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# Preparation of Ionic Liquids Containing Siloxane Frameworks

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Additional information is available at the end of the chapter

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## Abstract

This chapter deals with our recent researches on the preparation and properties of thermally stable ionic liquids (ILs) containing siloxane frameworks. ILs containing randomly structured oligosilsesquioxanes with quaternary ammonium side-chain groups (**Am-Random-SQ-IL**) and with imidazolium side-chain groups (**Im-Random-SQ-IL**) were successfully prepared by the hydrolytic condensation of the corresponding trifunctional alkoxy silanes in aqueous bis(trifluoromethanesulfonyl)imide (HNTf<sub>2</sub>) solution. It is also reported that ILs containing cage-like oligosilsesquioxanes (POSSs) with imidazolium side-chain groups (**Im-Cage-SQ-IL**) and with random distribution of quaternary ammonium and imidazolium side-chain groups (**Amim-Cage-SQ-IL**) were obtained, when the similar hydrolytic condensations were performed in a water/methanol (1 : 19 v/v) mixed solution of HNTf<sub>2</sub>. In addition, we investigated the preparation of ILs containing cyclic oligosiloxanes with various imidazolium side-chain groups (**MeIm-CyS-IL-NTf<sub>2</sub>**, **MeIm-CyS-IL-OTf**, **HIm-CyS-IL-NTf<sub>2</sub>**, **EtIm-CyS-IL-NTf<sub>2</sub>**, **PrIm-CyS-IL-NTf<sub>2</sub>**, and **BuIm-CyS-IL-NTf<sub>2</sub>**) by the hydrolytic condensation of the corresponding difunctional alkoxy silanes in the solutions of superacids, such as HNTf<sub>2</sub> and trifluoromethanesulfonic acid (HOTf).

**Keywords:** alkoxy silane, cyclic oligosiloxane, hydrolytic condensation, ionic liquid, POSS, siloxane, silsesquioxane, superacid

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## 1. Introduction

Ionic liquids (ILs), molten salts below 100°C or 150°C, have attracted much attention because of their potential application to green solvents [1–4] and electrolyte materials [5–7]. These

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compounds indicate the negligible vapor pressure, high thermal stability, and high ionic conductivity. Most ILs are regarded as organic compounds because of the presence of large amount of organic components in ILs. On the other hand, ILs with relatively more inorganic components could be applied to a wide range of materials research due to their significantly higher thermostability derived from the inorganic components.

Based on such considerations, some ILs containing inorganic frameworks, such as cage-like oligosilsesquioxanes (polyhedral oligomeric silsesquioxanes: POSSs) have been developed so far. A POSS IL (melting point ( $T_m$ ) = 23°C) was first developed by Chujo et al. [8]. This POSS IL had carboxylate anionic side-chain groups and imidazolium counter cations. In other cases, a POSS IL ( $T_m$  = 18°C) containing imidazolium cationic side-chain groups and dodecyl sulfate counter anions was prepared by Feng and coworkers [9]. However, these POSS ILs had relatively lower thermal decomposition (pyrolysis) temperatures ( $T_d$ s < 250°C) because of the large proportion of organic components in their side-chains or counter ions.

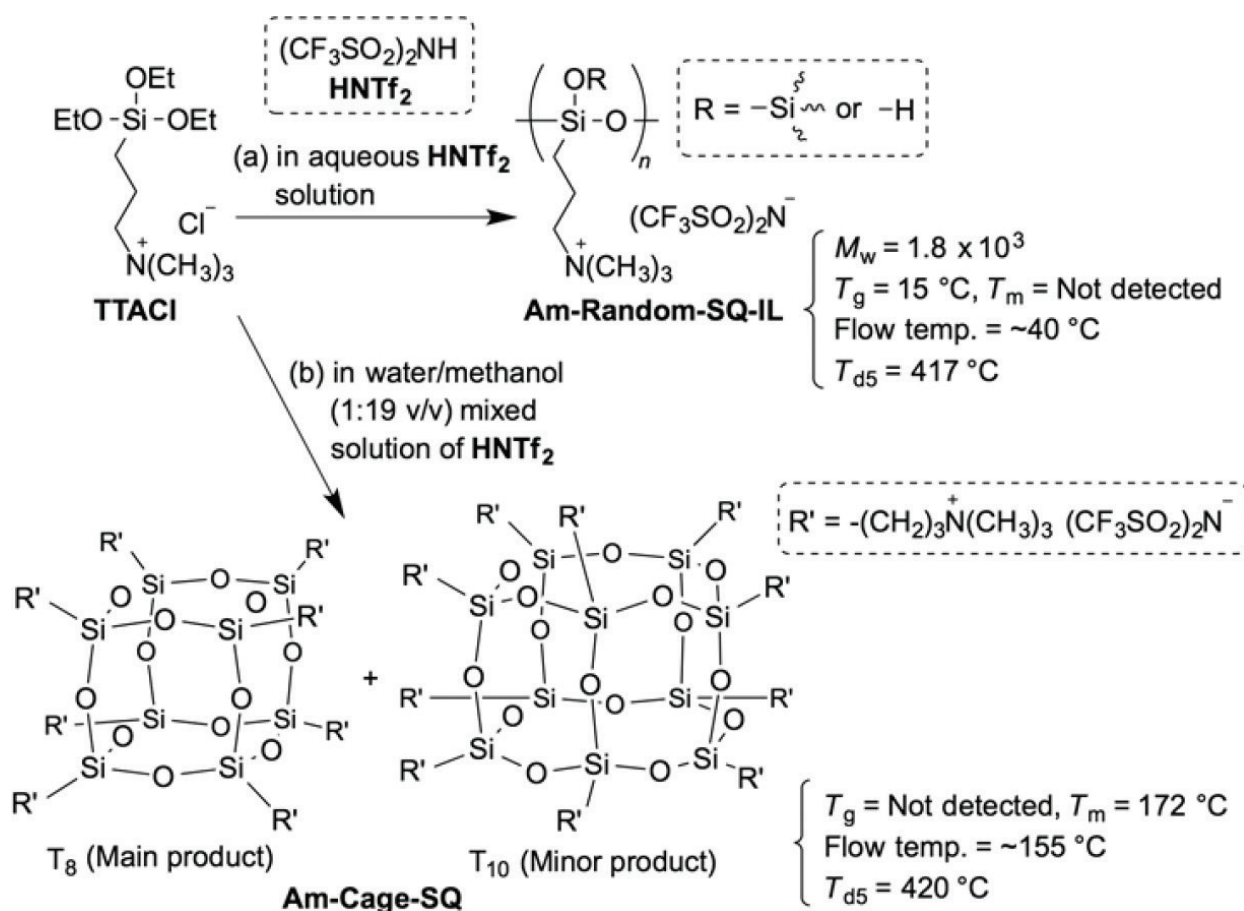
In this chapter, we would like to describe our recent work on the preparation of thermally stable ILs containing siloxane frameworks, such as randomly structured oligosilsesquioxanes, POSSs, and cyclic oligosiloxanes, by the hydrolytic condensation of the corresponding tri- and di-alkoxysilanes using superacid catalysts.

## 2. Preparation of a quaternary ammonium-type ionic liquid containing randomly structured oligosilsesquioxane

So far, we have prepared ionic siloxane compounds with regular structures, such as POSSs [10–12], ladder-like polysilsesquioxanes [13–19], and cyclic siloxanes [20], by the hydrolytic condensation of tri- and di-alkoxysilanes containing functional organic groups, which can be converted into ionic groups during the reactions. While performing these studies on the preparation of regularly structured ionic siloxane compounds, we fortuitously found a highly thermostable IL containing randomly structured oligosilsesquioxane, which has quaternary ammonium side-chain groups. We first describe the preparation and properties of this IL.

A quaternary ammonium-type IL containing randomly structured oligosilsesquioxane (**Am-Random-SQ-IL**) was successfully prepared by the hydrolytic condensation of the quaternary ammonium salt containing organotrialkoxysilane, trimethyl[3-(triethoxysilyl)propyl] ammonium chloride (TTACl), in aqueous bis(trifluoromethanesulfonyl)imide (HNTf<sub>2</sub>) solution under the following conditions (**Scheme 1a**) [21]: TTACl was stirred in aqueous HNTf<sub>2</sub> solution (0.5 mol/L) at room temperature for 2 h. Here, molar ratio of HNTf<sub>2</sub>/TTACl (= 1.5) is the important factor. The water-insoluble viscous product was isolated, washed with water, and dried under reduced pressure. Then, the crude product was dissolved in methanol and the resulting solution was heated in an open system until the solvent completely evaporated to remove the small amount of water remaining in the product. In addition, the resulting

viscous product was heated at 150°C for ca. 10 h. The product (**Am-Random-SQ-IL**) was soluble in dimethyl sulfoxide (DMSO), *N,N*-dimethylformamide (DMF), methanol, acetone, tetrahydrofuran (THF), and ethyl acetate, but insoluble in water, ethanol, 1-propanol, 2-propanol, chloroform, diethyl ether, toluene, and *n*-hexane.



Scheme 1. Preparation of (a) **Am-Random-SQ-IL** and (b) **Am-Cage-SQ**.

The energy dispersive X-ray (EDX) pattern of **Am-Random-SQ-IL** did not show the peaks due to Cl atom (2.6 and 2.8 keV). In addition, because the Si:S elemental ratio was 1:2.04, the molar ratio of quaternary ammonium cation to NTf<sub>2</sub> anion in **Am-Random-SQ-IL** was calculated to be ca. 1:1. The <sup>29</sup>Si NMR spectrum of **Am-Random-SQ-IL** in DMSO-*d*<sub>6</sub> at 60°C indicated two broad signals due to the T<sup>2</sup> (−56 to −61 ppm) and T<sup>3</sup> (−64 to −70 ppm) structures. The integrated ratio of these signals was estimated to be ca. 44:56. Although this compound had a relatively high proportion of the silanol groups, it was stable, i.e., without causing condensation and aggregation. The weight-average molecular weight (*M<sub>w</sub>*) of **Am-Random-SQ-IL** estimated by static light scattering (SLS) measurements in methanol was ca. 1.8 × 10<sup>3</sup>. Based on these results, it was concluded that **Am-Random-SQ-IL** was a randomly structured oligosilsesquioxane containing quaternary ammonium cations and NTf<sub>2</sub> anions.

When the differential scanning calorimetry (DSC) measurement of **Am-Random-SQ-IL** was performed, the baseline shift assigned to the glass-transition point ( $T_g$ ) was observed at 15°C (Run 1 in **Table 1**). On the other hand, the endothermic peak due to  $T_m$  could not be detected, indicating that **Am-Random-SQ-IL** is an amorphous compound. So far, ILs without  $T_m$  have been reported, e.g., 1-butyl-3-methylimidazolium tetrafluoroborate [22] and 1-ethyl-3-methylimidazolium phosphonate derivatives [23].

The flow temperature of **Am-Random-SQ-IL** was visually confirmed by the following procedure: **Am-Random-SQ-IL** was kept horizontal at 100°C for 15 min in a glass vessel, and the sample in the vessel was cooled to room temperature in the horizontal state. Then, the vessel stood at various temperatures for 15 min with tilting. Accordingly, **Am-Random-SQ-IL** showed obvious fluidity over 40°C (Run 1 in **Table 1**).

The thermal stability of **Am-Random-SQ-IL** on pyrolysis was investigated by thermogravimetric analyses (TGA). The temperatures of 3% ( $T_{d3}$ ), 5% ( $T_{d5}$ ), and 10% ( $T_{d10}$ ) weight losses of **Am-Random-SQ-IL** (411, 417, and 425°C, respectively) (Run 1 in **Table 1**) were higher than those of *N,N,N*-trimethyl-*N*-propylammonium bis(trifluoromethanesulfonyl) imide ([TMPA][NTf<sub>2</sub>]) (392, 400, and 411°C, respectively), which is an IL compound with the structure of the side-chains of **Am-Random-SQ-IL**. These results indicate that the thermal stability of **Am-Random-SQ-IL** was enhanced by connection to the silsesquioxane framework.

Run	IL	$T_g$ (°C) <sup>a</sup>	$T_m$ (°C) <sup>a</sup>	Flow temp. (°C) <sup>b</sup>	$T_{d5}$ (°C) <sup>c</sup>
1	<b>Am-Random-SQ-IL</b>	15	ND <sup>d</sup>	~40	417
2	<b>Am-Cage-SQ</b>	ND <sup>d</sup>	172	~155	420
3	<b>Im-Random-SQ-IL</b>	-25	ND <sup>d</sup>	~0	437
4	<b>Im-Cage-SQ-IL</b>	-21	106	~100	436
5	Mixture of <b>Am-Cage-SQ</b> and <b>Im-Cage-SQ-IL</b>	-7	164	~120	420
6	<b>Amim-Cage-SQ-IL</b>	-8	ND <sup>d</sup>	~30	420
7	<b>MeIm-CyS-IL-NTf<sub>2</sub></b>	-43	ND <sup>d</sup>	~0	415
8	<b>MeIm-CyS-IL-OTf</b>	-14	ND <sup>d</sup>	~20	391
9	<b>HIm-CyS-IL-NTf<sub>2</sub></b>	-38	ND <sup>d</sup>	~0	–
10	<b>EtIm-CyS-IL-NTf<sub>2</sub></b>	-44	ND <sup>d</sup>	~0	–
11	<b>PrIm-CyS-IL-NTf<sub>2</sub></b>	-44	ND <sup>d</sup>	~0	–
12	<b>BuIm-CyS-IL-NTf<sub>2</sub></b>	-45	ND <sup>d</sup>	~0	–

<sup>a</sup> Determined by DSC.

<sup>b</sup> Determined by visual observation.

<sup>c</sup> Determined by TGA.

<sup>d</sup> Not detected.

**Table 1.** Properties of ILs containing siloxane frameworks.

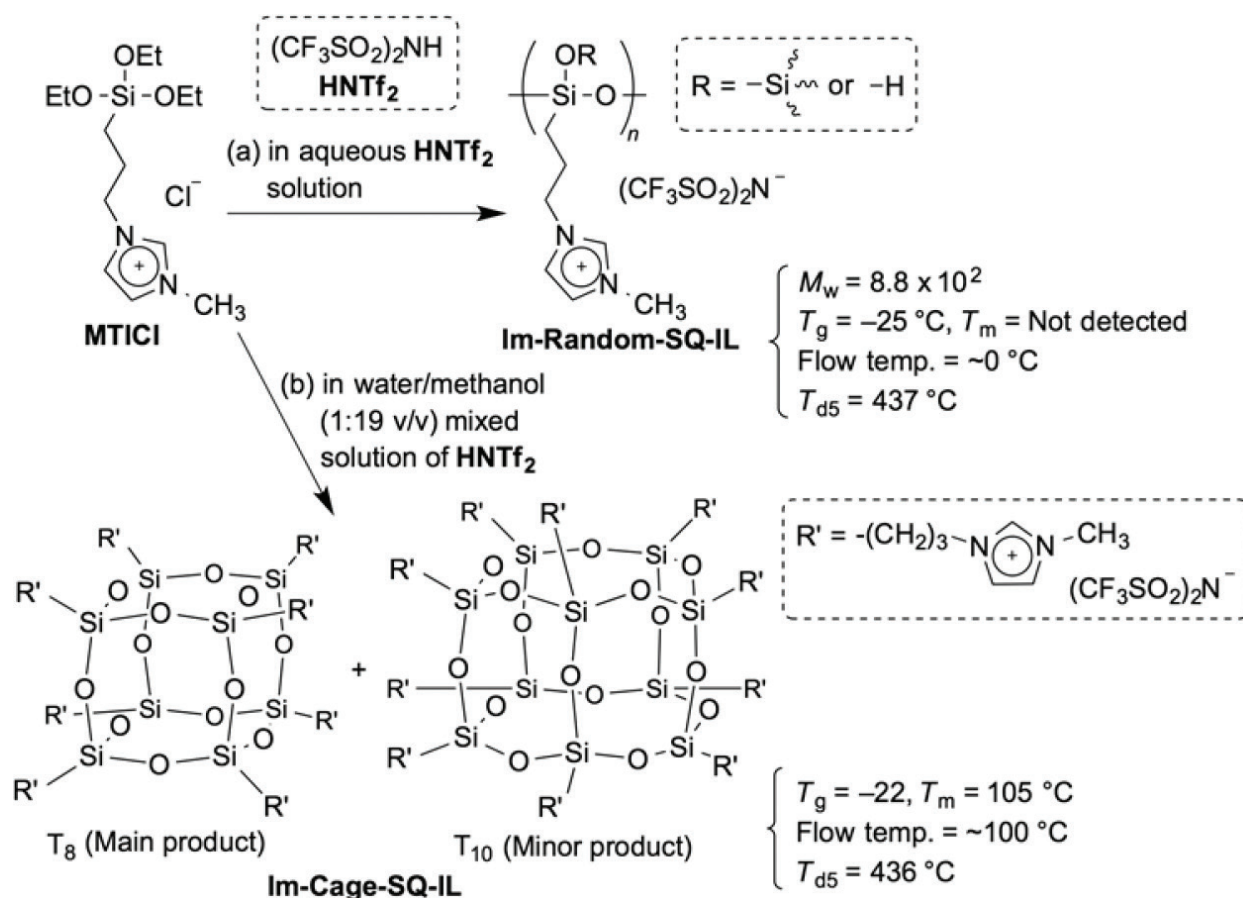
As described above, **Am-Random-SQ-IL** had an amorphous structure and displayed IL nature. Its amorphous structure is probably one of the most important factors for such IL properties. Therefore, to investigate the correlation between the IL nature and the structures of the silsesquioxanes, we investigated the preparation of a POSS compound with crystalline structure using the same reagent and superacid catalyst. When the hydrolytic condensation of TTACl was performed using HNTf<sub>2</sub> as a catalyst in water/methanol mixed solvent (1:19 v/v) instead of the aqueous solution as described above, a powdered POSS compound (**Am-Cage-SQ**) was prepared (**Scheme 1b**) [21]. A visual flow temperature of **Am-Cage-SQ** (~155°C) was much higher than that of **Am-Random-SQ-IL** because of the presence of higher  $T_m$  (172°C), although pyrolysis temperature was notably high ( $T_{d5} = 420^\circ\text{C}$ ) (Run 2 in **Table 1**). Such high  $T_{ms}$  and flow temperatures of these POSS compounds are probably derived from their highly symmetrical and crystalline structures.

### 3. Preparation of imidazolium-type ionic liquids containing random-structured and cage-like oligosilsesquioxanes

As described in the previous section, **Am-Random-SQ-IL** had  $T_g$  of 15°C and exhibited fluidity at ~40°C, i.e., it was not a room temperature IL (RT-IL). Generally, imidazolium-type ILs have relatively low  $T_m$  [24]. Therefore, to prepare a RT-IL containing a randomly structured oligosilsesquioxane framework (**Im-Random-SQ-IL**), the hydrolytic condensation of the imidazolium-group-containing organotrialkoxysilane using aqueous HNTf<sub>2</sub> was investigated [25]. **Im-Random-SQ-IL** could be prepared from 1-methyl-3-[3-(triethoxysilyl)propyl]imidazolium chloride (MTICl) as a starting material by the same procedure for the preparation of **Am-Random-SQ-IL** as described above (**Scheme 2a**). **Im-Random-SQ-IL** was soluble in DMSO, DMF, methanol, acetone, THF, and ethyl acetate, but insoluble in water, ethanol, 1-propanol, 2-propanol, chloroform, diethyl ether, toluene, and *n*-hexane.

The EDX pattern of **Im-Random-SQ-IL** also indicated the absence of Cl. In addition, the Si:S elemental ratio of **Im-Random-SQ-IL** was estimated to be 1:2.03, indicating that the molar ratio of imidazolium cations to NTf<sub>2</sub> anions was ca. 1:1. The <sup>29</sup>Si NMR spectrum of **Im-Random-SQ-IL** in DMSO-*d*<sub>6</sub> at 60°C exhibited two broad signals in the  $T^2$  (-53 to -61 ppm) and  $T^3$  (-64 to -70 ppm) regions with an integrated ratio of ca. 40:60. Similar to the aforementioned quaternary ammonium salt-type IL (**Am-Random-SQ-IL**), this compound was also stable, although it had a relatively high proportion of the silanol groups. The  $M_w$  of **Im-Random-SQ-IL** estimated by SLS data obtained in methanol was ca.  $8.8 \times 10^2$ . Based on these results, it was concluded that **Im-Random-SQ-IL** was a randomly structured oligosilsesquioxane compound composed of imidazolium cations and NTf<sub>2</sub> anions.

The DSC analysis of **Im-Random-SQ-IL** was performed. The baseline shift assigned to  $T_g$  was observed at -25°C (Run 3 in **Table 1**). Conversely, the endothermic peak due to  $T_m$  was not detected. The amorphous structure of **Im-Random-SQ-IL** may give rise to poor packing of the ions. The flow temperature of **Im-Random-SQ-IL** was confirmed by the same procedure for **Am-Random-SQ-IL** as described above. Consequently, it showed obvious fluidity at ~0°C, i.e., it is a RT-IL (Run 3 in **Table 1**).

Scheme 2. Preparation of (a) **Im-Random-SQ-IL** and (b) **Im-Cage-SQ-IL**.

We assumed that such IL properties were probably attributed to the amorphous structure. Therefore, as well as the quaternary ammonium-type ILs as described in the previous section, a POSS compound with crystalline structure was prepared. A POSS compound (**Im-Cage-SQ-IL**) was prepared by the hydrolytic condensation of MTICl using  $\text{HNTf}_2$  as a catalyst in water/methanol (1:19, v/v) mixed solvent (**Scheme 2b**) [25]. **Im-Cage-SQ-IL** was soluble in DMSO, DMF, methanol, acetone, THF, and ethyl acetate, but insoluble in water, ethanol, 1-propanol, 2-propanol, chloroform, diethyl ether, toluene, and *n*-hexane. The  $^1\text{H}$  NMR and EDX results for **Im-Cage-SQ-IL** were almost same as those for **Im-Random-SQ-IL**.

The  $^{29}\text{Si}$  NMR spectrum of **Im-Cage-SQ-IL** in  $\text{DMSO}-d_6$  at  $40^\circ\text{C}$  showed two signals assigned to the  $T^3$  structures at  $-66.5$  ppm (a main signal) and at  $-68.7$  ppm (a minor signal), indicating the absence of silanol groups. These signals were derived from cage-like octasilsesquioxane ( $T_8$ ) and cage-like decasilsesquioxane ( $T_{10}$ ), respectively. Because the integrated ratio of these signals was estimated to be 75:25, the molar ratio of  $T_8:T_{10}$  was calculated to be 79:21 ( $= 75/8:25/10$ ). In addition, the MALDI-TOF MS results supported the formation of such POSS structures. Finally, the XRD pattern of **Im-Cage-SQ-IL** showed many sharp diffraction peaks, indicating the formation of a crystalline structure, unlike that of **Im-Random-SQ-IL**, which did not exhibit any diffraction peaks.

The DSC curve for **Im-Cage-SQ-IL** indicated the baseline shift due to  $T_g$  at  $-22^\circ\text{C}$  and the endothermic peak due to  $T_m$  at  $105^\circ\text{C}$  (Run 4 in **Table 1**). In addition, **Im-Cage-SQ-IL** showed fluidity at  $\sim 100^\circ\text{C}$  (Run 4 in **Table 1**), confirmed by the same procedure as described above for **Im-Random-SQ-IL**. This indicated that **Im-Cage-SQ-IL** was not a RT-IL. Because **Im-Cage-SQ-IL** is a crystalline compound, its flow temperature was near its  $T_m$  ( $\sim 100^\circ\text{C}$ ). On the other hand, **Im-Random-SQ-IL** with an amorphous structure exhibited fluidity above its  $T_g$ . These results suggest that the amorphous structure of **Im-Random-SQ-IL** is essential for achieving RT-IL, in addition to the types of substituent groups in the silsesquioxanes.

The thermal stabilities of **Im-Random-SQ-IL** and **Im-Cage-SQ-IL** upon pyrolysis were investigated by TGA. The  $T_{d3'}$ ,  $T_{d5'}$  and  $T_{d10}$  values for **Im-Random-SQ-IL** were 429, 437, and  $447^\circ\text{C}$ , respectively (Run 3 in **Table 1**), while those of **Im-Cage-SQ-IL** were 427, 436, and  $446^\circ\text{C}$ , respectively (Run 4 in **Table 1**). These values were higher than those of 1-methyl-3-propyl-imidazolium bis(trifluoromethylsulfonyl)imide ([C3mim][NTf<sub>2</sub>]) ( $366$ ,  $380$ , and  $399^\circ\text{C}$ , respectively). This compound is an IL with the structure of the side-chains of **Im-Random-SQ-IL** and **Im-Cage-SQ-IL**. These results indicated that the thermal stabilities of **Im-Random-SQ-IL** and **Im-Cage-SQ-IL** were increased by incorporation of the silsesquioxane frameworks. Such a tendency was also observed in a quaternary ammonium-type IL, **Am-Random-SQ-IL**, as described above.

#### 4. Preparation of ionic liquids containing cage-like oligosilsesquioxane (POSS) with the random distribution of quaternary ammonium and imidazolium side-chain groups

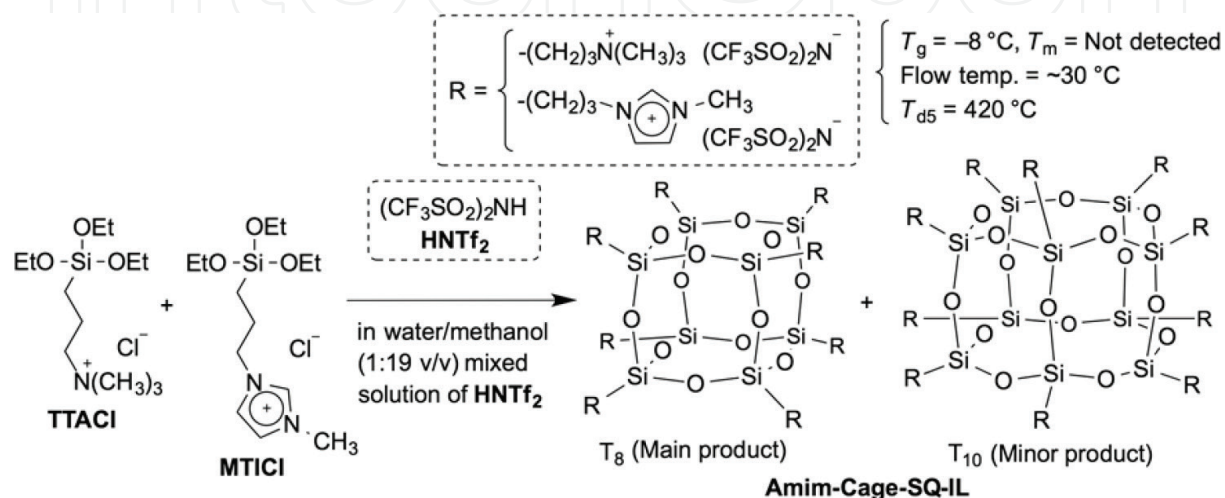
As described in Section 3, a highly thermostable POSS IL containing imidazolium cationic side-chains and NTf<sub>2</sub> anions as counter ions (**Im-Cage-SQ-IL**) could be successfully prepared by hydrolytic condensation of MTICl using superacid HNTf<sub>2</sub> as a catalyst. In addition, a quaternary ammonium-type POSS (**Am-Cage-SQ**) could also be prepared from TTACl as a starting material using the same procedure, as described in Section 2. However, visual flow temperatures of these compounds were relatively high ( $\sim 155^\circ\text{C}$  for **Am-Cage-SQ** and  $\sim 100^\circ\text{C}$  for **Im-Cage-SQ-IL**) because of their higher  $T_m$ s ( $172^\circ\text{C}$  for **Am-Cage-SQ** and  $105^\circ\text{C}$  for **Im-Cage-SQ-IL**) (Run 2, 4 in **Table 1**). Such high  $T_m$ s and flow temperatures of these POSS compounds are probably derived from their highly symmetrical and crystalline structures.

The development of POSS RT-ILs with high thermal stabilities is expected for both academic and application reasons because RT-ILs are particularly useful for many applications of green solvents and electrolyte materials. Therefore, to prepare such POSS ILs, we focused on our previous studies on the preparation of low-crystalline POSS [11] and amorphous POSS-linking polymer [12]. Their synthesis was achieved by hydrolytic condensation of a mixture of two types of amino-group-containing organotrialkoxysilanes. The molecular symmetry of the resulting POSS derivatives was low because of the random distribution of the two types of side-chain groups. Consequently, their crystallization was suppressed. In this section, we describe the preparation of a thermally stable POSS RT-IL (**Amim-Cage-SQ-IL**), which contained a



random distribution of the two types of side-chain groups, by the hydrolytic condensation of a mixture of TTACl and MTICl using HNTf<sub>2</sub> as a catalyst in water/methanol mixed solvent [26].

**Amim-Cage-SQ-IL** was prepared from a mixture of TTACl and MTICl (1:1 mol/mol) by same procedures for the preparation of **Im-Cage-SQ-IL** and **Am-Cage-SQ** as described above (Scheme 3). **Amim-Cage-SQ-IL** was soluble in DMSO, acetonitrile, DMF, methanol, acetone, THF, and ethyl acetate, but insoluble in water, ethanol, 1-propanol, 2-propanol, chloroform, diethyl ether, toluene, and *n*-hexane.



Scheme 3. Preparation of **Amim-Cage-SQ-IL**.

The <sup>1</sup>H NMR spectrum of **Amim-Cage-SQ-IL** in DMSO-*d*<sub>6</sub> showed the signals attributable to the side-chain groups of both the *N,N,N*-trimethyl-*N*-propylammonium group and the 1-methyl-3-propylimidazolium group. The average compositional ratio of TTACl to MTICl components in the product was estimated to be ca. 1:1 from the <sup>1</sup>H NMR spectrum. The EDX pattern of **Amim-Cage-SQ-IL** did not indicate any peaks originating from Cl, and the Si:S elemental ratio was estimated to be 1.00:2.03, indicating that the molar ratio of cation species (imidazolium and ammonium) to NTf<sub>2</sub> anions was ca. 1:1.

The <sup>29</sup>Si NMR spectrum of **Amim-Cage-SQ-IL** in DMSO-*d*<sub>6</sub> at 40°C only showed four sharp signals due to the *T*<sup>3</sup> structure at -66.8, -67.3, -68.8, and -69.3 ppm, indicating the absence of silanol groups. These signals could be attributed to the MTICl and TTACl components of *T*<sub>8</sub> and the MTICl and TTACl components of *T*<sub>10</sub> respectively, because these chemical shifts were almost same as those of **Am-Cage-SQ** and **Im-Cage-SQ-IL** as described in the previous sections. Because the integrated ratio of *T*<sub>8</sub>:*T*<sub>10</sub> signals was estimated to be 77:23, the molar ratio of *T*<sub>8</sub>:*T*<sub>10</sub> was calculated to be 81:19 (= 77/8:23/10), indicating that *T*<sub>8</sub> was the main product. The MALDI-TOF MS analysis of **Amim-Cage-SQ-IL** also supported the <sup>29</sup>Si NMR results.

The DSC curves of **Am-Cage-SQ** and **Im-Cage-SQ-IL** (POSS compounds as described in Sections 2 and 3) indicated the endothermic peaks for *T*<sub>m</sub>s at 172 and 105°C, respectively (Run 2, 4 in Table 1), i.e., **Am-Cage-SQ** and **Im-Cage-SQ-IL** are crystalline compounds.

The XRD patterns of **Am-Cage-SQ** and **Im-Cage-SQ-IL** supported that they were crystalline compounds. Therefore, **Am-Cage-SQ** and **Im-Cage-SQ-IL** showed relatively high flow temperatures ( $\sim 155$  and  $\sim 100^\circ\text{C}$ , respectively) because of their high crystallinity (Run 2, 4 in **Table 1**). In addition, a mixture of **Am-Cage-SQ** and **Im-Cage-SQ-IL** also maintained crystalline structure, because the endothermic peak due to  $T_m$  was observed at  $164^\circ\text{C}$ ; it showed fluidity at  $120^\circ\text{C}$  (Run 5 in **Table 1**).

Conversely, the DSC curve of **Amim-Cage-SQ-IL** showed a baseline shift at  $-8^\circ\text{C}$  due to  $T_g$ , whereas an endothermic peak due to  $T_m$  was not detected (Run 6 in **Table 1**), indicating that **Amim-Cage-SQ-IL** is an amorphous compound. The XRD pattern of **Amim-Cage-SQ-IL** did not show any diffraction peaks, supporting the amorphous structure of this compound. **Amim-Cage-SQ-IL** exhibited obvious fluidity at  $\sim 30^\circ\text{C}$  (Run 6 in **Table 1**). Because the molecular symmetry of the resulting POSS compound with a random distribution of the two types of side-chain groups was low, its crystallization was suppressed. Therefore, the phase transition from amorphous solid to fluid occurred above  $T_g$ . Based on these results, it was concluded that **Amim-Cage-SQ-IL** had  $T_g$  of  $-8^\circ\text{C}$  and showed fluidity at  $\sim 30^\circ\text{C}$ , i.e., it is a RT-IL.

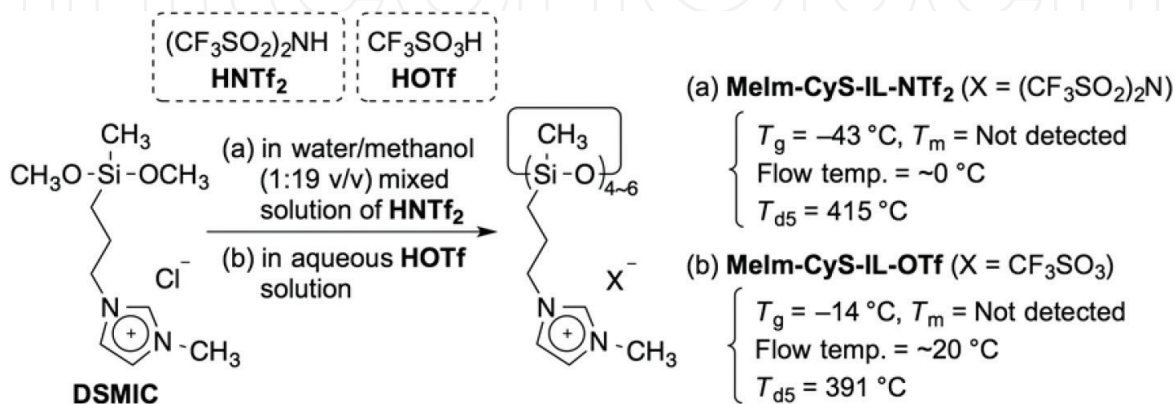
The  $T_{d3\%}$ ,  $T_{d5\%}$  and  $T_{d10\%}$  values estimated by TGA of **Amim-Cage-SQ-IL** were  $414^\circ\text{C}$ ,  $420^\circ\text{C}$ , and  $428^\circ\text{C}$ , respectively (Run 6 in **Table 1**). These values were higher than those of ILs with the side-chain structures of this IL: [TPMA][NTf<sub>2</sub>] ( $392$ ,  $400$ , and  $411^\circ\text{C}$ , respectively) and [C3mim][NTf<sub>2</sub>] ( $366$ ,  $380$ , and  $399^\circ\text{C}$ , respectively).

## 5. Preparation of ionic liquids containing cyclic oligosiloxanes

In the previous sections, we described that ILs containing silsesquioxane frameworks, such as randomly structured silsesquioxanes and POSSs, were successfully prepared. In particular, **Am-Random-SQ-IL**, **Im-Random-SQ-IL**, and **Amim-Cage-SQ-IL** had both relatively low flow temperatures ( $< \sim 40^\circ\text{C}$ ) and high thermal stabilities ( $T_{d5\%} > \sim 400^\circ\text{C}$ ). However, they also displayed high viscosities, probably because of the presence of silanol groups for randomly structured silsesquioxane ILs and relatively higher degrees of polymerization (DP) for all silsesquioxane ILs. It is assumed that siloxane-based ILs without silanol groups and with lower DP probably exhibit high thermal stability, low flow temperature, and low viscosity. In this section, therefore, we describe the preparation and properties of ILs containing cyclic oligosiloxanes as the siloxane frameworks.

To achieve the preparation of such ILs containing cyclic oligosiloxanes, we referred to our previous study for the facile preparation of cationic cyclotetrasiloxane (this is not an IL) by the hydrolytic condensation of 3-aminopropylmethyltriethoxysilane using the superacid trifluoromethanesulfonic acid (HOTf) [20]. Therefore, when the hydrolytic condensation of 1-[3-(dimethoxymethylsilyl)propyl]-3-methylimidazolium chloride (DSMIC) was performed using superacid catalysts such as HNTf<sub>2</sub> and HOTf, we found that imidazolium salt-type ILs containing cyclic oligosiloxane frameworks (**MeIm-CyS-IL-NTf<sub>2</sub>** and **MeIm-CyS-IL-OTf**) were successfully prepared [27].

**MeIm-CyS-IL-NTf<sub>2</sub>** was prepared by the following procedure (**Scheme 4a**): DSMIC was stirred in a water/methanol (1:19, v/v) mixed solution of HNTf<sub>2</sub> at room temperature. Then, the solvent was evaporated by heating at ~50°C in an open system. The resulting crude product was further heated at 100°C for 2 h, washed with water, and then dried at 150°C for ca. 5 h to obtain **MeIm-CyS-IL-NTf<sub>2</sub>**. On the other hand, **MeIm-CyS-IL-OTf** was prepared using almost same procedure as that of **MeIm-CyS-IL-NTf<sub>2</sub>** but using an aqueous HOTf as a catalyst (**Scheme 4b**). The EDX results of **MeIm-CyS-IL-NTf<sub>2</sub>** and **MeIm-CyS-IL-OTf** indicated the absence of Cl and the molar ratio of imidazolium cations to NTf<sub>2</sub> or OTf anions were ca. 1:1.



**Scheme 4.** Preparation of (a) **MeIm-CyS-IL-NTf<sub>2</sub>** and (b) **MeIm-CyS-IL-OTf**.

In the MALDI-TOF MS analysis of **MeIm-CyS-IL-NTf<sub>2</sub>**, several peaks assigned to cyclic siloxane tetramer (main peaks) and pentamer (minor peaks) were observed. Furthermore, the <sup>1</sup>H NMR spectrum exhibited multiplet signals due to methyl groups at 0.23 to -0.23 ppm. In addition, the <sup>29</sup>Si NMR spectrum of **MeIm-CyS-IL-NTf<sub>2</sub>** in DMSO-*d*<sub>6</sub> at 40°C also showed two multiplet signals due to the *D*<sup>2</sup> structure (-19.2 to -19.6 ppm for cyclic tetrasiloxane (main signals) and -21.4 to -21.9 ppm for cyclic pentasiloxane (minor signals)). On the other hand, the MALDI-TOF MS results of **MeIm-CyS-IL-OTf** indicated the existence of a mixture of cyclic siloxane tetramer (main product), pentamer (main product), and hexamer (minor product). In addition, **MeIm-CyS-IL-OTf** had some stereoisomers, confirmed by the <sup>1</sup>H NMR spectrum with multiplet signals assigned to the methyl groups at 0.16--0.23 ppm and the <sup>29</sup>Si NMR spectrum with three multiplet signals due to the *D*<sup>2</sup> structure (-19.1 to -19.7 ppm for cyclic tetrasiloxane (main signals), -21.3 to -21.9 ppm for cyclic pentasiloxane (main signals), and -22.2 to -22.5 ppm for cyclic hexasiloxane (minor signals)). These results indicated that **MeIm-CyS-IL-NTf<sub>2</sub>** was a mixture of cyclic tetrasiloxanes and cyclic pentasiloxanes, while **MeIm-CyS-IL-OTf** was a mixture of cyclic tetrasiloxanes, cyclic pentasiloxanes, and cyclic hexasiloxane, with some stereoisomers.

The DSC curves of the resulting products indicated the baseline shifts assigned to  $T_g$ s at -43°C for **MeIm-CyS-IL-NTf<sub>2</sub>** (Run 7 in **Table 1**) and at -14°C for **MeIm-CyS-IL-OTf** (Run 8 in **Table 1**), respectively. These values were newly estimated using different DSC equipment from that in the original paper [27] and were slightly different from the values in the original paper. Conversely, the endothermic peaks due to  $T_m$  were not detected. In addition, **MeIm-CyS-IL-NTf<sub>2</sub>** and **MeIm-CyS-IL-OTf** showed obvious fluidity at  $\sim 0$  and  $\sim 20^\circ\text{C}$ , respectively (Run 7, 8 in **Table 1**). On the basis of these results, it was concluded that **MeIm-CyS-IL-NTf<sub>2</sub>**

and **MeIm-CyS-IL-OTf** were RT-ILs. The  $T_{d3}$ ,  $T_{d5}$ , and  $T_{d10}$  values estimated by TGA were 407, 415, and 427°C for **MeIm-CyS-IL-NTf<sub>2</sub>** (Run 7 in Table 1) and 380, 391, and 402°C for **MeIm-CyS-IL-OTf** (Run 8 in Table 1).

The viscosity of **MeIm-CyS-IL-NTf<sub>2</sub>** was lower than that of **Im-Random-SQ-IL** containing randomly structured oligosilsesquioxane framework, as described in Section 3. Both ILs have same side-chain groups and showed low flow temperatures ( $\sim 0^\circ\text{C}$ ), yet the siloxane frameworks differed between the ILs. Figure 1 shows the photographs of these two samples after 0 and 10 s, with tilting at  $14^\circ\text{C}$ . **MeIm-CyS-IL-NTf<sub>2</sub>** obviously flowed after 10 s, while **Im-Random-SQ-IL** did not show fluidity after 10 s. These results indicated that cyclic oligosiloxane frameworks were important factors for the lower viscosity of **MeIm-CyS-IL-NTf<sub>2</sub>**. Further detailed studies for viscosity determination are currently in progress.

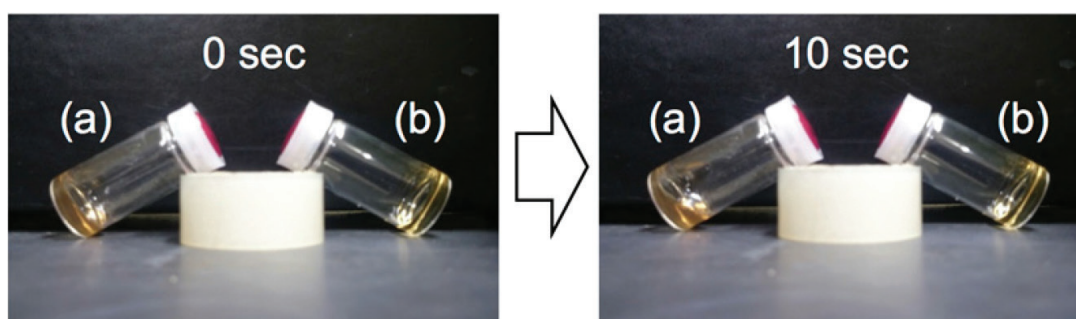
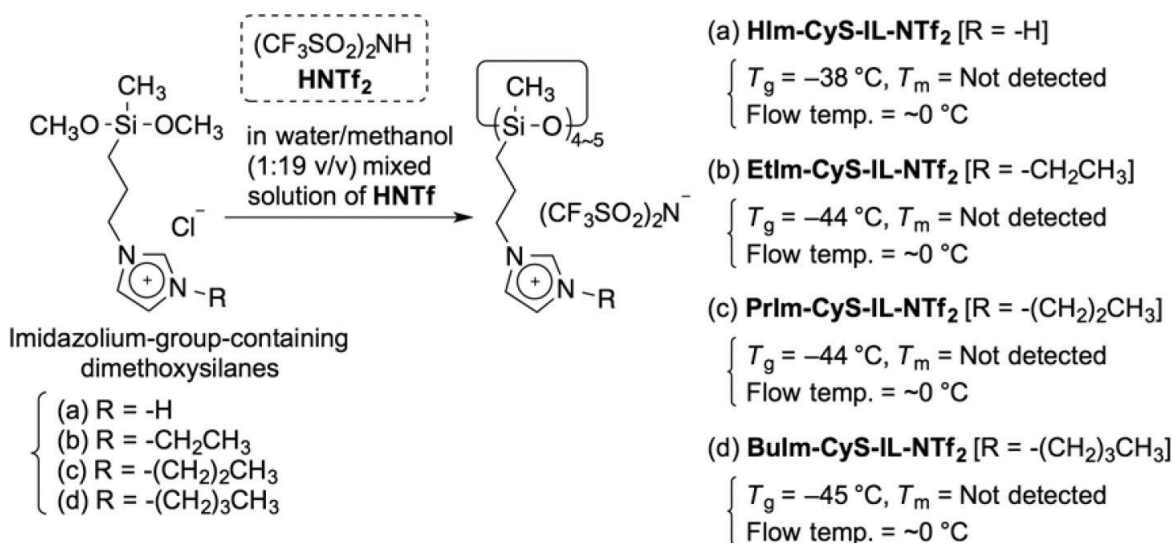


Figure 1. Photographs of (a) **MeIm-CyS-IL-NTf<sub>2</sub>** and (b) **Im-Random-SQ-IL** after 0 and 10 s with tilting at  $14^\circ\text{C}$ .

For this chapter, we newly investigated the effects of the alkyl chain length in the imidazolium groups of ILs containing cyclic oligosiloxane frameworks. Therefore, imidazolium salt-type ILs containing cyclic oligosiloxane with various lengths of alkyl chains ( $R = \text{H}$ ,  $\text{CH}_2\text{CH}_3$ ,  $(\text{CH}_2)_2\text{CH}_3$ , and  $(\text{CH}_2)_3\text{CH}_3$ ) were prepared by the hydrolytic condensation of the corresponding imidazolium-group-containing dimethoxysilanes using the superacid  $\text{HNTf}_2$  in a water/methanol (1:19, v/v) mixed solvent (Scheme 5). Based on the results of the  $^{29}\text{Si}$  NMR and MALDI-TOF MS analyses, we determined that the resulting products [**HIm-CyS-IL-NTf<sub>2</sub>** ( $R = \text{H}$ ), **EtIm-CyS-IL-NTf<sub>2</sub>** ( $R = \text{CH}_2\text{CH}_3$ ), **PrIm-CyS-IL-NTf<sub>2</sub>** ( $R = (\text{CH}_2)_2\text{CH}_3$ ), and **BuIm-CyS-IL-NTf<sub>2</sub>** ( $R = (\text{CH}_2)_3\text{CH}_3$ )] were mixtures of cyclic tetrasiloxanes (main product) and cyclic pentasiloxanes (minor product), with some stereoisomers, respectively.

The DSC curves of the resulting ILs showed the baseline shifts assigned to  $T_g$ s were observed at  $-38^\circ\text{C}$  for **HIm-CyS-IL-NTf<sub>2</sub>** (Figure 2a, Run 9 in Table 1),  $-44^\circ\text{C}$  for **EtIm-CyS-IL-NTf<sub>2</sub>** (Figure 2b, Run 10 in Table 1),  $-44^\circ\text{C}$  for **PrIm-CyS-IL-NTf<sub>2</sub>** (Figure 2c, Run 11 in Table 1), and  $-45^\circ\text{C}$  for **BuIm-CyS-IL-NTf<sub>2</sub>** (Figure 2d, Run 12 in Table 1). These values were almost same as that of **MeIm-CyS-IL-NTf<sub>2</sub>** ( $-43^\circ\text{C}$ ) (Run 7 in Table 1). Conversely, the endothermic peaks due to the  $T_m$ s were not detected for all ILs. In addition, all ILs showed obvious fluidity at  $\sim 0^\circ\text{C}$  (Figure 2a–d inset, Run 9–12 in Table 1). On the basis of these results, we concluded that the alkyl chain lengths in imidazolium groups of ILs containing cyclic oligosiloxane frameworks had an insignificant effect on the IL natures, such as  $T_g$  and flow temperatures.



Scheme 5. Preparation of (a) HIm-CyS-IL-NTf<sub>2</sub>, (b) EtIm-CyS-IL-NTf<sub>2</sub>, (c) PrIm-CyS-IL-NTf<sub>2</sub>, and (d) BuIm-CyS-IL-NTf<sub>2</sub>.

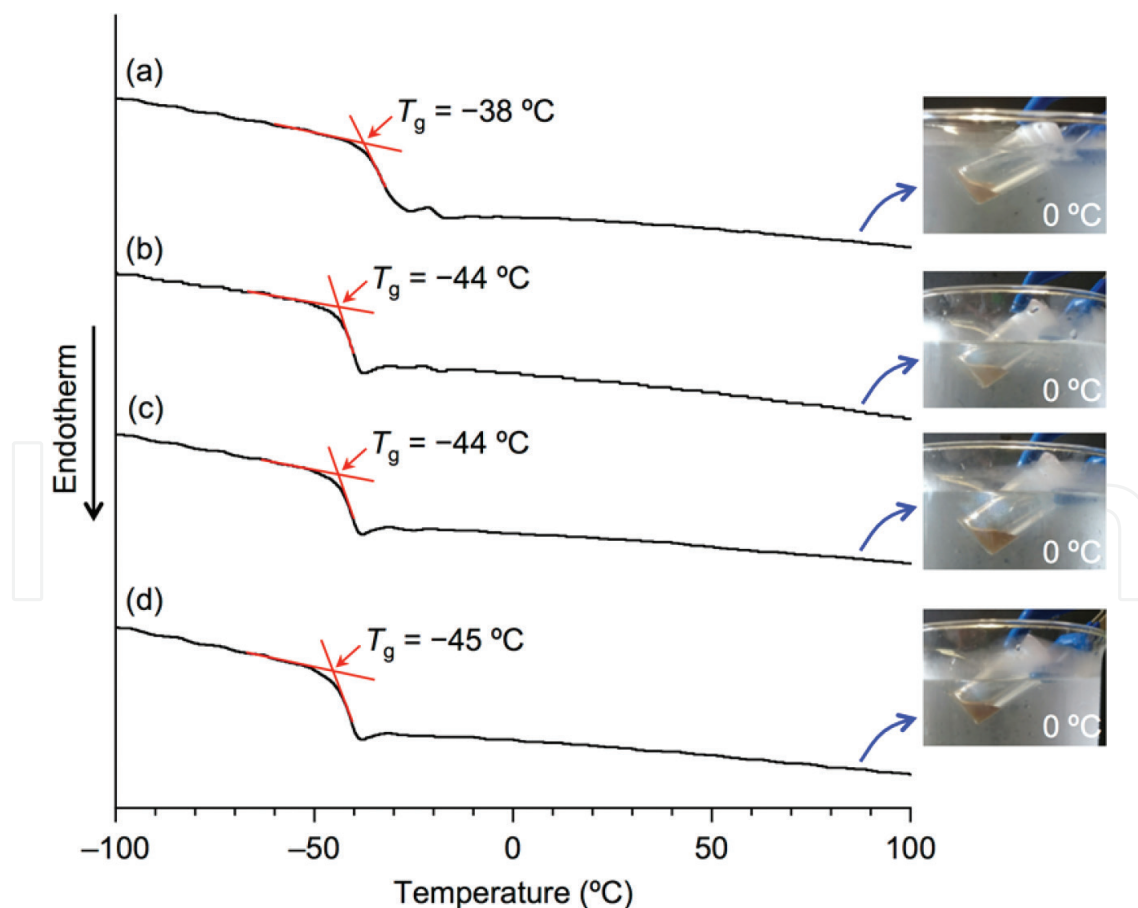


Figure 2. DSC curves and photographs of (a) HIm-CyS-IL-NTf<sub>2</sub>, (b) EtIm-CyS-IL-NTf<sub>2</sub>, (c) PrIm-CyS-IL-NTf<sub>2</sub>, and (d) BuIm-CyS-IL-NTf<sub>2</sub>.

## 6. Conclusions

In this chapter, we described the preparation and properties of thermally stable ILs containing siloxane frameworks, such as randomly structured oligosilsesquioxanes (**Am-Random-SQ-IL** and **Im-Random-SQ-IL**), POSSs (**Im-Cage-SQ-IL** and **Amim-Cage-SQ-IL**), and cyclic oligosiloxanes (**MeIm-CyS-IL-NTf<sub>2</sub>**, **MeIm-CyS-IL-OTf**, **HIm-CyS-IL-NTf<sub>2</sub>**, **EtIm-CyS-IL-NTf<sub>2</sub>**, **PrIm-CyS-IL-NTf<sub>2</sub>**, and **BuIm-CyS-IL-NTf<sub>2</sub>**). We are expecting that new applications of these siloxane-based ILs are found.

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