

動的粘弾性測定とシミュレーションによる天然高分子/イオン液体系の物性研究

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Study on Physical Properties of Natural Polymer in Ionic Liquid Solutions
by Dynamic Viscoelastic Measurement and Simulation.

(動的粘弾性測定とシミュレーションによる天然高分子/イオン液体系の物性研究)

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Contents

Chapter 1. Introduction.	5
1.1 Natural Polymer and Ionic Liquids.	5
1.1.1 Natural Polymer in Ionic Liquids.	5
1.1.2 Cellulose.	5
1.1.3 Silk.	6
1.1.4 Natural Rubber.	6
1.1.5 Ionic Liquids.	7
1.2 Rheology.	8
1.2.1 Concepts of Rheology.	8
1.2.2 Viscoelasticity by Maxwell Element and Voigt Element.	8
1.2.3 Theory of Dynamic Viscoelasticity.	9
1.2.4 Dynamic Viscoelasticity of Polymer Solutions.	10
1.2.5 Polymer Solution.	11
1.2.6 Intrinsic Viscosity of Polymer.	12
1.3 Molecular Simulation.	14
1.3.1 Selection of Modeling Software.	14
1.3.2 Mechanism of Molecular Simulation.	14

Chapter 2. Experiments. 15

2.1 Polymer Materials. 15

2.2 Synthetic Process of Ionic Liquid by Reflux Heating. 15

2.3 Synthetic Process of Ionic Liquids by Microwave Heating. 17

 2.3.1 Microwave Reactor. 17

 2.3.2 Heating Time Test by [BMIM][Br]. 18

 2.3.3 Huge Mass Synthesis Test by [BMIM][Br]. 19

 2.3.4 Purity Test by [AMIM][Cl]. 20

2.4 Sample Preparation for Dilute Solution. 23

2.5 Density Measurement. 23

2.6 Water Content Measurement. 23

2.7 Viscoelastic Measurement. 24

2.8 Molecular Simulation by Material Studio. 24

Chapter 3. Intrinsic Viscosity of Natural Polymer/Ionic Liquid. 25

3.1 Introduction. 25

3.2 Results and Discussion. 25

 3.2.1 Cellulose/[AMIM][Cl]. 25

 3.2.2 Silk/[AMIM][Cl]. 27

3.3 Summary. 28

Chapter 4. Ionic Liquids Synthesis Compared with Reflux and Microwave. 29

4.1 Introduction. 29

4.2 Results and Discussion. 29

 4.2.1 Heating Time Test by [BMIM][Br]. 29

 4.2.2 Huge Mass Synthesis Test by [BMIM][Br]. 30

 4.2.3 Purity Test by [AMIM][Cl]. 30

4.3 Summary. 31

Chapter 5. Molecular Simulation. 32

5.1 Introduction. 32

5.2 Results and Discussion. 32

 5.2.1 Density of Ionic Liquids. 32

 5.2.2 Mean Square Displacement and Diffusion Coefficient. 33

 5.2.3 Radial Distribution Function. 33

 5.2.4 Concentration Fluctuations. 35

5.3 Summary. 36

Chapter 6. Conclusion. 37

References 39

Acknowledgement 42

Chapter 1. Introduction.

1.1 Natural Polymer and Ionic Liquids.

1.1.1 Natural polymer in Ionic Liquids.

Natural polymer is applied to use as biomaterial⁽¹⁾⁽²⁾ and environmentally friendly materials⁽³⁾⁽⁴⁾ in recent years. In general, natural polymer is difficult to dissolve in water and ordinary solvents by their special structures.

In 2002, Rogers⁽⁵⁾ reported that ionic liquids (ILs)⁽⁶⁾⁽⁷⁾

can dissolve natural polymer such as cellulose. Moreover, ILs are very useful solvents by their unique properties. In Takahashi laboratory, we study about the physical properties of natural polymers to clarify the characterization for future application. In 2014, Hu⁽⁸⁾ reported the experimental results of dynamic viscoelastic behavior of pullulan/IL solution as standard polymer solution for comparison with natural polymer, because physical properties of pullulan⁽⁹⁾ (Fig. 1) is well known. Based on the result of pullulan, we started to study about the physical properties of cellulose and silk fibroin. However, we still have difficulty in the reproducibility of data even when preparation conditions are slightly different. Therefore, I tried to prepare homogeneous samples for improvement by comparing reflux heating with microwave heating.

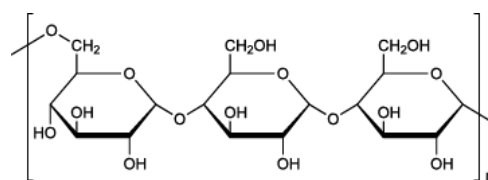


Figure 1. Structural formula of pullulan.

1.1.2 Cellulose.

Cellulose⁽¹⁰⁾ has number of beta-linked D glucose and these units construct linear polysaccharide chain. The chain has amount of intramolecular and intermolecular interaction by hydroxy group, so that it is difficult to dissolve in ordinary solvents⁽¹¹⁾. In 2017, Xu⁽¹²⁾ reported

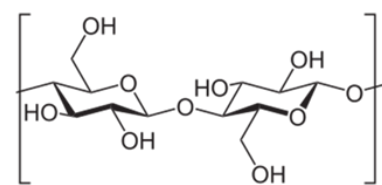


Figure 2. Structural formula of beta-linked D cellulose.

intrinsic viscosity of cellulose (Fig. 2) in 1-allyl-3-methylimidazolium chloride ([AMIM][Cl]) when he controlled the bubble burst speed at pre-heating. In this study, I prepared samples of cellulose in [AMIM][Cl] to get reproducibility, and I measured the dynamic viscoelasticity by using rheometer.

1.1.3 Silk.

Silk ⁽¹³⁾ consists of fibroin, sericin and a few mineral materials (Fig. 3). Fibroin has heavy chain about 350K of molecular weight and attached chain about 25K of molecular weight. Removing sericin and a few mineral materials are suitable to study on the physical properties of fibroin. In 2011, Ichikawa ⁽¹⁴⁾ reported viscoelastic behavior

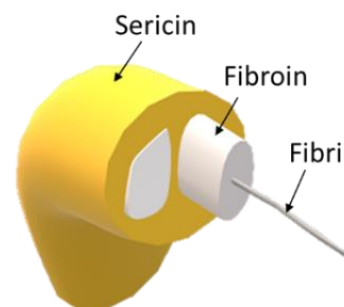


Figure 3. Structure of silk.

of silk fibroin in 1-butyl-3-methylimidazolium chloride ([BMIM][Cl]), and the measurement data has consistency by using recovered sample. However, the elastic behavior was not typical in comparison with ordinary polymer solutions. In 2015, Oka ⁽¹⁵⁾ reported that purification of fibroin is possible by dripping the mixture solution into 0.5% Na₂CO₃ and acetonitrile, and she gained the data of intrinsic viscosity of fibroin in [AMIM][Cl]. She also reported the viscoelasticity slightly increase by removing sericin, and the feature of data is similar to the result of Ichikawa. In this study, I prepared sample of silk in [AMIM][Cl] to test reproducibility, and I measured viscoelasticity by using rheometer.

1.1.4 Natural Rubber.

Natural rubber ⁽¹⁶⁾ is covered by protein and phospholipids (Fig. 4), and natural rubber has many cis-1,4-polyisoprene (PI) in its structure. Therefore, purification by using ILs may be a good method for extraction from rubber emulsion. In 2016, Sato ⁽¹⁷⁾ studied about natural rubber in

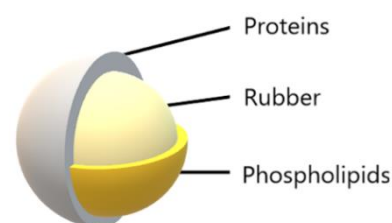


Figure 4. Structure of natural rubber.

[AMIM][Cl], and he reported that [AMIM][Cl] can remove some materials covering rubber, but it

cannot remove all phospholipids. In 2018, Matsumoto ⁽¹⁸⁾ reported 1-butyl-3-methylimidazolium bromide ([BMIM][Br]) can remove extra phospholipids more than [AMIM][Cl]. In this study, I tried to synthesize [BMIM][Br] by microwave heating for future work of natural rubber.

1.1.5 Ionic Liquids.

In 1914, Walden ⁽¹⁹⁾ found the first ionic liquid of ethylamine nitrate. In nowadays, ILs are composed by organic anions and counter cations, and many types of ILs are synthesized by these ion pair ⁽²⁰⁾. Besides that, ILs have unique properties such as liquid state in wide temperature range, almost non-vapor pressure, nonflammability, and designable polarity ⁽²¹⁾. Therefore, ILs are very useful liquid materials not only electrochemistry but also biochemistry. In Takahashi laboratory, we synthesized ILs to dissolve natural polymer. However, the purity of ILs are different in each batch, thus the properties, such as water content, density, and viscosity, are not constant. Therefore, purification of ILs kept the physical properties in the permissible range ^{(8) (12)} is important for researching physical properties of natural materials. For that reason, I studied about ordinally heating method by reflux and new heating method by microwave synthetic instrument to decrease heating time, to try huge mass synthesis and to improve the purity of ILs. In this study, I synthesized [AMIM][Cl] and [BMIM][Cl] to dissolve cellulose and silk fibroin, and I synthesized [BMIM][Br] to extract rubber (Fig. 5).

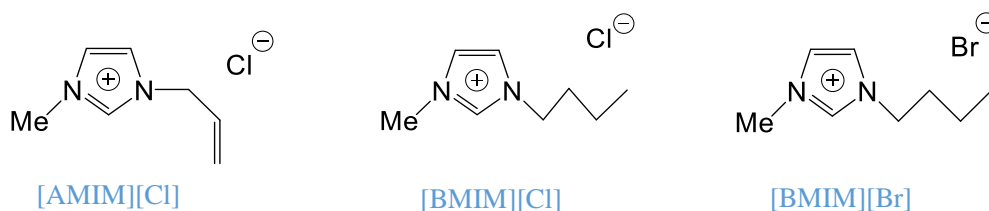


Figure 5. Ionic liquids for this research.

1.2 Rheology. ⁽²²⁾

1.2.1 Concepts of Rheology.

Rheology is one of the sciences to consider about transformation and flow of materials, and it targets all materials like elastic solid, liquid and viscous liquid. Rheology is related to a lot of study fields such as industry, medical science, biology, agriculture and food science. In other words, rheology has no limitation of target of materials and fields, and it can treat complex materials. Especially in the industry, rheology is needed for forming process and making products. In our research, we use the study of rheology to elucidate the physical properties of polymer materials in ionic liquid solutions by using rheometer for future application.

1.2.2 Viscoelasticity by Maxwell Element and Voigt Element.

We can consider about two kinds of simple dynamic model to explain the viscoelastic behavior by using the spring model (as elastic modulus G) and the dashpot model (as viscosity η). One model is shown Maxwell element for the liquid property by connecting with spring and dashpot in series, another model is shown Voigt element for the solid properties by connecting with spring and dashpot in parallel (Fig. 6).

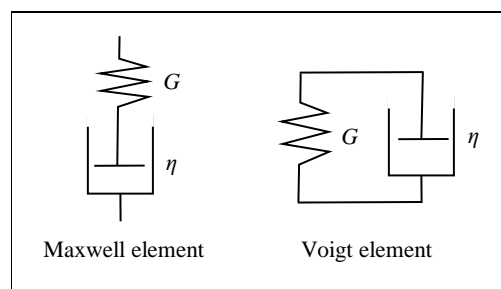


Figure 6. Dynamic Models; Maxwell element and Voigt element.

In Maxwell element, since the stress (σ) becomes equal for both spring part and dashpot part, total strain (γ) consist of spring strain (γ_1) and dashpot strain (γ_2) becomes like equation (1.1) and equation (1.2). Strain ratio ($\dot{\gamma}$) is the sum of spring strain ratio and dashpot strain ratio like equation (1.3).

$$\sigma = G\gamma_1 = \eta \frac{d\gamma_2}{dt} \quad (1.1)$$

$$\gamma = \gamma_1 + \gamma_2 \quad (1.2)$$

$$\dot{\gamma} = \frac{d\gamma}{dt} = \frac{1}{G} \frac{d\sigma}{dt} + \frac{\sigma}{\eta} \quad (1.3) / (\text{Maxwell element})$$

In Voigt element, since the strain becomes equal for both spring part and dashpot part, the stress is the sum of spring stress and dashpot stress like equation (1.4) and equation (1.5).

$$\sigma = \sigma_1 + \sigma_2 \quad (1.4)$$

$$\sigma = G\gamma + \eta \frac{d\gamma}{dt} \quad (1.5) / (\text{Voight element})$$

Equation (1.3) and equation (1.5) are basic formula to state dynamic viscoelasticity.

1.2.3 Theory of Dynamic Viscoelasticity. ⁽²³⁾

Viscoelastic materials usually have many relaxation mechanisms. Dynamic viscoelastic measurement is observation of response for viscoelastic materials by giving oscillation displacement or stress. Also, frequency (f) and amplitude frequency (ω) is indicated $\omega = 2\pi f$. Perfect elastic body is indicated by sine curve, and phase difference (δ) is 0° (Eq. (1.6)). Also, the sine curve is shown as storage modulus (G'). Moreover, perfect viscous body is indicated by cosine curve, and phase difference is 90° (Eq. (1.7)) (Fig. 7). The cosine curve is shown as loss modulus (G''). Viscoelastic body can construct by these two components of G' and G'' .

$$\text{Elastic body (as } G' \text{)} \quad \delta = 0 \quad (1.6)$$

$$\text{Viscous body (as } G'' \text{)} \quad \delta = \pi/2 \quad (1.7)$$

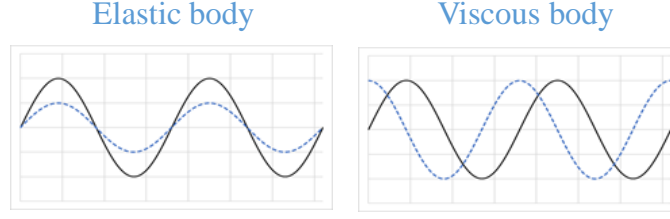


Figure 7. Response of elastic body and viscous body.

Time $t = 0$ and strain $\gamma = \gamma_0$ are given to equation (1.3), and we get the formula of stress relaxation (Eq. (1.8)).

$$G(t) = \frac{\sigma}{\gamma_0} = Ge^{-t/\tau} \quad (1.8)$$

1.2.4 Dynamic Viscoelasticity of Polymer Solutions.

In general, viscoelastic behavior of amorphous polymer has unique four regions as glass region, glass-rubber transition region, rubber plateau region and flow region. Especially in liquid state, plateau region and flow region are remarkable as their feature, and Maxwell element has great relationship with liquid state. Oscillation strain $\gamma(t) = \gamma_0 e^{i\omega t}$ are given to Maxwell element, and the steady state oscillation term shows σ^* , therefore we can get another Maxwell element (Eq. (1.9)).

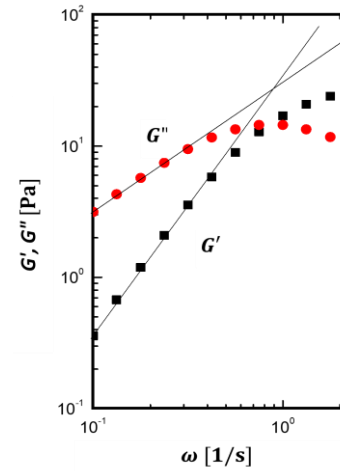


Figure 8. G' and G'' of Homogeneous polymer solution.

$$\sigma^* = G \frac{1}{1-i/\omega\tau} \gamma_0 e^{i\omega t} = G \left(\frac{\omega^2 \tau^2}{1+\omega^2 \tau^2} + i \frac{\omega \tau}{1+\omega^2 \tau^2} \right) r_0 e^{i\omega t} \quad (1.9)$$

The formula can divide to real part and imaginary part as equation (1.10), and G^* means complex modulus. Therefore, storage modulus and loss modulus become equation (1.11) as angular frequency

function. When G' is the second power of ω , G'' is the first power of ω in dynamic viscoelastic measurement (Fig. 8), the polymer solution sample can be considered homogeneous solution.

$$G^*(\omega) = G'(\omega) + iG''(\omega) \quad (1.10)$$

$$G'(\omega) = G \frac{\omega^2 \tau^2}{1 + \omega^2 \tau^2}, \quad G''(\omega) = G \frac{\omega \tau}{1 + \omega^2 \tau^2} \quad (1.11)$$

1.2.5 Polymer Solution.

Flexible polymer in solvent can be classified into three regions (Fig. 9). When polymer coil begins to overlap with each other, the polymer solution reaches the critical concentration, and it is said overlapping concentration (c^*) (Eq. (1.12)). ^{(24) (25) (26) (27)}

$$c^* = 3M / (4\pi N_A R_g^3) \quad (1.12)$$

M is the polymer molecular weight, N_A is the Avogadro's number, R_g is the radius of gyration about polymer chain. When the polymer solution concentration (c) does not reach c^* , the polymer chain is separated from each other. The polymer chains primarily interact with the solvent, and this state in the solution is approaching dilute solution.

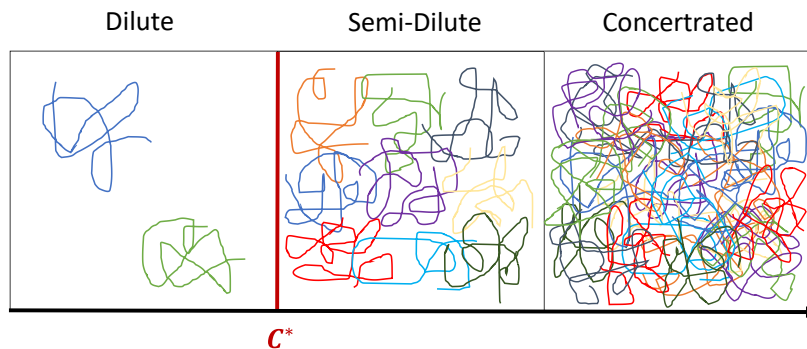


Figure 9. Polymer regions in solution.

Even polymer dissolve slightly in low molecular solvent, the polymer solution viscosity increases well. The viscosity increment is useful to estimate the molecular weight and molecular size.

1.2.6 Intrinsic Viscosity of Polymer.

Intrinsic viscosity ($[\eta]$) is important information for physical properties to understand the increment of viscosity ratio by single polymer chain. However, making polymer solution by single polymer chain is quite difficult, so dilute solution is used to determine intrinsic viscosity, and the estimation is used by solvent viscosity (η_s) and polymer solution viscosity (η). Specific viscosity (η_{sp} ; viscosity increment by some polymer chains.) and relative viscosity (η_r ; viscosity ratio against solvent viscosity.) are shown as equation (1.13) by using these viscosities (η_s and η).

$$\begin{aligned}\eta_{sp} &= (\eta - \eta_s) / \eta_s \\ \eta_r &= \eta / \eta_s\end{aligned}\tag{1.13}$$

Ratio of viscosity increment per unit mass polymer concentration is shown as η_{sp}/c , and the extrapolated value ($c \rightarrow 0$) leads $[\eta]$ in the polymer solution. Also, $(\ln \eta_r)/c$ of the extrapolated value ($c \rightarrow 0$) leads $[\eta]$ in the polymer solution (Eq. (1.14)) (Fig. 10).

$$\begin{aligned}\lim_{c \rightarrow 0} \left(\frac{\eta_{sp}}{c} \right) &= [\eta] \\ \lim_{c \rightarrow 0} \left(\frac{\ln \eta_r}{c} \right) &= [\eta]\end{aligned}\tag{1.14}$$

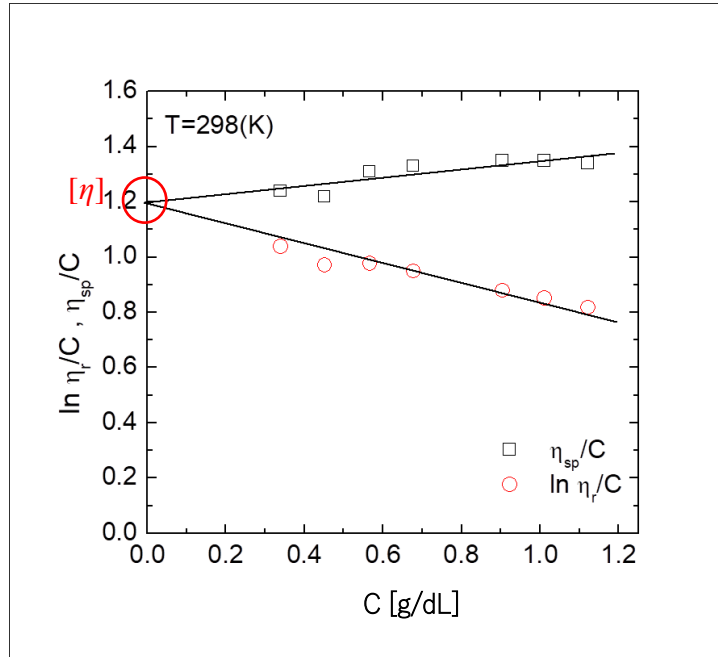


Figure 10. Intrinsic viscosity to extrapolated value. ⁽¹⁵⁾

Strictly, in low concentration until c^* , η_{sp} is typically shown as (Eq. (1.15)).

$$\eta_{sp} = [\eta]c + K_H[\eta]^2c^2 \cdot \cdot \cdot = \frac{(\eta - \eta_s)}{\eta_s} \quad (1.15)$$

K_H is Huggins's constant, it means two molecules interaction, and the value is almost 0.3 – 0.6 in molecular dispersing solution.

1.3 Molecular Simulation.

1.3.1 Selection of Modeling Software.

Simulation is very useful method to find the answer of question, because it is faster, cheaper and easier than laboratory experiment. In nowadays, several modeling software are used by simulation time and simulation size. In this study, I tried elementary simulation for polymer/IL solutions modeling by using the Hyper Chem. Professional software⁽²⁸⁾ and Material Studio software⁽²⁹⁾ to improve our laboratory experiment. After simulation, I compared with the results of laboratory experiment and computer simulation.

1.3.2 Mechanism of Molecular Simulation.

In this study, I selected the theory of Molecular Mechanics (MM) and Molecular Dynamics (MD) for ILs and natural polymer, because molecular modeling is suitable for polymer and polymer solution in monomer size level. Also, the theory of MM has five potential energy (U) categorized by bond stretch, torsional, valance angle bend, intramolecular nonbonded and intermolecular interaction (Eq. (1.16)). MM is the process of finding the minimum protentional energy by mathematics. On MD method, we should initialize parameter and variables, then we read the initial coordinate, and we choose an ensemble like NPT, NVE and NVT. These ensembles are the formal statistical mechanics designations, and these mean the system variables such as constant number (N), volume (V), energy (E), temperature (T) and pressure (P).

$$U = \sum_{i < j} \sum_{i < j} 4\varepsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \sum_{i < j} \sum_{i < j} \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}} \\ + \sum_{bonds} \frac{1}{2} k_b (r - r_0)^2 + \sum_{angles} \frac{1}{2} k_a (\theta - \theta_0)^2 + \sum_{torsions} k_\phi [1 + \cos(n\phi - \delta)] \quad (1.16)$$

Chapter 2. Experiment.

2.1 Polymer Materials.

I used cosmetic cotton (purity; 98%) purchased from Cotton Lab. as cellulose sample. Also, I used silk fibroin from cocoon of *Bombyx mori* (Fig. 11). After loosening these materials, I dried them in vacuum oven at 60 °C more than 12 hours.

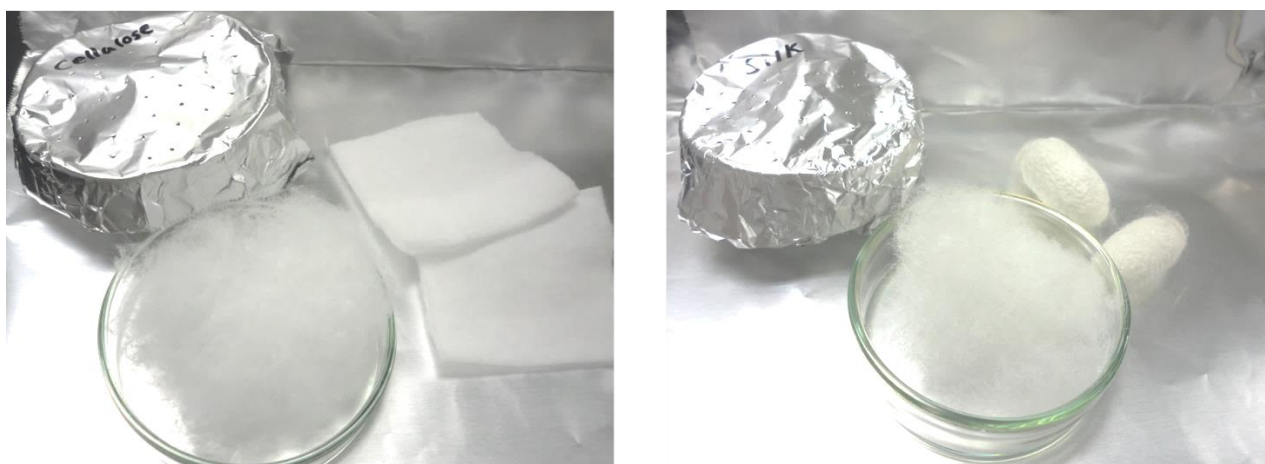
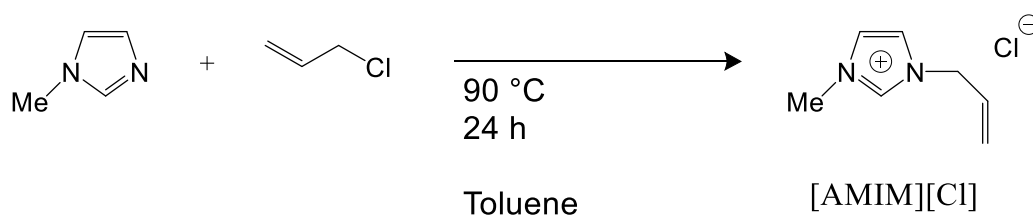


Figure 11. Cellulose (left) and silk fibroin (right).

2.2 Synthetic Process of Ionic Liquid by Reflux Heating.

I synthesized [AMIM][Cl] by using 1-methylimidazole (100 mL), allylchloride (101 mL) and toluene (125 mL) in a round bottom flask by reflux at 90 °C for 24 hours (Scheme 1).



Scheme 1. Synthetic process of [AMIM][Cl] by using reflux.

After that, the solution was crystallized in refrigerator for 24 hours. Then I removed toluene by discarding the supernatant and further evaporated at 90 °C in vacuo. Next, I shook the solution with ethyl acetate (about 200 mL x3), after then I removed ethyl acetate by evaporation at 60 °C in vacuo.

Furthermore, I did additional purification by using 2 spoons of active carbon and methanol to remove impurities for 2 days. After removing the active carbon by suction filtration, I removed methanol by evaporation at 60 °C and 110 °C in vacuo. Finally, I checked all reactants by ^1H NMR (400 MHz) using CDCl_3 and TMS (Fig. 12). In addition, I checked the physical properties of ILs such as density, water content and solvent viscosity. The purification procedure was repeated until the physical properties of ILs become stable in the allowed range to use as solvent.

[Experiment] ^1H NMR (400 MHz, CDCl_3) *Spectroscopic data* ; $\delta = 5.14$ (s, 3H), 5.50 (d, 2H), 5.54 (d, 1H), 6.10 (m, 1H), 7.88 (s, 1H), 8.05 (s, 1H), 10.36 (s, 1H)

[Reference] ⁽³⁰⁾ ^1H NMR (300 MHz, CDCl_3) *Spectroscopic data* ; $\delta = 4.06$ (s, 3H), 4.94 (d, 2H), 5.40 (d, 1H), 5.91–5.97 (m, 1H), 7.42 (s, 1H), 7.65 (s, 1H), 10.44 (s, 1H).

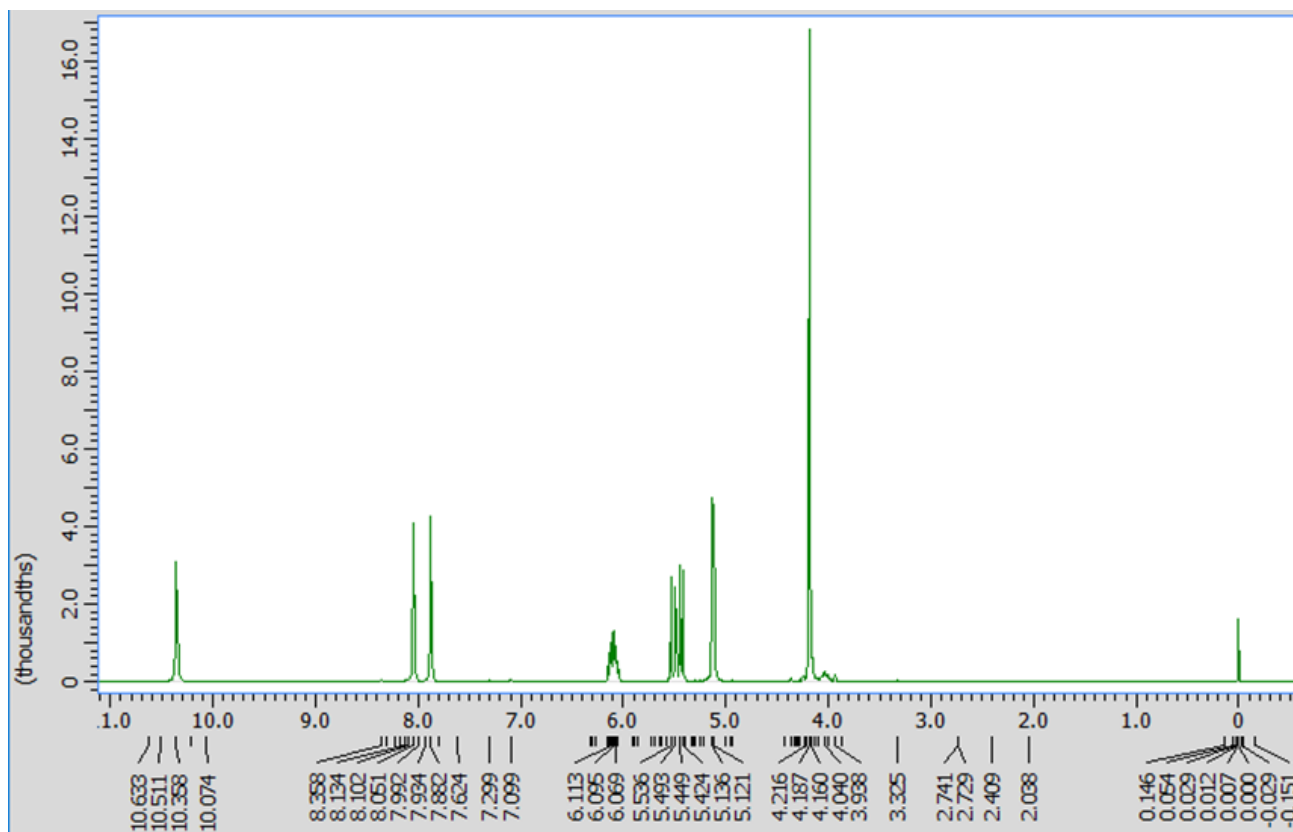


Fig 12. ^1H NMR spectra chart (in CDCl_3) of $[\text{AMIM}][\text{Cl}]$ by reflux.

2.3 Synthetic Process of Ionic Liquids by Microwave Heating.

2.3.1 Microwave Reactor

Microwave is effective heating method using ion rotation and vibration by electromagnetic field, therefore heating speed is faster than ordinary heating. Household microwave oven causes large complicated cavity, so that microwave energy reflects many places in cavity, and the sample cannot absorb all energy (Fig. 13). However, microwave reactor for synthetic heating has simple small cavity, so that microwave energy hardly reflects, and sample can absorb microwave energy directly (Fig. 14).

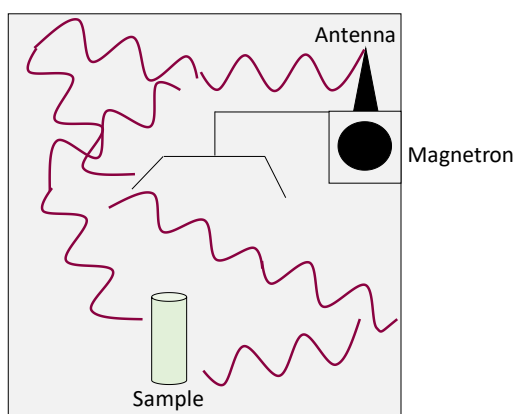


Figure 13. Construction of household microwave oven.

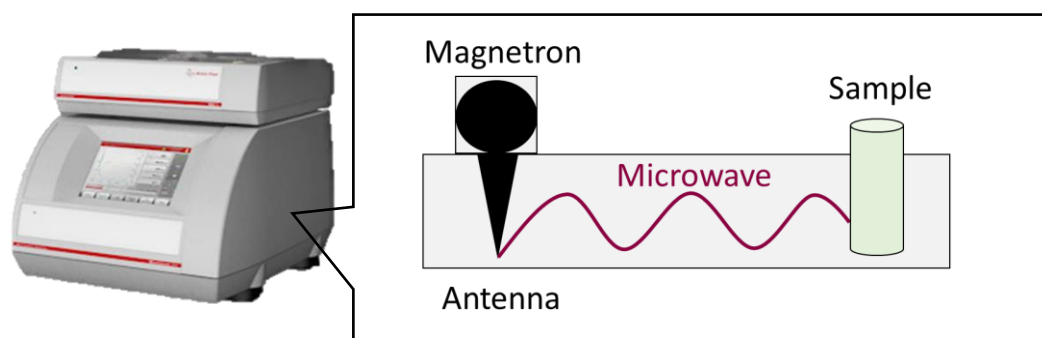
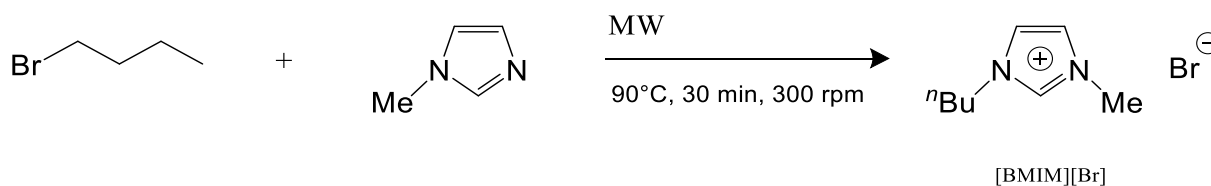


Figure 14. Construction of microwave reactor.

In this research, I used Monowave-400 (Anton-Paar) as microwave reactor. The reactor can control heating condition such as method, temperature, time and stirring speed, the reactor also irradiate microwave to sample directly. I treated each reagent to synthesize ILs by microwave heating.

2.3.2 Heating Time Test by [BMIM][Br].



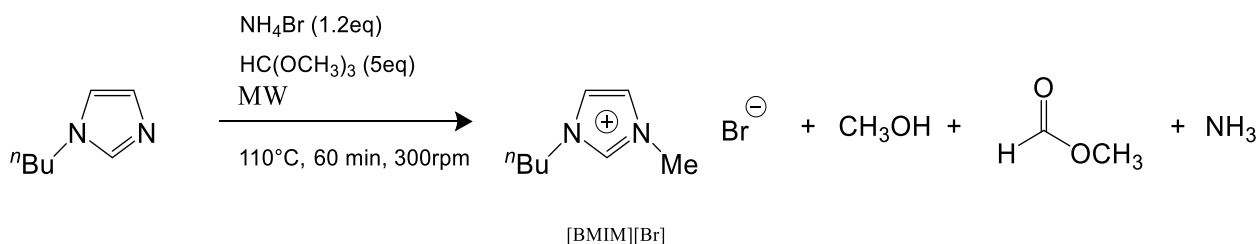
Scheme 2. Synthetic process of [BMIM][Br] on Rajender's method ⁽³¹⁾⁽³²⁾ by microwave instrument.

I used 1-bromo butane (2.2 mmol) and 1-methyl imidazole (2.0 mmol) to synthesize [BMIM][Br]. I chose G10 vial tube (for 10 mL), and microwave heated the sample at 90 °C (heating method; heat as fast as possible), and microwave kept heating the sample for 30 minutes with 300 rpm stirring, after then the reactor cold the sample to 70 °C (Scheme 2). Since I gained single phase liquid, I removed unreacted matter by ethyl acetate (2 mL x3), and I purified the product by vacuum drying. Finally, I checked all reactants by ¹H NMR (400 MHz) using DMSO-d₆ (Fig. 15). The yield is 98.6% (440 mg) on this process.

[Experiment] ¹H NMR (400 MHz, DMSO-d₆) *Spectroscopic data*; δ = 0.90 (t, 3H), 1.27 (s, 2H), 1.76 (quin, 2H), 3.85 (s, 3H), 4.16 (t, 2H), 7.71 (s, 1H), 7.78 (s, 1H), 9.14 (s, 1H)

[Reference] ⁽³³⁾ ¹H NMR (400 MHz, DMSO-d₆) *Spectroscopic data*; δ = 0.90 (t, 3H, CH₃), 1.26 (s, 2H, CH₂), 1.76 (quin, 2H, CH₂), 3.84 (s, 3H, CH₃), 4.15 (t, 2H, CH₂), 7.70 (s, 1H, CH), 7.77 (s, 1H, CH), 9.11 (s, 1H, CH).

2.3.3 Huge Mass Synthesis Test by [BMIM][Br].



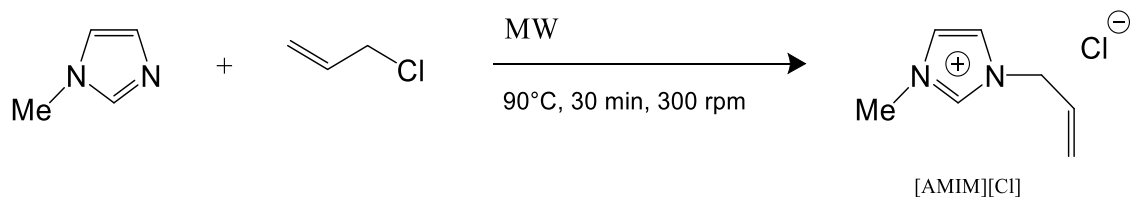
Scheme 3. Synthetic process of [BMIM][Br] on Matsumoto's method ⁽³⁴⁾ by microwave instrument.

I used 1-butylimidazole (10.0 mmol), ammonium bromide and trimethyl orthoformate at a mixing ratio of 1 : 1.2 : 5 to synthesize [BMIM][Br]. I used G30 vial tube (for 30 mL), and microwave heated the sample at 110°C (heat in 10 minutes) waiting for 60 minutes at 300 rpm, after then the reactor cold the sample to 70°C (Scheme 3). After finish cooling, I purified the ionic liquid to remove extra ammonium bromide by alumina column chromatography (methanol : ethyl acetate = 1 : 1), and then I obtained yellow liquid by vacuum drying. Finally, I compared with reactants and reference by ^1H NMR (400 MHz) using DMSO-d_6 (Fig. 16). The yield is 90.3% (2.00 g) on this process.

[Experiment] ^1H NMR (400 MHz, DMSO) *Spectroscopic data*; $\delta = 0.90$ (t, 3H), 1.26 (sxtet, 2H), 1.75 (quin, 2H), 3.85 (s, 3H), 4.16 (t, 2H), 7.71 (s, 1H), 7.78 (s, 1H), 9.16 (s, 1H)

[Reference] ⁽³³⁾ ^1H NMR (400 MHz) *Spectroscopic data*; $\delta = 0.90$ (t, 3H, CH_3), 1.26 (sxtet, 2H, CH_2), 1.76 (quin, 2H, CH_2), 3.84 (s, 3H, CH_3), 4.15 (t, 2H, CH_2), 7.70 (s, 1H, CH), 7.77 (s, 1H, CH), 9.11 (s, 1H, CH).

2.3.4 Purity Test by [AMIM][Cl].



Scheme 4. Synthetic process of [AMIM][Cl] on Takahashi lab. method ⁽³⁵⁾ by microwave instrument.

I treated 1-methylimidazole (60.0 mmol) and allylchloride (65.0 mmol) to synthesize [AMIM][Cl]. I used G30 vial tube, and microwave heated the sample at 90 °C (heat in 10 minutes) waiting for 30 minutes on 300 rpm, after then the reactor cold the sample to 40 °C (Scheme 4). After finish cooling, since I gained yellow liquid, I removed unreacted matter by ethyl acetate (10 mL x 3), and I obtained light brown liquid by vacuum drying. Finally, I checked reactants by ¹H NMR (400 MHz) using DMSO-d₆ (Fig. 17). The yield is 85.1% (8.6 g) on this process.

[Experiment] ¹H NMR (400 MHz, DMSO-d₆) *Spectroscopic data*; δ = 3.87 (s, 3H), 4.85 (d, 2H), 5.27 - 5.37 (m, 2H), 5.99 – 6.09 (m, 1H), 7.74 (d, 2H), 9.21 (s, 1H)

[Reference] ⁽³⁶⁾ ¹H NMR (400 MHz, DMSO-d₆) *Spectroscopic data* ; δ = 3.88 (s, 3H), 4.88 - 4.89 (d, J = 4.4 Hz, 2H), 5.28 - 5.35 (m, 2H), 5.99 - 6.08 (m, 1H), 7.78 (d, 2H), 9.37 (s, 1H).

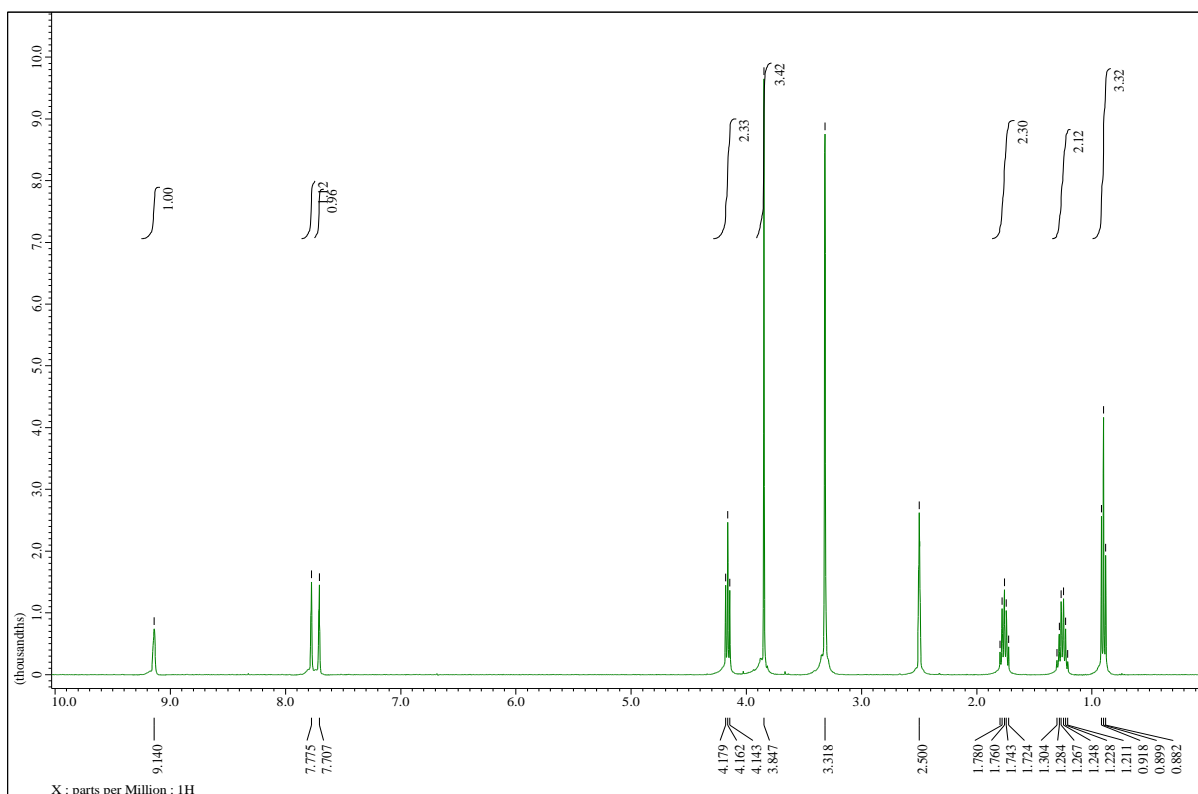


Figure 15. ^1H NMR spectra chart (in DMSO- d_6) of [BMIM][Br] on Raiender's method by MW.

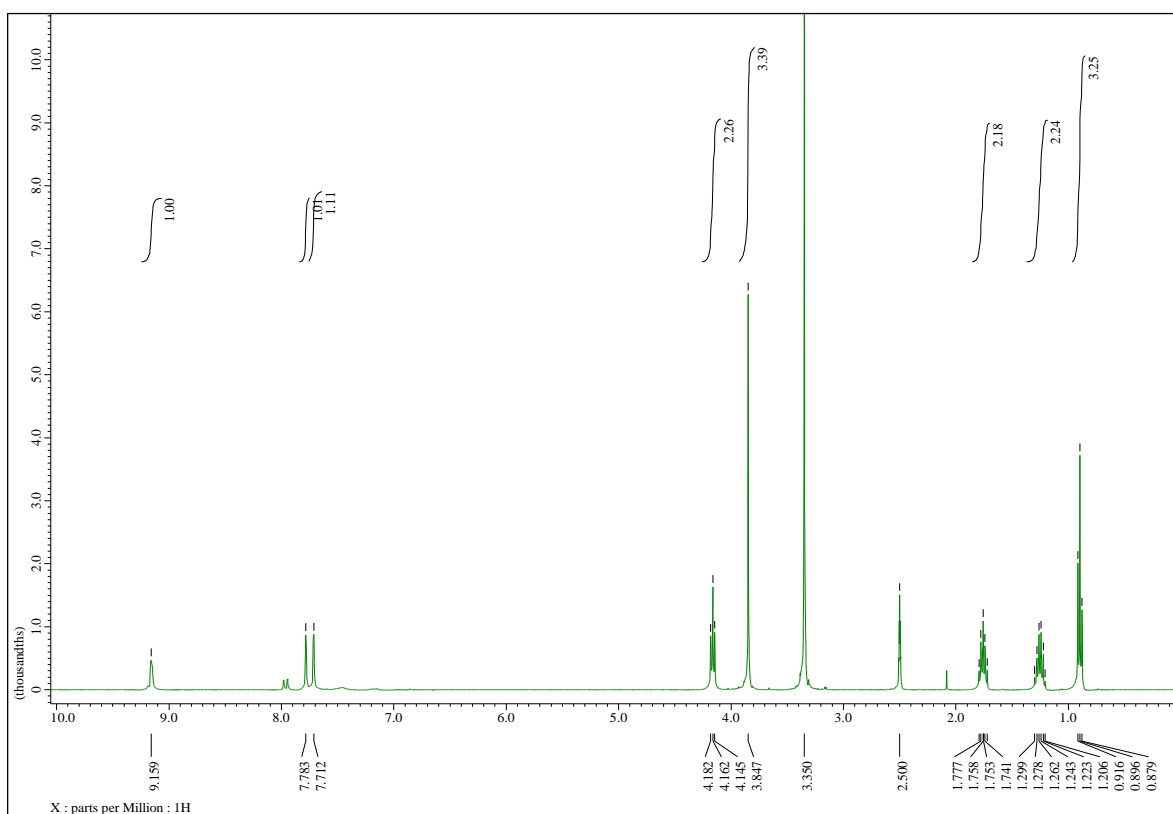


Figure 16. ^1H NMR spectra chart (in DMSO- d_6) of [BMIM][Br] on Matsumoto's method by MW.

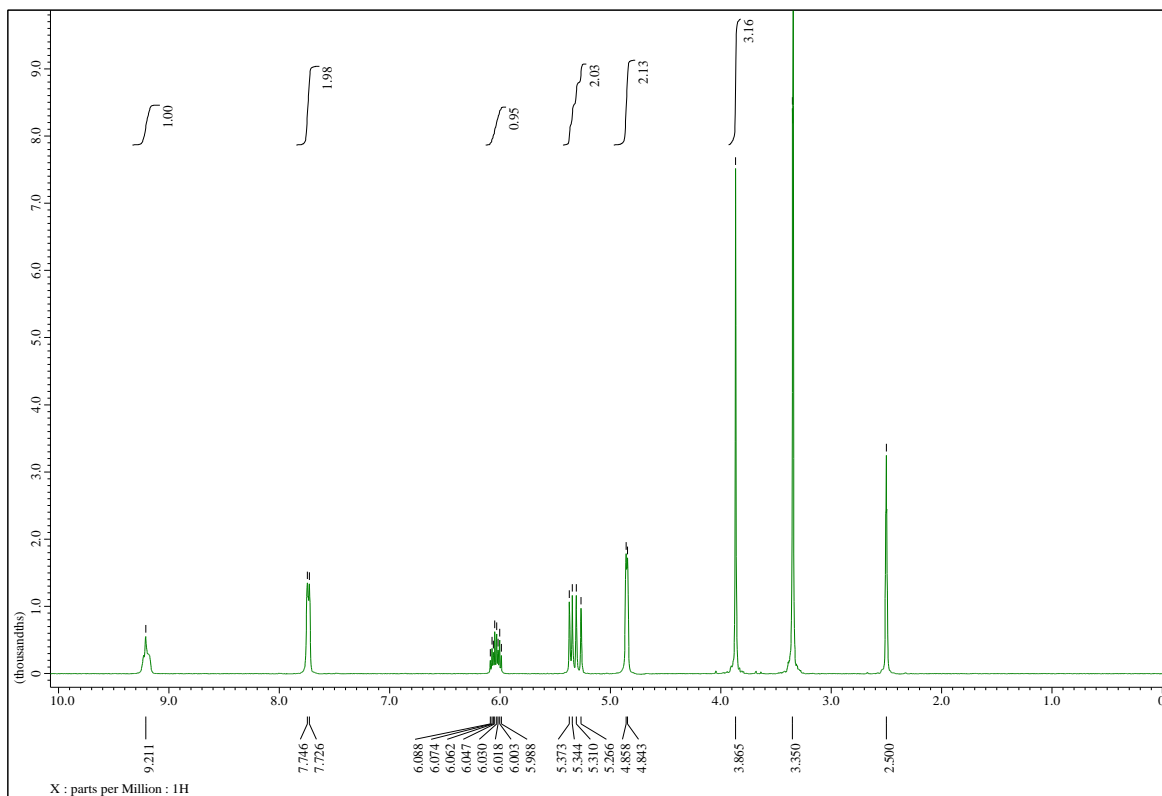


Figure 17. ^1H NMR spectra chart (in DMSO-d_6) of [AMIM][Cl] on Takahashi lab method by MW.

2.4 Sample Preparation for Dilute Solution.

I prepared mother sample by using the pre-treated polymer sample and the synthesized [AMIM][Cl], and I mixed into vial bottle under nitrogen gas atmosphere. During the process, I prepared mother sample (about 50 g) at about 1.0 wt%. Then I dried the mother sample by vacuum at 100 °C for 12 hours. I stirred the sample slowly to homogenize by my hand at 60 °C for several days. Finally, I diluted the mother sample to get sample solutions at different weight concentrations [g/dL] to measure viscoelastic properties. The homogenization procedure was done for each sample until it looks homogenous (Fig. 18).



Figure 18. Sample preparation.

2.5 Density Measurement.

I measured the density of ILs and polymer/ILs solutions for different concentrations at 25 °C, 40 °C and 10 °C at atmospheric pressure by using density meter DMA-4500 (Anton Paar). I determined the density when I got the same value at three times. I used the value of density (ρ) [g/cm³].

2.6 Water Content Measurement.

I measured the water content of ILs and polymer/ILs solutions by using Karl Fischer titration MKC-501 (Kyoto Electronics Manufacturing) after the drying process. I determined the water content by average from three to five results, and I calculated the ratio of water content [wt%] by the results of water content [μ g] and the solution weight [g].

2.7 Viscoelastic Measurement.

I measured dynamic viscoelasticity of ILs and polymer/IL solutions by using rheometer MCR-300 (Anton Paar) with cone plate of diameter 50 mm and 1-degree cone angle under nitrogen gas atmosphere. I set the measurement mode to frequency sweep, then I set the condition that measuring temperature (T) at 25.0 °C , amplitude strain (γ) 5~10%, and frequency (ω) 100~0.1 rad/s.

2.8 Molecular Simulation.

At first, I checked ⁽³⁷⁾(38) ideal structure of polymer and ILs by Hyper Chem Professional software. Then I constructed each material such as 10 units cellulose (x4), 10 units silk (x8), [AMIM][Cl] and [BMIM][Cl] by Material Studio. Then I tried to simulate whole bulk solution in small time scale, and I analyzed the simulation result. For minimization, I used conjugated gradient method, and I used MD-NPT run for equilibration by 1000 ps. For data collecting stage, I used MD run by 1.0 ns. Finally, I simulated by longer time scale and analyzed by NPT and NBT, and I got basic data of each material. After simulation, I combined with polymer and ILs, and I gained simulation data of polymer solution such as density, mean square displacement, radial distribution function, and concentration fluctuations.

Chapter 3. Intrinsic Viscosity of Natural Polymer/Ionic Liquid.

3.1 Introduction.

Natural polymer material is difficult to dissolve in water and ordinary solvents because of the special structures, so that their physical properties at molecular level are still needed to be elucidate. In 2002, ionic liquid was first used as solvent for cellulose. In 2011, the dynamic viscoelastic behavior of pullulan/IL solution as standard polymer solution indicated typical polymer behavior. Based on the result, our laboratory studied about the physical properties of cellulose and silk fibroin in ionic liquid solutions to clarify these characterizations. However, the reproducibility of data still has difficulty. Therefore, in this study, I tried to prepare homogeneous sample by reflux heating, and I observed dynamic viscoelasticity for clarification of intrinsic viscosity.

3.2 Results and Discussion.

3.2.1 Cellulose/[AMIM][Cl].

I observed that G' is the second power of frequency (ω) and G'' is the first power of ω in dynamic viscoelastic measurement for five solutions, 0.38 g/dL, 0.56 g/dL, 0.59 g/dL, 0.85 g/dL and 1.10 g/dL (Fig. 19). Therefore, I confirmed that these cellulose/[AMIM][Cl] solutions are homogeneous viscoelastic liquid. However, I could not get the definite result in intrinsic viscosity ($[\eta]$), because the data has wide dispersion (Fig. 20) (Table 1). By the result, we considered two causes about the dispersion. One is the mother solution of cellulose/[AMIM][Cl], because it might not have been homogenous. Another is the polymer chain cessation in the dilution process. In anyway, I could not confirm the protocol of intrinsic viscosity measurement.

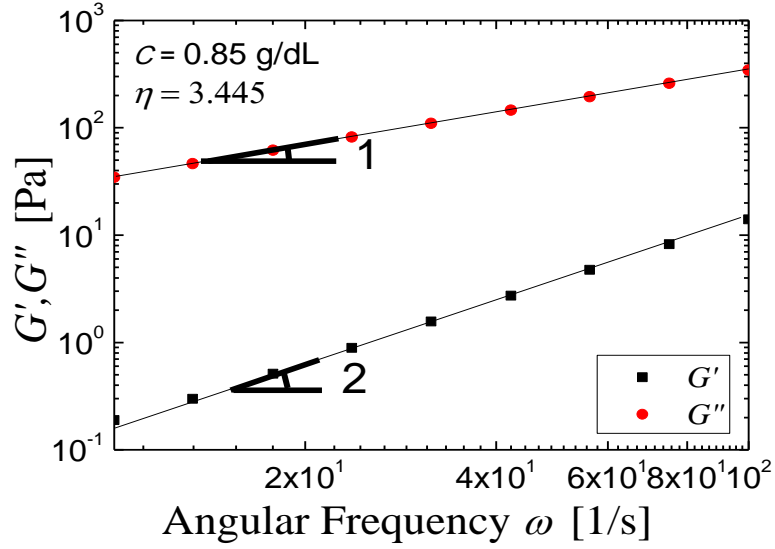


Figure 19. Dynamic viscoelasticity of cellulose/[AMIM][Cl].

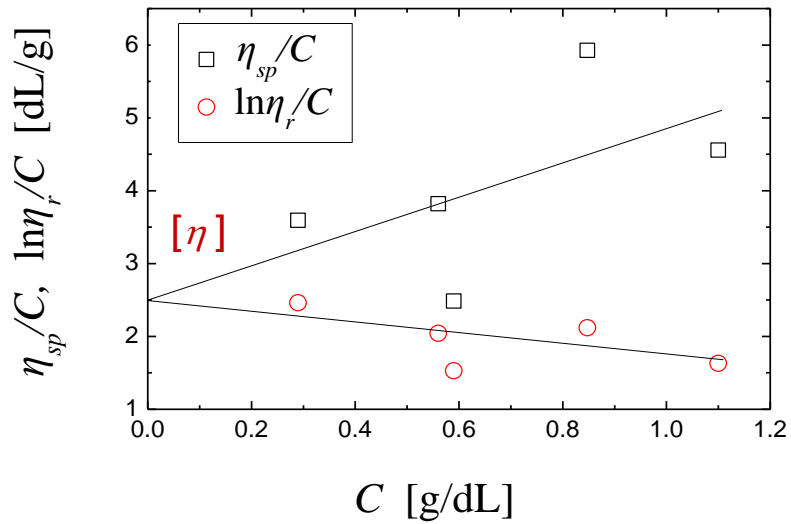


Figure 20. Intrinsic viscosity of cellulose/[AMIM][Cl].

Table 1. Intrinsic viscosity of cellulose/[AMIM][Cl].

[AMIM][Cl]	η_s	0.572
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Cellulose in [AMIM][Cl]	C	η	η_{sp}	η_r	η_{sp}/C	$\ln \eta_r/C$
	g/dL					
	1.100	3.440	5.014	6.014	4.558	1.631
	0.848	3.445	5.023	6.023	5.926	2.118
	0.590	1.410	1.465	2.465	2.483	1.529
	0.560	1.796	2.140	3.140	3.821	2.043
	0.290	1.168	1.042	2.042	3.593	2.462

3.2.2 Silk/[AMIM][Cl].

I also observed the value that G' is the second power of frequency (ω) and G'' is the first power of ω in dynamic viscoelastic measurement for four solutions, 0.36 g/dL, 0.57 g/dL, 0.84 g/dL and 1.15 g/dL. Therefore, I confirmed that these silk/[AMIM][Cl] solutions are homogeneous viscoelastic liquid. However, I could not get the definite result in intrinsic viscosity ($[\eta]$), because the data has wide dispersion (Fig. 21) (Table 2). By the result, we considered two causes about the dispersion. One is the mother solution of silk/[AMIM][Cl], because it might not have been homogenous. Another is the polymer chain cessation in the dilution process. In anyway, I could not confirm the protocol of intrinsic viscosity measurement and elastic property different from well studied ones.

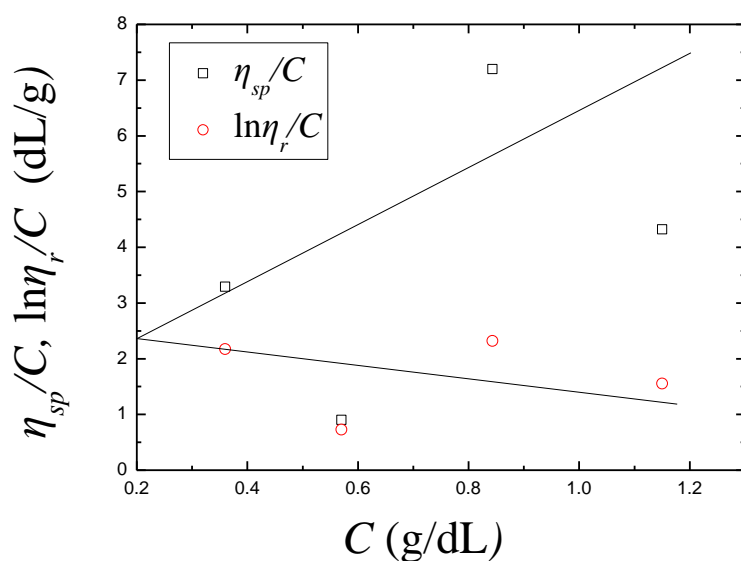


Figure 21. Intrinsic viscosity of silk/[AMIM][Cl].

Table 2. Intrinsic viscosity of silk/[AMIM][Cl].

[AMIM][Cl]	η_s	0.572				
Silk in [AMIM][Cl]	C	η	η_{sp}	η_r	η_{sp}/C	$\ln \eta_r/C$
	g/dL					
	1.150	3.413	4.967	5.967	4.319	1.553
	0.843	4.043	6.068	7.068	7.195	2.319
	0.570	0.866	0.514	1.514	0.902	0.728
0.360	1.250	1.185	2.185	3.293	2.172	

3.3 Summary.

I observed the value of G' is the second power of frequency (ω) and G'' is the first power of ω in dynamic viscoelastic measurement for both cellulose/[AMIM][Cl] and silk/[AMIM][Cl]. However, I could not get the definite result of intrinsic viscosity ($[\eta]$) by wide dispersion of data. By the result, we considered about two causes of the dispersion. One is the mother solution of cellulose/[AMIM][Cl] and silk/[AMIM][Cl], because it might not have been homogenous. Another is the polymer chain cessation in the dilution process. In anyway, I could not confirm the protocol of intrinsic viscosity measurement. Henceforth, I should improve sample preparation and measurement skill for reproducibility.

Chapter 4. Ionic Liquids Synthesis Compared with Reflux and Microwave..

4.1 Introduction.

Natural polymer is suitable materials for industry, but these are difficult to dissolve in ordinary solvents. In Takahashi laboratory, I use ionic liquids (ILs) as solvents for natural polymer, because ILs have good characteristics. In this chapter, I report the result of synthetic process about two kinds of ILs, 1-butyl-3-methylimidazolium bromide ([BMIM][Br]) and 1-allyl-3-methylimidazolium chloride ([AMIM][Cl]), according to three different synthetic routes to improve heating time, try huge mass synthesis and improvement of purity by microwave (MW) reactor. I estimated comparison between conventional reflux method and MW heating method to improve the dispersion of physical properties.

4.2 Results and Discussion.

4.2.1 Heating Time Test by [BMIM][Br].

I got the information of changing yield of [BMIM][Br] by heating time by using MW reactor. Normally, reflux heating takes time for 24 hours to synthesis [BMIM][Br]. However, heating by MW reactor takes time only 30 minutes (Fig. 22) (yield; 98.6% (Table 3)). Also heating by household MW oven is difficult to make the same condition. Therefore, MW reactor is useful for heating, and it is easier relatively and efficiently in a shorter time than using conventional reflux and household MW oven.

Table 3. The yield of [BMIM][Br] by heating time by using microwave synthetic instrument.

Program	Temperature ° C	Time hh:mm:ss	Stirrer Speed rpm	Yield %
Heat AFAP	90	0:05:00	300	81.3
Heat AFAP	90	0:10:00	300	95.3
Heat AFAP	90	0:20:00	300	96.3
Heat AFAP	90	0:30:00	300	98.6

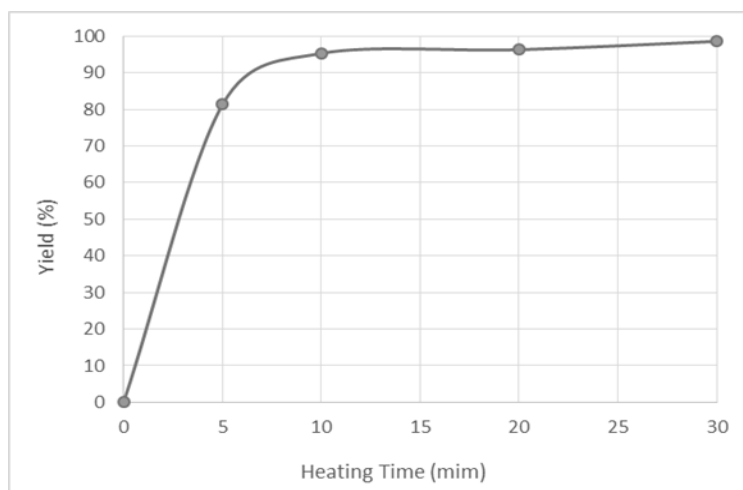


Figure 22. The yield of [BMIM][Br] by heating time using microwave heating.

4.2.2 Huge Mass Synthesis Test by [BMIM][Br].

[BMIM][Br] was not obtained only 2.00 g (yield; 90.3%). This synthetic route was not suitable for huge mass synthesis, since some byproduct are also generated with the target substance when heating. When trying huge mass synthesis of [BMIM][Br], I need to prepare a larger vial tube, to use another route getting only the target, or alternatively use MW reactor for industrial use.

4.2.3 Purity Test by [AMIM][Cl].

The purity of [AMIM][Cl] was improved by using microwave reactor compared with reflux heating (Table 4) (Fig. 23). However, I should try additional purification of [AMIM][Cl] to keep the physical properties in the permissible range, and it becomes important for researching physical properties of natural materials.

Table 4. The physical properties of [AMIM][Cl] by microwave heating.

	Sample 1	Sample 2	Sample 3	Sample 4
Water contain [wt%]	0.254	0.241	0.499	0.080
Density (25°C) [g/cm ³]	1.1467	1.1465	1.1464	1.1468
Dynamic viscoelastic	1.528	1.120	1.402	1.714

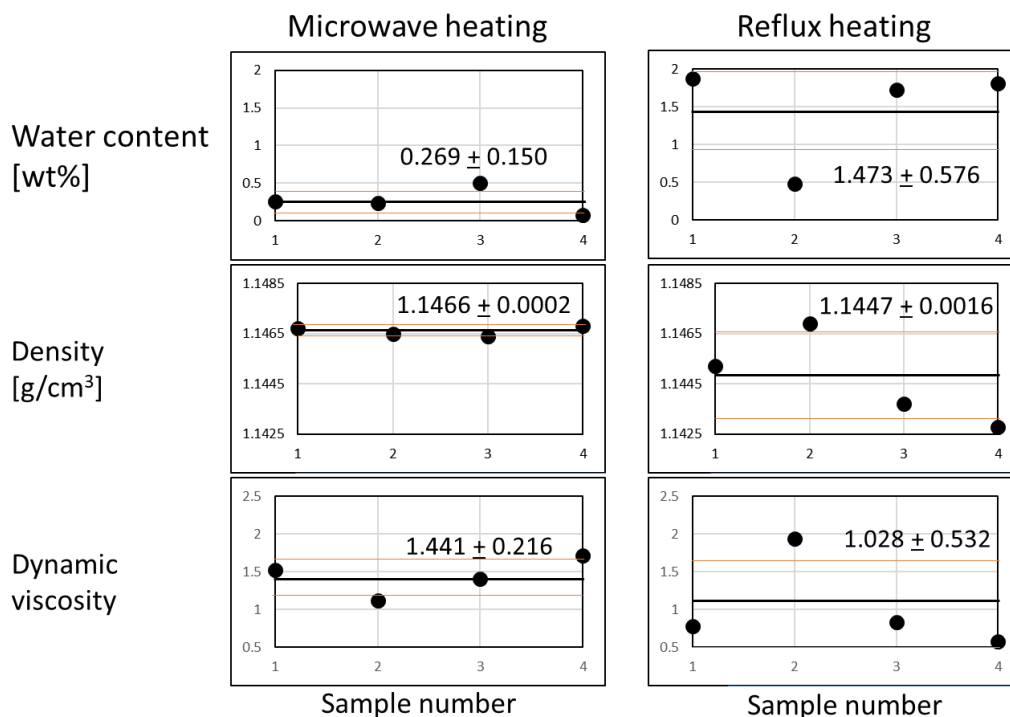


Figure 23. Physical properties (water content, density, viscosity) of [AMIM][Cl] synthesized by microwave heating and reflux heating (after four times purification).

4.3 Summary.

I synthesized [BMIM][Br] and [AMIM][Cl] according to three different synthetic routes by microwave reactor. I also compared with conventional reflux method and MW heating method by physical properties. In chapter 4.2.1, the heating time of [BMIM][Br] was reduced from 24 hours to 30 minutes by using microwave reactor. Therefore, MW reactor is useful for heating, and it is easier than using conventional reflux and household MW oven. In chapter 4.2.2, huge mass synthesis of [BMIM][Br] was not available for this MW reactor, because the MW reactor has special size of vial tube. Therefore, I should seek bigger vial or other synthetic process, or use MW reactor for industrial use. In chapter 4.2.3, the purity of [AMIM][Cl] such as water content, density and viscosity were improved by using MW reactor compared with reflux heating. However, I still need additional purification of [AMIM][Cl] to keep the physical properties in the permissible range, because stability of physical properties important for researching natural materials.

Chapter 5. Molecular Simulation.

5.1 Introduction.

Simulation is very useful method to find the answer for question, and several modeling software are used to make the same condition at laboratory experiment. In Takahashi laboratory, we studied the physical properties of cellulose and silk fibroin in ionic liquid by experiment. However, getting the measurement reproducibility was difficult and confirmation by other experiments are very difficult. Therefore, in this chapter, I tried to elementary simulate for modeling polymer/IL solutions by using the software of Hyper Chem. Professional and Material Studio. After simulation, I compared with the results of experiment and simulation.

5.2 Results and Discussion.

5.2.1 Density of Ionic Liquids.

The density data of [BMIM][Cl] and [AMIM][Cl] were simulated by NPT-MD run (Fig. 24). The average density of [AMIM][Cl] is $1.0078 \pm 0.0093 \text{ g/cm}^3$, the average density of [BMIM][Cl] is $0.965 \pm 0.0081 \text{ g/cm}^3$. Therefore, [AMIM][Cl] is larger density than [BMIM][Cl], and this trend is same as our experiment

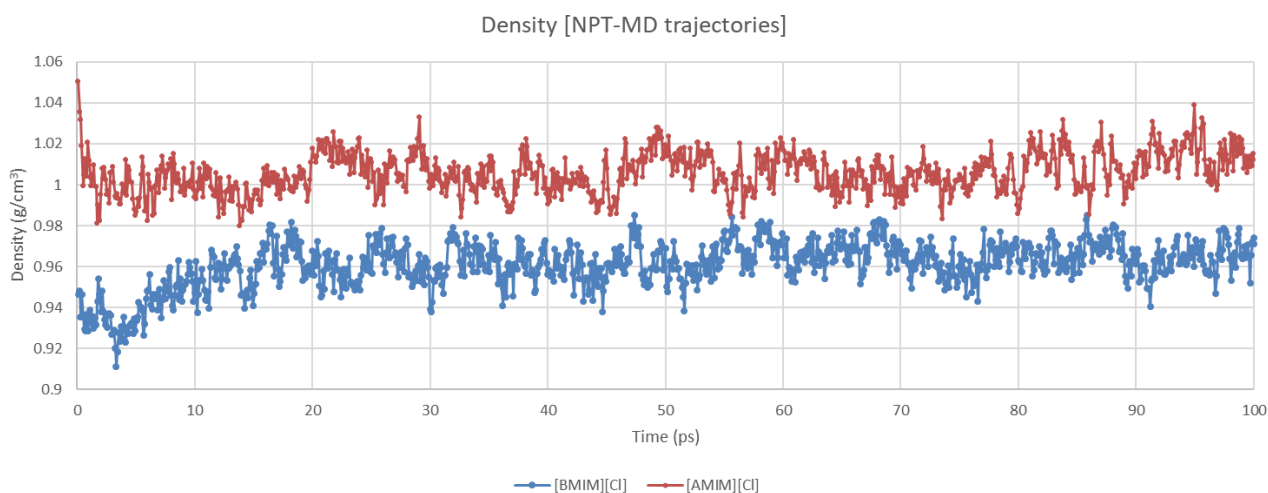


Figure 24. Density simulation of ILs.

5.2.2 Mean Square Displacement and Diffusion Coefficient.

The mean square displacement of ILs and diffusion coefficient (Fig. 25) were simulated by NPT-MD run. The data shows, [BMIM][Cl] has lower local viscosity than [AMIM][Cl], and this trend is different with our experiment. I should consider about the effect of electrostatic interaction, steric barrier and so on, because this simulation was elementary modeling and further apply the model to more coarse-grained simulation.

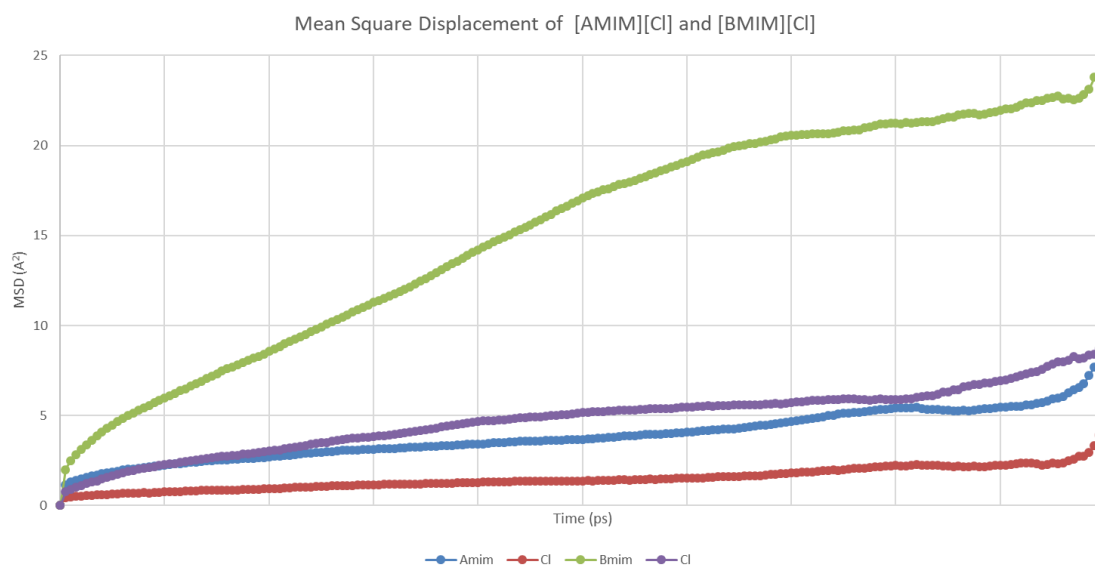


Figure 25. Mean squared displacement of ILs.

5.2.3 Radial Distribution Function.

The three kind of radial distribution function data were simulated by NPT-MD run. These data mean [AMIM][Cl] has higher density than [BMIM][Cl], because [AMIM]⁺ and Cl⁻ is closer than [BMIM]⁺ and Cl⁻ (Fig. 26), the distance of each Cl⁻ in [AMIM][Cl] solution is closer than [BMIM][Cl] (Fig. 27) and the distance of pair of [AMIM][Cl] is closer than pair of [BMIM][Cl] (Fig. 28). The result of this data can reinforce the result of density.

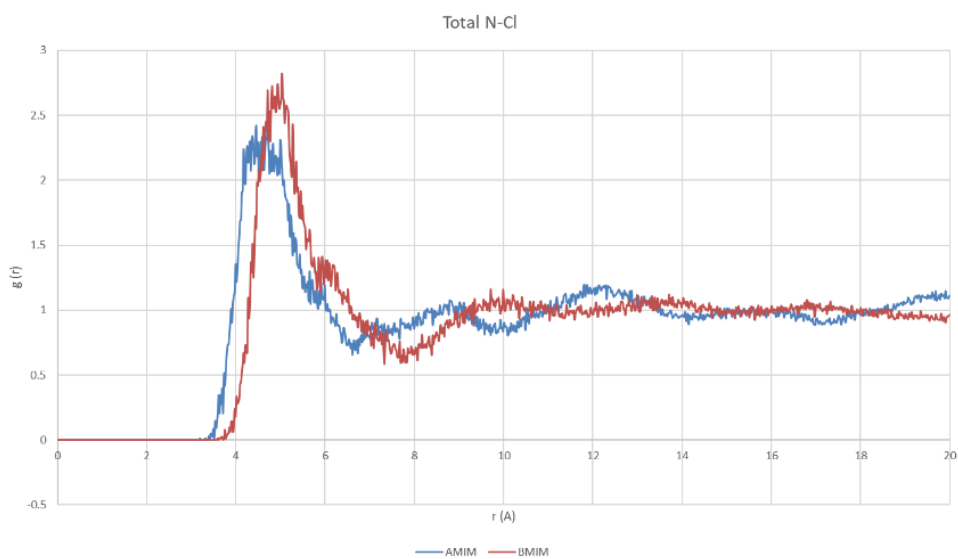


Figure 26. Radial distribution function on [AMIM]⁺ and [BMIM]⁺ with chloride ion.

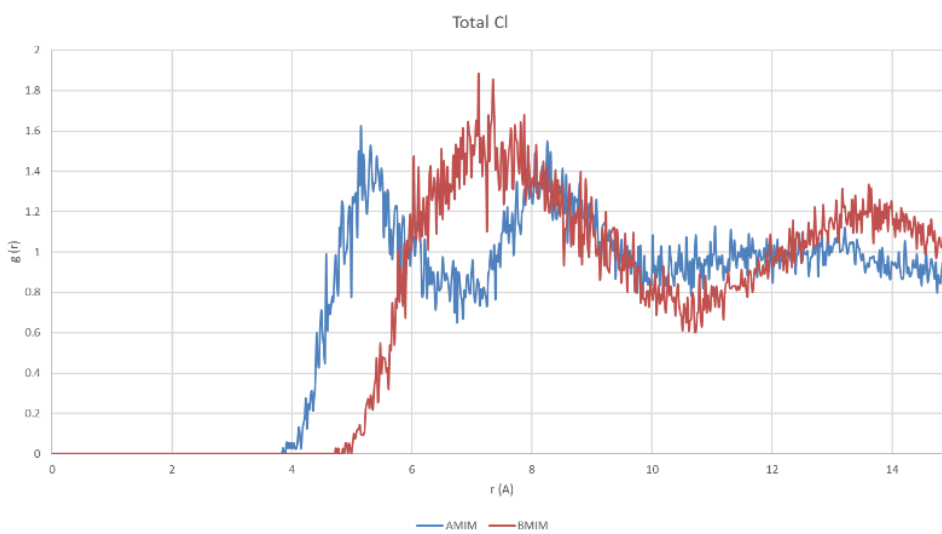


Figure 27. Radial distribution function on pair of chloride.

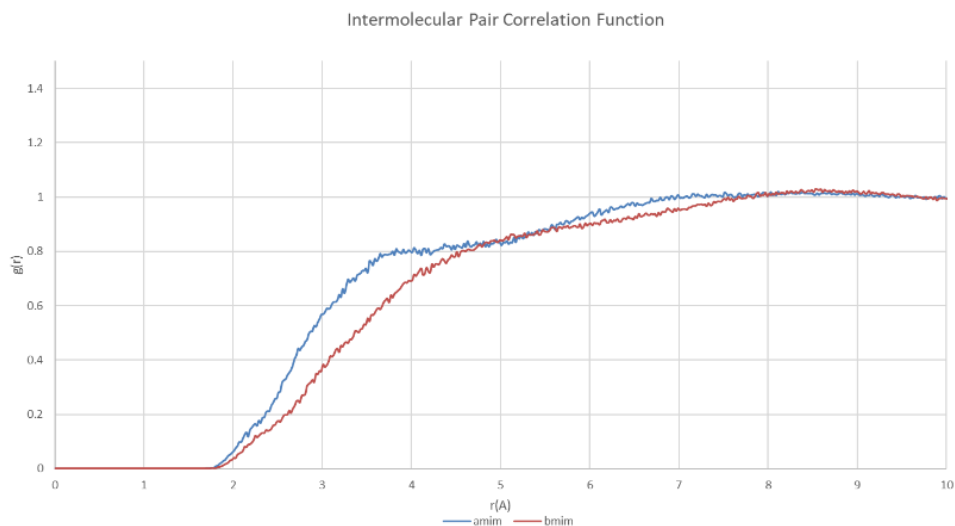


Figure 28. Radial distribution function on pair of [AMIM][Cl] and [BMIM][Cl].

5.2.4 Concentration Fluctuations.

I got the data of cellulose/[BMIM][Cl] and cellulose/[AMIM][Cl] by the simulation of NVT-MD run (Fig. 29) (Fig. 30). The data shows [AMIM][Cl] is better solubility than [BMIM][Cl] for cellulose, because Cl⁻ of [AMIM][Cl] is easy to move in natural polymer compared with Cl⁻ of [BMIM][Cl]. This result is same trend as our experiment. Although the run of simulation was short time, so I should try longer time run again.



Figure 29. Concentration profile of cellulose/[BMIM][Cl].

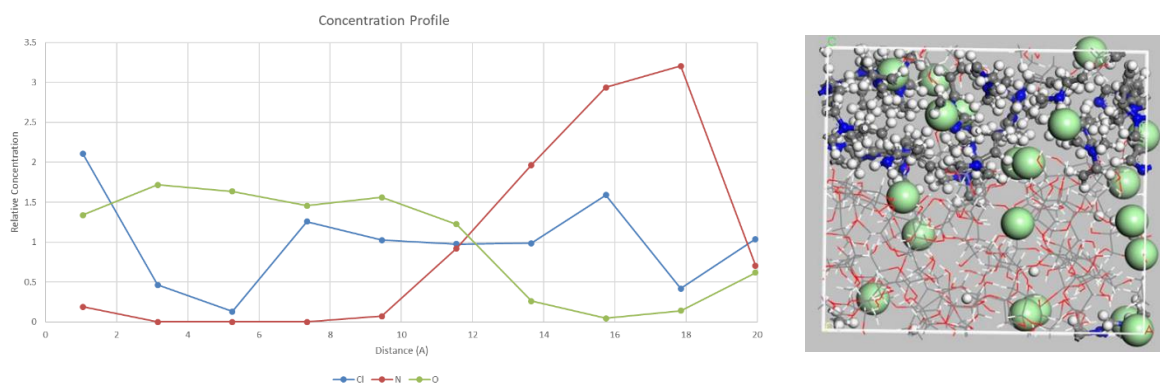


Figure 30. Concentration profile of cellulose/[AMIM][Cl].

In addition, silk/[BMIM][Cl] and silk/[AMIM][Cl] were simulated by NVT-MD run. The data shows [AMIM][Cl] is better solubility than [BMIM][Cl] for silk by same reason as cellulose. Also, this result is same trend as our experiment. The run of simulation was short time, so I should try longer time run again.

5.3 Summary.

The density of [AMIM][Cl] is higher than [BMIM][Cl], and this trend is same as our experiment. [AMIM][Cl] has better solubility than [BMIM][Cl] for cellulose and silk, and thus trend is the same as our experiment. Although, I should try the simulation by longer time run for getting closer to experimental data. However, I got the different simulation data with our experiment in concentration fluctuations. In this simulation, viscosity of [AMIM][Cl] is higher than [BMIM][Cl], but in our experiment, viscosity value of [BMIM][Cl] is higher one digit than [AMIM][Cl]. Therefore, I should consider about the effects like electrostatic interaction and steric barrier. I also should run by larger scale and coarse-grained simulation for dynamically stable for high order structure in samples.

Chapter 6. Conclusion.

In chapter 3, I observed viscoelastic trend that the value of G' is in the second power of ω and G'' is the first power of ω for both cellulose/[AMIM][Cl] and silk/[AMIM][Cl] by dynamic viscoelastic measurement. However, I could not get the definite result of intrinsic viscosity $[\eta]$, because of these wide dispersions. By the result, we considered two causes about the dispersion. One is the mother solution, which might not have been homogenous. And another possibility is polymer chain cessation in the dilution process. In anyway, I could not confirm the protocol of intrinsic viscosity measurement. Henceforth, I should improve sample preparation and measurement skill for reproducibility.

In chapter 4, I synthesized [BMIM][Br] and [AMIM][Cl] according to three different synthetic routes by microwave reactor. I also compared with conventional reflux method and MW heating method by physical properties. Heating time of [BMIM][Br] was reduced from 24 hours to 30 minutes by using microwave reactor. For huge mass synthesis of [BMIM][Br], it was not succeeded by this MW reactor, because the MW reactor has special size vial tube. Therefore, I should seek bigger vial or other synthetic process, or use MW reactor for industrial use. In the purity of [AMIM][Cl] such as water content, density and viscosity were improved by using MW reactor compared with reflux heating. However, I still need additional purification of [AMIM][Cl] to keep the physical properties in the permissible range become important for researching physical properties of natural materials.

In chapter 5, density of [AMIM][Cl] is higher than [BMIM][Cl], and solubility of [AMIM][Cl] is better than [BMIM][Cl] for cellulose and silk dissolution, these trends are same as our experiment. However, I got the different simulation data with our experiment in concentration fluctuations. Viscosity of [AMIM][Cl] is higher than [BMIM][Cl], but in our experiment, viscosity value of

[BMIM][Cl] is higher one digit than [AMIM][Cl]. Therefore, I should consider about the effect like electrostatic interaction and steric barrier. Then I also need to try the molecular model of larger scale and coarse-grained for dynamically stable and high order structure in samples. I also should try the simulation by longer time run for getting closer to experimental data.

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