# Melting and Crystallization Behaviors of an Ionic Liquid, 1-Isopropyl-3-methylimidazolium Bromide, Studied by Using Nanowatt-Stabilized Differential Scanning Calorimetry

**Keiko Nishikawa,**[*1] **Shaolan Wang,**[1,†] **Takatsugu Endo,**[1] **and Ken-ichi Tozaki**[2]

[1]Graduate School of Advanced Integration Science, Chiba University, Chiba 263-8522

[2]Faculty of Education, Chiba University, Chiba 263-8522

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We studied the melting and crystallization behaviors of 1-isopropyl-3-methylimidazolium bromide ([$i$-C$_3$mim]Br) using a laboratory-made differential scanning calorimeter (DSC) with nanowatt stability and sensitivity. In addition to common behaviors for many ionic liquids such as premelting over a wide temperature range and excessive supercooling, we observed unique thermal phenomena: reversible phase transitions of domains in the premelting region, rhythmic crystallization and melting, and intermittent crystallization. The latter two phenomena were observed in the returning experiments from the premelting region at a cooling rate as slow as 0.05 mK s$^{-1}$. It is considered that these phenomena occurred because an [$i$-C$_3$mim]$^+$ ion is capable of taking plural stable conformations and the conformational changes occurred linking with melting and crystallization. We interpret these curious phenomena as the phase changes of the locally melted domains composed of different conformers, which significantly hindered the overall phase changes.

Room-temperature ionic liquids are a new class of compounds with low melting temperatures despite the fact that they are composed only of ions.[1] They are attracting much attention because of their characteristic properties[2–4] and potential utilities as functional liquids.[5–10] Unique properties are remarkably manifested in their thermal behaviors such as premelting over a wide temperature range, excessive supercooling, and the existence of complex thermal histories.[11–17]

Researchers have performed thermal analyses of ionic liquids and their crystals by differential scanning calorimetry (DSC), thermal gravity analysis, and so on.[11–16] These methods have provided useful information regarding thermal properties of ionic liquids. However, more sensitive measurements in more sophisticated conditions are necessary to minutely elucidate the thermal phenomena and the complex structural changes of ionic liquids. We developed a nanowatt-stabilized DSC,[18,19] which is capable of measuring an extremely small heat flow with a small baseline fluctuation and a quick response time. The apparatus is also designed to scan as slowly as 0.01 mK s$^{-1}$, enabling us to mimic a nearly quasi-static process. These performances well fit the demand for thermal analyses of ionic liquids.

Many experimental results have suggested that the existence of plural conformers for a constituent ion seriously affects the structural and thermal properties of the ionic liquid. For example, in the studies on crystal polymorphisms, Holbrey et al. concluded that the plural conformers inhibit the easy crystallization of ionic liquids.[20] Berg reviewed the existence of various conformers in many ionic liquids and their crystals.[21] Raman spectroscopic studies backed up by density functional theory (DFT) calculations revealed that the occurrences of the conformers of imidazolium-based ions and their populations are different in the liquid and crystalline states.[2,22–26] Using the above-mentioned DSC, we also confirmed that the melting and crystallization of 1-butyl-3-methylimidazolium bromide ([C$_4$mim]Br) and its chloride ([C$_4$mim]Cl) occurred linking with the cooperative conformational change of the butyl group in the cation.[17,25] In addition, we have recently observed "rhythmic melting and crystallization" in the premelting region during the heating process of [C$_4$mim]Br.[27] From our preceding studies by calorimetry and Raman spectroscopy,[17,25] we believe that this curious thermal behavior is also due to the link between the phase transitions and the conformational changes of alkyl chains bonded to the imidazolium ring.

The present study is a part of our ongoing systematic study aimed at developing a deeper understanding of the underlying mechanism, especially the relationship between the conformational structures of imidazolium-based cations and the phase transitions of their salts that in turn lead to their dynamics. Our recent experimental measurements covered the following: crystal structures by X-ray diffraction,[28–30] phase transitions by the above-mentioned DSC with super-high sensitivity[17,27] and by Raman spectroscopy joined with calorimetry,[25,26] and relaxation times by NMR,[31,32] all with variations of the alkyl groups bonded to the imidazolium ring. In the present study, we selected 1-isopropyl-3-methylimidazolium bromide ([$i$-C$_3$mim]Br) for thermal measurements to precisely examine whether the steric interaction of the isopropyl group influences the conformational changes and causes the characteristic thermal behaviors. This is a report on the overall thermal behaviors of melting and crystallization, including the previous

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[†] Present address: Analytical and Testing Center, Sichuan University, Chengdu, Sichuan 610064, P. R. China

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short report on a hitherto unknown phenomenon, "intermittent crystallization."[33]

## Experimental

We used the DSC made in our laboratory,[18,19] which is a nanowatt-stabilized DSC of the heat-flux type. The schematic diagram of the DSC can be found in the literature.[17–19] The design is based on the following concepts: thermoelectric modules are utilized for a heat-flux sensor (the Seebeck effect) and heat pumps (the Peltier effect), and the system adopted for temperature regulation is a type of predictive controller[34] instead of a proportional-integral-derivative (PID) controller. In this system, the amount of the current electrified into the Peltier elements to supply or remove heat is predicted both from the difference between the actual sample temperature and the set temperature and from the temperature history up to the starting point of regulation. We have programmed this procedure to repeat every 2 s. This controller causes no ripples because no on–off switching is used.

This DSC can measure a heat-flow with a baseline fluctuation within ±3 nW. This baseline stability, that corresponds to the sensitivity of the DSC, is $10^2$–$10^3$ times higher than that of commercially available DSCs.[19] This apparatus is also designed to scan as slowly as ca. 0.01 $\mathrm{mK\,s^{-1}}$; enabling us to mimic a nearly quasi-static process. As the relaxation time of the apparatus is estimated to be ca. 2 s,[19] the dynamics of a thermal process can be traced with a relaxation time exceeding 2 s. Measurements can be made during either process, heating or cooling, by changing the direction of the electric current through the thermoelectric modules. This performance is essential for thermal measurements on ionic liquids since many of them often display different behaviors during the cooling and heating processes.[11–17,27,33] The measurable temperature-region of the DSC is from 220 to 453 K, and the rate of cooling or heating is controllable in the range from 0.01 to 10 $\mathrm{mK\,s^{-1}}$. The temperature of the sample was measured using a Pt resistance thermometer. The temperature calibration for the Pt sensor was performed by measuring the melting points of several standard materials, such as docosane, biphenyl, Ga, and $H_2O$. The calibration of heat-flow was performed by measuring the specific heat capacity of the standard sample of a single-crystalline alumina. The heat-flow measurement was performed with a 1% margin. The temperature was controlled within ±0.15 mK.

The procedures of synthesis and purification of [$i$-$C_3$mim]Br were reported in our previous study.[26] The purity of the obtained crystalline solid was checked by $^1$H NMR (JEOL, JNM-LA400). We detected no signal resulting from impurities. As a result, the purity of the present sample was guaranteed within the sensitivities of the NMR spectrometer. As for most ionic liquids, it is commonly known that even a trace amount of impurity, particularly adventitious water, immensely affects their physical and chemical properties and sometimes hinders the liquids from crystallizing. To prepare the present sample as purely as possible, we further attempted to obtain single crystals of [$i$-$C_3$mim]Br by recrystallization from an acetonitrile/ethyl acetate solution. The single crystal thus prepared was transparent and needle-like. Because it was very hygroscopic, several single crystals were dried under vacuum for 6 h and then sealed hermetically into an Al pan in a dry $N_2$ atmosphere. The amount of the sample was 2.3 mg. An empty Al pan was used as a reference. These measurements were made several times and it was found that the DSC traces were almost the same under similar experimental conditions. The widest temperature range for the measurements was from 223 to 423 K.

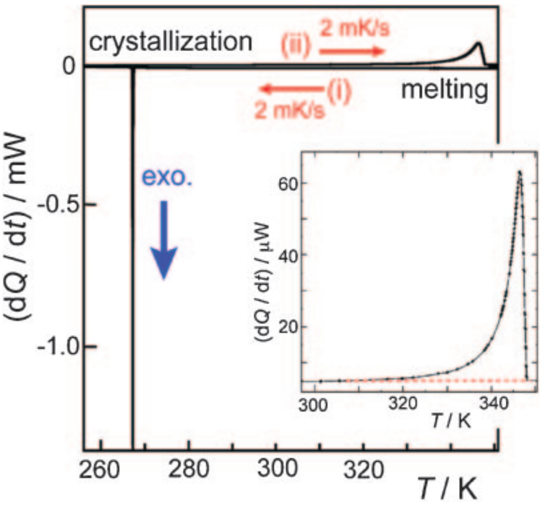

**Figure 1.** The DSC traces for [$i$-$C_3$mim]Br with cooling and heating rates of 2 $\mathrm{mK\,s^{-1}}$. The magnified drawing around the melting point is shown as the inset.

## Results and Discussion

**Overall DSC Traces and Conformational Changes Linking to Phase Transitions.** The sample, several single crystals of [$i$-$C_3$mim]Br, was first heated to 360 K to ensure complete melting although no trace was displayed. Figure 1 indicates the overall DSC traces obtained at the cooling and heating rates of 2 $\mathrm{mK\,s^{-1}}$. The exothermic crystallization peak appeared at about 267 K in the cooling process (Process (i)), and the endothermic melting peak appeared at about 346 K in the heating process (Process (ii)). In the case of [$C_4$mim]Br, there was no thermal activity in the cooling process, and crystallization from the supercooled liquid occurs only in the heating process.[17] Comparing with [$C_4$mim]Br, the behavior of [$i$-$C_3$mim]Br is more normal. According to the definition by Fredlake et al. for melting and crystallization behaviors,[16] [$C_4$mim]Br and [$i$-$C_3$mim]Br are classified as the third and first types, respectively. The crystallization of [$i$-$C_3$mim]Br occurs at about 80 K lower than melting, indicating the stable existence of a supercooled state and that it is hard to crystallize. The same characteristic feature has been reported for many ionic liquids.[11–17]

As shown in Figure 1, the melting peak has a very broad range, extending beyond 20 K, while the crystallization peak is sharp. The magnified drawing around the melting peak is the inset in Figure 1. Contamination in a sample commonly causes the broadening of the DSC melting curve. Therefore, we selected several single crystals as the present sample; the sample was pure enough to crystallize as single crystals. However, the peak is too broad to regard this melting as a simple process of loosing of the crystalline lattices. We suggest that this broadening is due to premelting, characteristic of the present sample as well as other ionic liquids. The details of the premelting phenomenon will be discussed later.

The melting point of [$i$-$C_3$mim]Br is about 346.3 K, if considered to be the peak-top temperature.[17] The dashed line in the magnified drawing is the baseline drawn from the crystal phase to the liquid phase for approximate estimation of the

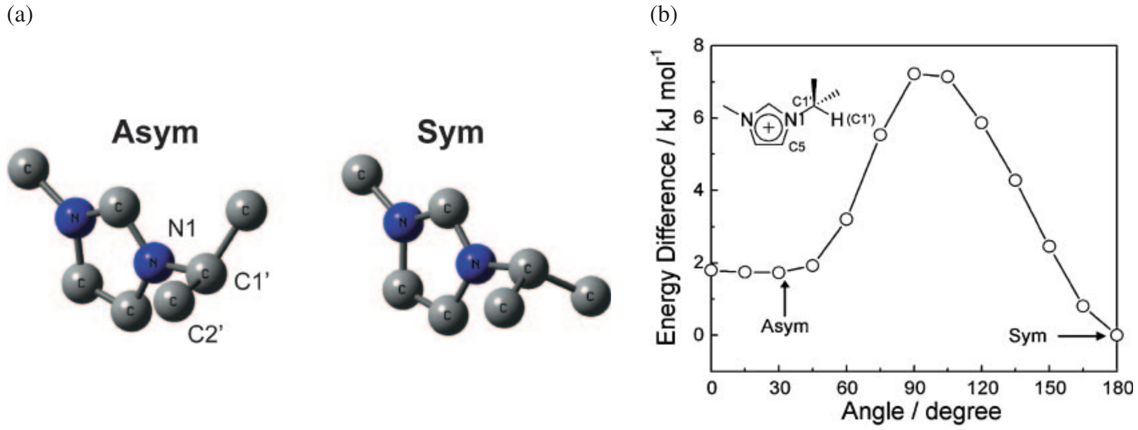

**Figure 2.** (a) Structures of two stable conformers of [*i*-$C_3$mim]$^+$, Asym and Sym. (b) Potential energies as a function of the rotational angle around the N1–C1′ axis. The torsion angle is defined as the dihedral angle of C5–N1–C1′–H(C1′).

enthalpy change of melting. The value obtained by integrating the area of the peak is 13.9 kJ mol$^{-1}$, which is about 0.6 times that of [$C_4$mim]Br.[17,35]

In comparison with a similar broad temperature range during the premelting of the [$C_4$mim]$^+$ ion,[17,27] we assumed that the structural changes of [*i*-$C_3$mim]$^+$ ions also occurred during the melting and crystallization processes. Our Raman spectroscopic experiments, which were backed up by DFT calculations,[26] confirmed that the conformation of the [*i*-$C_3$mim]$^+$ ions in the crystalline state are asymmetric while symmetric and asymmetric conformers coexist in the liquid and supercooled liquid states and that a conformational change between the two occur in the premelting region, as expected. Here, the symmetric conformer (Sym) refers to the arrangement where two methyl groups in the isopropyl group are positioned symmetrically with respect to the imidazolium ring, as shown in Figure 2a. In the asymmetric conformer (Asym), also shown, the plane formed by N1–C1′–C2′ is nearly perpendicular to that of the imidazolium ring.

In the previous study,[26] we also calculated the potential energy change for the rotation of the isopropyl group of a free [*i*-$C_3$mim]$^+$ ion around the N1–C1′ axis. Energy differences from the most stable one are shown in Figure 2b. Calculations indicated the following results. First, there are two local minima at rotational angles, ca. 30 and 180°. These rotational isomers correspond to Asym and Sym, respectively. Second, the energy deference between Asym and Sym is about 2 kJ mol$^{-1}$, which is slightly greater compared to that between the most occurring conformers for the [$C_4$mim]$^+$ ion, about 0.0–0.5 kJ mol$^{-1}$.[36,37] Third, the activation energy barrier for rotational isomerization from Asym was calculated to be about 5 kJ mol$^{-1}$. Fourth, there is little energy difference between −40 and 40° of the rotational angle of the isopropyl group (energy difference is ca. 0.1 kJ mol$^{-1}$), meaning that there is the possibility of various rotational isomers existing with little rotation from Asym. In fact, three types of conformations for [*i*-$C_3$mim]$^+$ exist in the crystalline state.[38] However, they are almost the same as the arrangement of Asym shown in Figure 2a and differ from each other only in slightly different rotation angles around the N1–C1′ axis. Therefore, gathering the three rotational conformers together, we can nearly say that the conformation of [*i*-$C_3$mim]$^+$ ions in the crystalline state is asymmetric. On the other hand, the symmetric and asymmetric conformers coexist in the liquid state. As a result, the premelting is due to loosing the crystalline lattice accompanied with a cooperative change of a part of the asymmetric conformers to the symmetric ones. Such conformational changes, in the boundary of the liquid and the crystalline phases, have been reported for ionic liquids with [$C_2$mim],[23] [$C_4$mim],[2,17,22,25] and 1-hexyl-3-methylimidazolium [$C_6$mim][24] cations.

**Thermal Phenomena in the Premelting Region.** To investigate the details of the premelting phenomenon of [*i*-$C_3$mim]Br, we performed the returning experiments. The sample was heated at the rate of 2 mK s$^{-1}$ from room temperature to the preset temperature (Process (1)) and then cooled down (Process (2)). The temperature, set at a specific point in the premelting region, is hereafter denoted as the "returning temperature." We performed numerous experiments varying the returning temperature and the cooling rate, and some curious phenomena were observed depending on the experimental conditions as indicated below.

**Reversible Melting and Crystallization:** The first experiments were performed at the heating and cooling rates of 2 mK s$^{-1}$, changing the returning temperatures. The highest returning temperature was 346.0 K, 0.3 K lower than the peak-top temperature of the melting curve. However, the heat flow from the heat bath raised the sample temperature, and the sample was cooled down from approximately 0.2–0.3 K higher temperature than the preset one. Since the traces of the heating runs overlapped perfectly with the complete heating run, they are shown by the solid black lines in Figures 3a and 3b. The cooling traces were classified into two patterns depending on the returning temperature. When the temperatures were lower, simple and smooth exothermic curves were obtained, as shown in Figure 3a. Unlike [$C_4$mim]Br,[17] the exothermal peaks were not separated. Only some small indents were found in the trace cooled from 345.15 K. On the other hand, as shown in Figure 3b, the exothermal peaks became rougher and rougher as the returning temperatures approach the peak-top temperature. Finally, the signal separated into two, as shown by the green and pink curves in Figure 3b. We emphasize here that these notched peaks including small indents are not electronic noises but intrinsically arise from the present sample. The validity of this data was confirmed by the fact that we detected

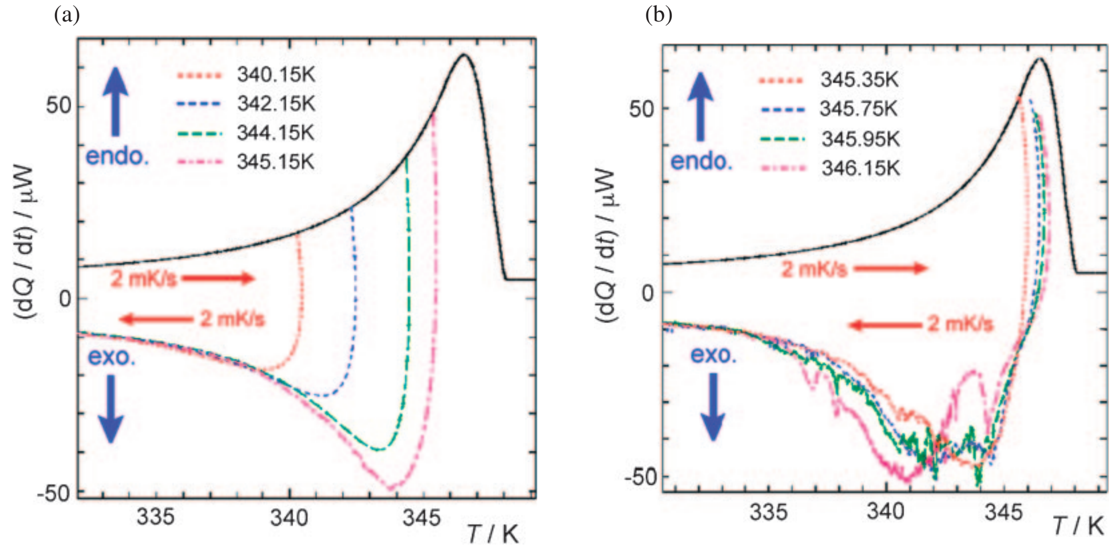

**Figure 3.** The DSC traces for [$i$-$C_3$mim]Br around the melting point. The black solid curve is the trace of a complete run. Others are the traces where the sample is cooled down from a specific point in the premelting region. (a) The returning temperatures are lower, and (b) the temperatures are higher. The heating and cooling rates for all the runs were 2 mK $s^{-1}$.

no thermal anomaly for the standard sample such as alumina under the same experimental conditions.

The phenomena can be explained by the model for melting and crystallization of ionic liquids based on our preceding studies of [$C_4$mim]Br.[17,25,27] In a crystalline state, ions with a certain specific conformation are arranged regularly. In the heating process, small domains in a crystalline area start to melt first, accompanied by conformational changes of the ions, probably at the regions with crystalline defects or at the surface of the crystals, i.e, local melting occurs, and the regions are composed of mixtures of different conformers. These premelting domains grow as the temperature increases until percolation of the crystal areas finally breaks off. Up to such a temperature, local melting and crystallization in the premelting region can occur reversibly by heating or cooling.[17] We may assume that many small crystalline domains remain even after the melting where the DSC trace falls to the baseline level of the liquid. In fact, we have observed periodically repeated endothermic and exothermic processes for [$C_4$mim]Br just after melting.[27] In the crystallization process from the supercooled liquid, the conformational change is also accompanied. Depending on the samples and experimental conditions, the division of the crystallization peak may be observed just as in the case of [$C_4$mim]Br.[17]

As for the [$i$-$C_3$mim]Br case, when the returning temperature is not too close to the peak-top temperature, the portion of the ions that change their structure from Asym to Sym is very small. When the sample is cooled down from this temperature, almost all of the ions crystallize directly. For this reason, the separation of the exothermal peak did not appear in the cooling run. As the returning temperature approaches the peak-top temperature, the number of [$i$-$C_3$mim] ions in the Sym conformation increases. When the sample is cooled down from this temperature, a portion of these should crystallize after changing back from Sym to Asym. We observed local crystallization accompanied with the conformational changes as the spiky exothermal peaks on the broad exothermal peak. As the returning temperature approaches the peak-top temperature, the number of the ions that have to change their conformations becomes greater and greater.[26] Therefore, the thermal behavior due to the change in molecular structure became conspicuous, and finally the exothermal peak largely divided into two, as shown in Figure 3b. These experimental results demonstrate that the premelting domains enlarge gradually as temperature increases to the peak-top and that the phase changes of melting and crystallization occur reversibly in the premelting domains. This is the same behavior as that of the model based on the phase transition of [$C_4$mim]Br.[17,25,27] This behavior also confirmed that the crystallization peak at about 267 K is never observed when the sample is cooled down from the premelting region. This result suggests that the nucleuses for crystallization remain at the peak-top of the melting curves. As a result, we can assign the endothermic and exothermic phenomena in the premelting region to the local melting and crystallization, respectively.

**Intermittent Crystallization:** In our previous study on [$C_4$mim]Br,[27] we detected many notched peaks on the usual melting trace on the heating run when the rate was extremely slow, i.e., 0.02 mK $s^{-1}$. We named this phenomenon "rhythmic melting and crystallization" and showed that it occurs due to the linking of melting/crystallization and cooperative conformational changes of the [$C_4$mim]$^+$ ion, i.e, melting and crystallization are periodically repeated with endothermic or exothermic heat transfer cycles that alternately trigger subsequent changes.

As for [$i$-$C_3$mim]Br, we focused on the cooling process after we detected very notched peaks, as shown in Figure 3b. We repeated several experiments, fixing the returning temperature at 346.0 K and changing the cooling rate. As mentioned above, due to the heat flow from the heat bath, the sample temperature rose by 0.2–0.3 K. For this reason, the sample was cooled down approximately from the peak-top temperature in the returning experiment from 346.0 K. As slowing down the cooling rate, the DSC signals of the reversible crystallization did not separated largely but traced simple curves accompanying fine exothermal notched peaks. The result for the cooling rate of

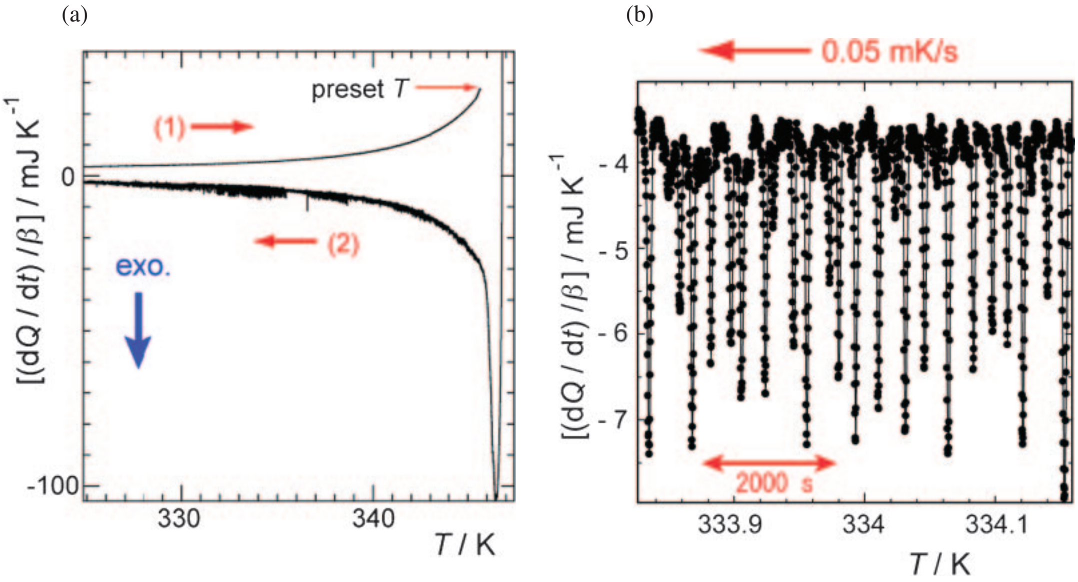

**Figure 4.** The DSC traces for [$i$-C$_3$mim]Br around the melting point. The curve shows the trace wherein the sample was cooled down from 346.0 K. (a) Full scale drawing and (b) magnified drawing around 334 K in the cooling run.

0.05 mK s$^{-1}$ is shown in Figure 4a, where the values of the vertical axis are divided by the heating or cooling rate ($\beta$) to normalize the rate differences. The magnified drawing around 334 K is shown in Figure 4b. The small peaks were sharp, and were separated piece by piece. Moreover, all of them were exothermic peaks. In the latter figure, data are plotted as dots every 4 s. As emphasized above, these notched peaks are not due to electronic noise, but intrinsically arise from the present sample. As reported in our previous short report,[33] we have named this phenomenon "intermittent crystallization." The present DSC with super-high sensitivity and quick response time has enabled us to detect this phenomenon. These results reveal that there exist local melting domains in the premelting region and that the domains with almost the same order in size are spatially separated from each other at about 334 K. The notched peaks refer to the crystallization of the domains.

As for the present sample, more than 90% of the crystalline area seemed to melt up to the returning temperature as estimated from the amount of absorbed heat. Being cooled down suddenly, most of the [$i$-C$_3$mim]$^+$ and Br$^-$ ions appear to be smoothly crystallized because the DSC trace is smooth just after returning, as shown in Figure 4a. The exothermal notched peaks appear after 70–80% emission of the total enthalpy of crystallization. This behavior implies that a large number of [$i$-C$_3$mim]$^+$ ions in the premelting region maintained the asymmetric conformation (i.e., the conformation in the crystalline phase) that leads to smooth crystallization. This speculation is supported by our preceding experimental studies performed using an apparatus designed for simultaneous measurements of Raman spectroscopy and calorimetry.[25] The results for [$i$-C$_3$mim]Br[26] and [C$_4$mim]Br[25] showed that a major portion of the conformational changes occurred at the temperature at the peak-top of the melting DSC trace or just after this point. In the cooling process of [$i$-C$_3$mim]Br, these domains seemed to remain where the symmetric and asymmetric conformers are mixed together so that the symmetric isomer cannot easily turn to the asymmetric conformation.

We estimated the order of enthalpy for a piece in the intermittent crystallization to be $0.7 \times 10^{-5}$ J, ca. $0.5 \times 10^{-9}$ times the molar crystallization enthalpy of 13.9 kJ mol$^{-1}$, i.e., the average number of ion pairs in the domains was estimated to be ca. $3 \times 10^{14}$. This order is 10–100 times larger than that in the domain for the rhythmic melting and crystallization of [C$_4$mim]Br.[27]

Prior to the discussion on the time scale of this phenomenon, let us refer to the relaxation time of our measurement system. As mentioned in the preceding study,[19,33] it is about 2 s. Therefore, the dynamics of a thermal process can be traced with a relaxation time exceeding 2 s. The time scale of crystallization can be estimated from Figure 4b. As the cooling rate is 0.05 mK s$^{-1}$, the horizontal temperature axis refers to the time axis. The interval of intermittent crystallization was about 200–230 s, and about 100 s is required for each domain to crystallize under the present experimental conditions. These values are much longer than the relaxation time of the apparatus.

We attribute the intermittent crystallization to the processes of melting and crystallization linking with the conformational change of [$i$-C$_3$mim]$^+$. This phenomenon occurs as a very slow dynamic process because of the involvement of a large number (ca. $10^{14}$) of ion pairs. Plural conformers for a constituent ion commonly exist in the ionic liquid.[21] Due to the Coulomb interactions, the density of an ionic liquid is generally 10–20% higher than that of a molecular substance with similar components. The decrease in the free volume for conformational changes is probably the major origin of the retarded phase transition for ionic liquids.

**Rhythmic Crystallization and Melting:** Once the returning temperature exceeded the peak-top temperature of the DSC trace, the observed phenomena altered drastically. First, we confirmed that the sample cooled from the temperature exceeding the peak-top did not entirely crystallize in the premelting region but overall crystallization occurred at about 267 K. This shows that the upper limit for the reversible melting and crystallization is nearly at the peak-top temperature.

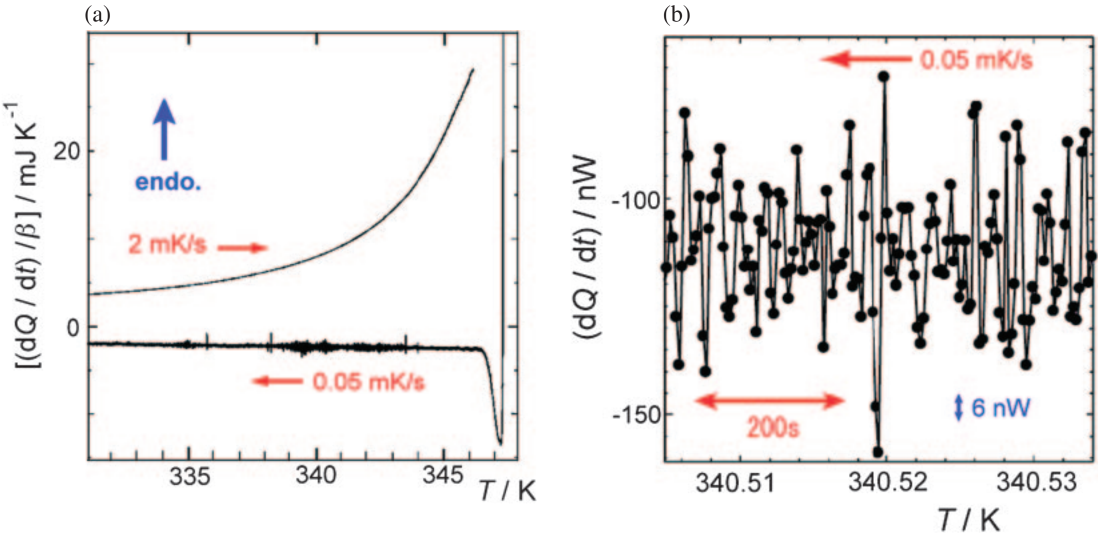

**Figure 5.** The DSC traces for [$i$-$C_3$mim]Br around the melting point. The sample was cooled down with a cooling rate of 0.05 mK s$^{-1}$ from 346.5 K, which is 0.2 K higher than the peak-top of the melting trace. (a) Full scale drawing and (b) magnified drawing around 340.52 K.

We discovered a curious phenomenon in the measurement performed at the returning temperature of 346.5 K and with a cooling rate of 0.05 mK s$^{-1}$. This temperature was just 0.2 K higher than the peak-top temperature. As shown in Figure 1, at this temperature, the melting curve did not drop to the baseline of the liquid state, meaning that the sample did not become liquid completely. The overall DSC traces of this experiment are shown in Figure 5a. As shown in this figure, a small exothermic peak first appeared at ca. 347.2 K in the cooling process. This seems to be assigned to the crystallization of a very small portion. Crystalline grains remains at this temperature, and Asym conformers, whose amount is enough to form crystals, remains.[26] However, the crystalline grains cannot grow up to become a overall crystalline state. We consider that this is because the percolation of the crystalline area breaks off. It is speculated that the flat region of the baseline in the cooling process refers to the coexisting state of supercooled liquid and crystalline grains. Although this may be thought to be a curious phenomenon, we often observe the stable coexistence of supercooled liquid and crystals for many ionic liquids.

Although overall crystallization did not occur in the premelting region, the DSC trace was very noisy in some temperature ranges as shown in Figure 5a. The magnified drawing around 340.52 K is shown in Figure 5b, where data for every 4 s are plotted as dots. The noise intrinsic to the apparatus was ±3 nW. The observed notched peaks were about 10 times larger than the 6 nW margin shown by the blue arrow and indicated that they were attributed to the thermal phenomenon characteristic of the sample. It is clear that the pattern of periodic endothermic and exothermic heat transfers is different from the pattern of intermittent exothermic heat transfers; the latter is shown in Figure 4b. The notched peaks are rhythmic crystallization and melting, and we observed the same phenomenon for [$C_4$mim]Br in the premelting region and in the liquid region just after melting during the heating process.[27] At the temperature slightly exceeding the peak-top for the case of [$i$-$C_3$mim]Br, it is thought that crystalline domains remain surrounded by a large amount of liquid areas and that the percolation of the crystalline area breaks off. However, it is supposed that thermal fluctuations easily occur around the left crystalline domains. The melted region around the left crystalline grains crystallizes as cooling occurs. The heat released during crystallization melts the neighboring domains. Due to the endothermic process of melting, crystallization occurs in turn. Crystallization and melting are thereby repeated rhythmically. These were observed as the periodic notched peaks in the DSC trace, as shown in Figures 5a and 5b.

In the domains where the rhythmic crystallization and melting occurred, about 5–9 × $10^{12}$ ion pairs were contained. The time scale of the phenomenon was estimated to be 10–20 s. Compared with the intermittent crystallization where the returning temperature was preset at 346.0 K (Figure 4b), the released or absorbed heat in the rhythmic crystallization and melting was smaller, and the time scale was shorter. These results may be contradictory to the expectation that the premelting domains should become larger in the returning experiment from 346.5 K (Figure 5a). However, as for the sample heated up to the temperature exceeding the peak-top, a large number of [$i$-$C_3$mim]$^+$ ions changed to Sym,[26] and they mixed with the Asym ions. As a result, it seems to be harder for larger domains to crystallize during the extremely slow cooling process. On the other hand, even a small amount of the heat released during local crystallization will easily melt the small crystallizing domains because of the large mixture of Sym and Asym conformations. This seems to be the reason for rhythmic crystallization and melting occurring in the smaller size regions and in a shorter periodicity. By repeating rhythmic crystallization and melting, the whole sample seems to relax into the supercooled liquid state.

## Concluding Remarks

We have investigated the thermal behaviors of the ionic liquid [$i$-$C_3$mim]Br, especially focusing on the premelting region, using a laboratory-made DSC with nanowatt stability and sensitivity. In addition to the common thermal phenomena for most ionic liquids such as premelting over a wide temperature range and excessive supercooling, we observed the following curious thermal phenomena:

1) The sample reversibly crystallizes or melts in the premelting region.

2) When the sample was cooled down from the peak-top temperature of the melting trace and at a cooling rate as slow as $0.05\,\mathrm{mK\,s^{-1}}$, we observed many separate exothermal peaks. We have designated this phenomenon "intermittent crystallization." This phenomenon suggests that melting domains are left separately in the cooling process and that these domains crystallize piece by piece. The average number of ions in the domains is ca. $3 \times 10^{14}$. For the ions in the domain to crystallize, a large number of ions should change their conformation cooperatively and in accord with each other. This is because it takes $10^2\,\mathrm{s}$ for the intermittent crystallization to occur.

3) In the returning experiment slightly exceeded the peak-top temperature, the most portion of sample never crystallizes and becomes to supercooled liquids with rhythmic crystallization and melting.

Although the above-mentioned aspects are different, the origins of these anomalous behaviors must be closely related, i.e., the conformational changes in the dense field are likely to affect melting and crystallization and cause these phenomena. That is to say, the states just before and after the phase transitions are the coexisting state of plural conformers. Whether or not one of these phenomena occurs and is observable may depend on factors, such as the enthalpies and activation energies of the phase transitions, conformational energy differences, the amount of heat flow from the outside of the system, heat conductivities, and the relative fractions of different conformers and their mixing states as determined by thermal histories.

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