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POSS Ionic Liquid

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Abstract: We report the synthesis of a stable room-temperature ionic liquid consisting of an octacarboxy polyhedral oligomeric silsesquioxane (POSS) anion and an imidazolium cation. The introduction of the POSS moiety enhances the thermal stability and reduces the melting temperature. From an evaluation of the thermodynamic parameters during the melting, it was found that the rigidity and cubic structure of POSS can contribute to the enhancement of these thermal properties.

An ionic liquid (IL) is a nonvolatile salt with a melting temperature below 100 °C. The first reported air-stable ILs were molten salts of imidazolium ions; since their discovery, many researchers have synthesized various types of ionic compounds to obtain stable room-temperature ILs (RT-ILs).[1,2] Recently, nanostructured materials have attracted much attention as the components of ILs because not only their structural but also their morphological features have great potential to show advanced functions that are distinctly different from those of small molecules.[3] However, the increase in molecular weight and the presence of charges often cause an increase in the melting temperature. In addition, the molecular weight distribution affects the evaluation of their net properties.

Polyhedral oligomeric silsesquioxane (POSS) can serve as a nanobuilding block for constructing functional materials.[4] The rigid silica cube shows high thermal stability.[5] Moreover, POSS can form star-shaped structures and isolate each substitution group on the vertices.[6] As a result, such structural features often show particular characteristics different from those of planar molecules.[7] Several reports have shown that the POSS-containing ILs can function as high-performance electrolytes.[8] However, the transformation of octa-substituted POSS to a pure IL has not been achieved to date.

Herein, we report the synthesis of an RT-IL consisting of the octacarboxy-POSS[9] anion [POSS-$(COO^-)_8$] and the imidazolium cation [$Bmim^+$] (Figure 1a). Connecting the IL to POSS simultaneously accomplished a lowering of the melting temperature and an enhancement of the thermal stability. Thermodynamic analysis revealed that the rigidity and cubic structure of POSS can contribute to POSS-enhanced thermal properties. This is the first example demonstrating the properties of an RT-IL using octa-substituted POSS and the contribution of the structural characteristics of POSS to the thermal properties of an IL.

Initially, we tried to prepare [POSS-$(COO^-)_8$][$Bmim^+$]$_8$ from halide salt precursors via a metathesis reaction.[10] However, detachment of [$Bmim^+$] and defects of the ion pairs occurred during the purification step. Therefore, the synthetic route was changed to the acid−base neutralization between POSS-$(COOH)_8$ and [Bmim]OH. To avoid the degradation of the POSS cage in the presence of excess [Bmim]OH, the reaction was performed by titration of the diluted [Bmim]OH with a suspension of POSS-$(COOH)_8$.[11] Finally, we obtained a pure, transparent product (Figure 1b). We synthesized [Arm-COO^-][$Bmim^+$] (Figure 1a) for comparison purposes to evaluate how the connection with POSS affects the properties.

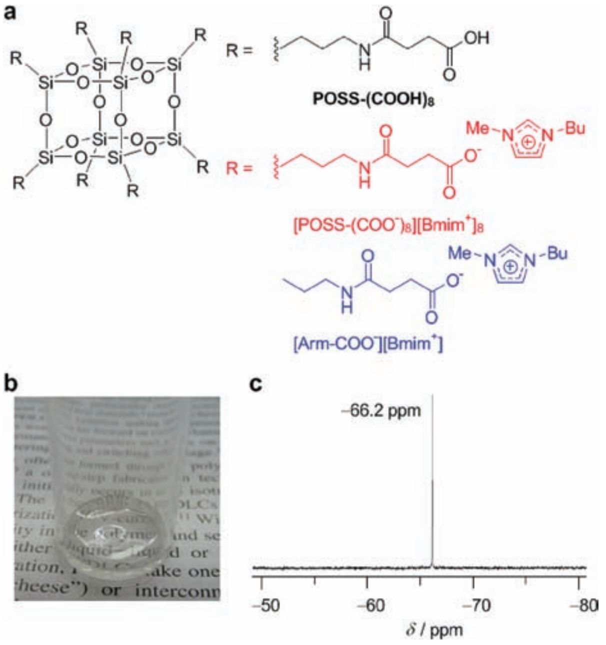

Figure 1. (a) Chemical structures of the ionic pairs used in this study. (b) Appearance of [POSS-$(COO^-)_8$][$Bmim^+$]$_8$ at 25 °C. (c) ^{29}Si NMR spectrum of [POSS-$(COO^-)_8$][$Bmim^+$]$_8$.

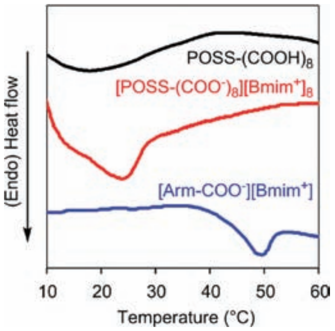

Figure 2. DSC curves of the salts for the fifth scan.

A single peak at −66.2 ppm was observed in the ^{29}Si NMR spectrum and was assigned to the T_8 POSS structure (Figure 1c). Integration of the peaks in the ^{1}H NMR spectrum indicated the formation of the 1:8 ion pairs of POSS and imidazolium cation.[12] The water abundance was kept below 1.5 wt %, as determined by the Karl Fischer method. In addition, the bromide ion component was below the detectable level in the elemental analysis. Therefore,

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Table 1. Thermodynamic Parameters of the ILs Determined from the DSC and TGA Curves

anion	T_g (°C)[a]	T_m (°C)[a]	T_d (°C)[b]	ΔH_{fus} (kJ mol^{-1})[c]	ΔS_{fus} (J mol^{-1} K^{-1})[d]
[POSS-(COO$^-$)$_8$]	−52	23	234	6.8 ± 2	21
[Arm-COO$^-$]	−40	48	202	15 ± 2	47

[a] Obtained from the fifth heating curves in Figure 2. [b] Determined from the sudden decrease in the TGA curves in Figure 3. [c] Determined from the first heating curves in the DSC experiments. The reported errors are standard deviations. [d] Calculated from the following relation: $\Delta S_{fus} = \Delta H_{fus}/T_m$.

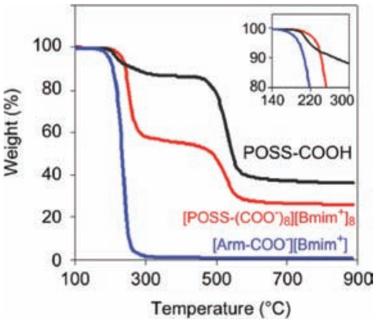

Figure 3. TGA thermograms of the ILs under flowing nitrogen.

we concluded that the colorless products were sufficiently pure for the following thermal analysis.

Differential scanning calorimetry (DSC) was performed at a heating rate of 10 °C/min (Figure 2).[13] The glass transition temperatures (T_g) and melting temperatures (T_m) of the ILs are listed in Table 1. Endothermic peaks assigned as the melting processes were observed below 100 °C. Therefore, [POSS-(COO$^-$)$_8$][Bmim$^+$]$_8$ and [Arm-COO$^-$][Bmim$^+$] were confirmed as ILs. Remarkably, [POSS-(COO$^-$)$_8$][Bmim$^+$]$_8$ has a melting temperature that is 25 °C lower than that of [Arm-COO$^-$][Bmim$^+$]; as a result, [POSS-(COO$^-$)$_8$][Bmim$^+$]$_8$ can be classified as an RT-IL.

To understand the thermodynamics of the melting process of the ILs, the enthalpies and entropies of fusion (ΔH_{fus} and ΔS_{fus}) were evaluated from the areas of the endothermic peaks observed in the DSC profiles (Table 1). The ΔH_{fus} value for [POSS-(COO$^-$)$_8$][Bmim$^+$]$_8$ was smaller than that of [Arm-COO$^-$][Bmim$^+$], contributing to the lower T_m value. The globular structure of [POSS-(COO$^-$)$_8$][Bmim$^+$]$_8$ molecules could reduce the packing density[4b] and isolate the distal ion pairs. These isolated groups should disrupt the formation of the thermally stable conformation. Thus, the interaction between the IL molecules could be weakened by the introduction of POSS. In contrast, the entropy change for [POSS-(COO$^-$)$_8$][Bmim$^+$]$_8$ showed a smaller value, which would contribute to an increase in the T_m value. This can be explained by the restriction of the molecular rotation and the reduction of the conformational variety of the ion pairs by the connection to the symmetric silica cube.[14,15] These data can be summarized as follows: the isolation of the side chains by POSS can contribute to the decrease in the enthalpy of fusion and compensate for the entropy disadvantage. Thus, the T_m of [POSS-(COO$^-$)$_8$][Bmim$^+$]$_8$ was lowered.

The thermal stability of the ILs against pyrolysis was investigated by thermogravimetric analysis (TGA). Figure 3 shows the TGA profiles of the ILs, and Table 1 summarizes the thermal degradation temperatures (T_d) estimated from the TGA profiles. The T_d value of [POSS-(COO$^-$)$_8$][Bmim$^+$]$_8$ was 32 °C higher than that of [Arm-COO$^-$][Bmim$^+$]. This result clearly indicates that thermal stability is enhanced by the connection to POSS. The rigid silica cage could suppress the molecular tumbling and prevent the degradation.[5]

In conclusion, we have presented here the synthesis of a stable IL containing octa-substituted POSS. From the TGA and DSC analyses, we found that the rigid cubic structure of POSS can play a significant role in the decrease of the melting temperature and the enhancement of thermal stability. Finally, we obtained a POSS-based RT-IL for the first time. Previous work successfully showed that the introduction of POSS into ILs can improve their conductivity.[8] In addition, the distinct spaces around the POSS core have the potential to generate characteristic optical properties. Our findings are useful not only for modulating these functions but also for designing new advanced ILs based on POSS.

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Supporting Information Available: Detailed experimental data from the syntheses and NMR experiments on the ILs. This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) The synthetic scheme is shown in Scheme S1, and experimental details are described in the Supporting Information.
(12) The ^{1}H NMR spectrum of the POSS IL is shown in Figure S1 in the Supporting Information.
(13) The multicycle scanning DSC curves are shown in Figure S3 in the Supporting Information.
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