ILs are glass forming liquids and BmimCl showed apparent shear thinning at high shear rate, effect of viscoelastic properties of ILs for polymer solutions are also examined. Figure 2 shows double logarithmic plots of storage ($G'$) and loss ($G''$) moduli against $\omega$ for BmimCl. The observed $G'$ values are close to the lower detection limit of the rheometer, while oscillatory measurements itself was difficult for EmimAc because of the low viscosity. Thus, we can conclude that $G'$ of ILs are negligibly small compared to those of dilute polymer solutions shown below. Together with the steady flow data shown later, we can conclude that ILs can be treated as ordinary solvents for the viscoelastic measurements even for dilute solutions in our experimental $T$ range.

Figure 3a and 3b shows examples of double logarithmic plots of $G'$ and $G''$ vs $\omega$ for pullulan/BmimCl and pullulan/EmimAc solutions, respectively. The data are shifted along the vertical axis by $10^{2}$ to avoid overlapping. In the lower $\omega$ region, typical terminal region behaviors ($G' \propto \omega^{n}$ and $G'' \propto \omega^{n}$) for uniform viscoelastic liquid is observed. In the higher $\omega$ region, the $\omega$ dependencies of $G'$ and $G''$ changed from $\omega^{2.3}$ to $\omega^{1.2}$ with the increase of concentrations. It can be considered that the viscoelastic properties of pullulan in ILs change from Zimm-like to Rouse-like behaviors.\(^{19}\)

![Double logarithmic plots of $G'$ and $G''$ vs $\omega$ for (a) pullulan (P-400)/BmimCl and (b) pullulan (P-800)/EmimAc solutions with different concentrations at 25 °C and 10 °C, respectively. Symbols are denoted in the figure.](image)

**Fig. 2.** Double logarithmic plots of $G'$ and $G''$ for BmimCl (water content 0.6 %) at 25 °C.
Figure 4a and b show examples of shear rate ($\dot{\gamma}$) dependences of steady shear viscosity $\eta(\dot{\gamma})$ for (a) pullulan (P-400, P-100)/BmimCl solutions with different concentrations at 25 °C and (b) at different temperatures for $C = 0.019$ g/cm$^3$ (P-400, 1.8 wt%). Figure 5 shows examples of $\dot{\gamma}$ dependence of $\eta(\dot{\gamma})$ for pullulan (P-400, P-100)/EmimAc solutions. The Newtonian behaviors are clearly observed in lower shear rate region as denoted by horizontal lines, while shear thinning is observed in higher shear rate region for all of the BmimCl solutions. With the increase of the concentration or decrease of the temperature, the Newtonian viscosities increase and the shear thinning regions shift to slightly lower shear rates. For the lower molecular weight sample (P-100) at lower concentrations, shear thinning become less evident. For the pullulan (P-100)/EmimAc solutions, no shear thinning behavior is observed even in higher concentrations than in BmimCl, which can be attributed to the lower viscosity of EmimAc compared to that of BmimCl. In these figures, typical $\eta(\dot{\gamma})$ data for solvent ILs are shown for comparison. It is clear that solvents do not show shear thinning and solvent viscosity $\eta_s$ can be obtained with good accuracy. Above mentioned shear thinning behavior can be regarded as the behavior of ordinary polymer solutions. All these features are typical ones observed for the ordinary dilute polymer solutions.

Figure 6 shows comparison between complex viscosity $\eta^* (\omega)$ and $\eta(\dot{\gamma})$ for pullulan/BmimCl solutions. In this figure, data for higher concentration expected to be close to entangled region are also shown for comparison. It is clear that both data well coincide with each other at low $\omega$ and $\dot{\gamma}$. In this case, the deviation from Cox-Mertz rule is only small. The deviations
from the Cox-Mertz rule become more apparent with decrease of concentration. At $C = 0.019 \, g/cm^3$, shear thinning behavior of $\eta(\dot{\gamma})$ becomes comparable to that observed for polystyrene solutions at concentration slightly higher than the thermodynamic overlapping concentration but well below from critical concentration for entanglement effects. For pullulan/EmimAc solution, qualitatively the same behavior was observed.

The details of dynamic viscoelastic properties at relatively higher concentrations will be reported in elsewhere. In this paper, only zero shear viscosity $\eta^0$ obtained in the terminal region for relatively lower concentrations (corresponding to $C[\eta] < 4$) are discussed. It is clear from Figure 6 that steady shear measurements can cover wide range of $\dot{\gamma}$ in Newtonian region. At still lower $C$, where the oscillatory data are not obtained with good accuracy, $\eta^s$ are obtained by steady shear measurements alone and used to obtain $[\eta]$.

3.2 Intrinsic Viscosity and Mark-Houwink-Sakurada Equations of Pullulan in ILs

From $\eta$ and $\eta^0$, relative viscosity $\eta_{rel} (= \eta^0/\eta)$ and specific viscosity $\eta_s (= \eta_{rel} - 1)$ are calculated to obtain intrinsic viscosity of polymers in IL solutions. Figure 7 shows an example of plots of $\eta_{rel}/C$ and $\ln \eta_{rel}/C$ vs $C$, in which $[\eta]$ is determined by extrapolation to zero concentration shown by two straight lines. For all of the solutions, $[\eta]$ at 25 °C were determined while $[\eta]$ at 10 °C and 40 °C are obtained for selected solutions. The obtained $[\eta]$ are tabulated in Table I. It is clear that $[\eta]$ in both ILs do not show apparent change with the temperature, implying that solvent power of BmimCl and EmimAc for pullulan are constant in the tested range of temperature.

Figure 8 shows double logarithmic plots of $[\eta]$ against $M_w$ in two IL solutions at 25 °C. The data for aqueous solutions\(^{20}\) and the Mark-Houwink-Sakurada (MHS) equations determined at above $M_w = 48 \, kg/mol$ (slope: 0.67) and below $M_w \geq 30 \, kg/mol$ (slope: 0.5) are also shown for comparison. It is evident that $[\eta]_{EmimAc} > [\eta]_{BmimCl} > [\eta]_{water}$ where subscripts denote the solvent, in high $M_w$ region, say higher than 20 – 30 kg/mol. In low $M_w$ region, $[\eta]_{BmimCl}$ and $[\eta]_{EmimAc}$ almost coincide with but very slightly higher than $[\eta]_{water}$ compared at the same $M_w$. The data at $M_w < 30 \, kg/mol$ can be represented by $M_w^{0.5}$ dependence. It can be concluded that pullulan molecules behave as typical flexible polymer in ILs. The excluded volume effects in ILs are somewhat stronger than in aqueous solution and become negligible at somewhat lower $M_w$ than in aqueous solution.

By using the data at $M_w > 20 \, kg/mol$, the MHS equation in BmimCl and EmimAc is obtained as eqs (1) and (2), respectively, by the least square method.

$$[\eta] = (0.038 \pm 0.02)M^{0.65\pm0.05} \quad \text{(cm}^3 \text{g}^{-1}) \quad (1)$$

$$[\eta] = (0.034 \pm 0.01)M^{0.67\pm0.02} \quad \text{(cm}^3 \text{g}^{-1}) \quad (2)$$

Since the data in Figure 8 for IL solutions are scarce and slightly scattered compared to the data in aqueous solutions, the uncertainty of the above equations become somewhat larger than those for aqueous solutions. But we can still conclude that measurement of $[\eta]$ by rheometer is a promising method for characterization of so-called insoluble polymers in ILs.
REFERENCES