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Rhythmic melting and crystallizing of ionic liquid 1-butyl-3-methylimidazolium bromide

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ARTICLE INFO

ABSTRACT

We measured heat flow processes near the melting point of a typical ionic liquid, 1-butyl-3-methylimidazolium bromide ($[C_4mim]Br$), using a laboratory-made differential scanning calorimeter with the base line stability of ±3 nW. We discovered the rhythmical exothermic and endothermic processes with the time scale of 10^1 s in the pre-melting region and in the region just after melting. This novel phenomenon is attributed to the link of the melting/crystallizing in domains and cooperative conformational change of the $[C_4mim]^+$ ion. It is also confirmed that about 10^{12}–10^{13} ion pairs of $[C_4mim]Br$ are involved in the domains.

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1. Introduction

Room temperature ionic liquids have attracted much attention of late. Because of their unique properties, they have been used as functional liquids in a wide variety of applications such as electrochemical materials and chemical reaction media. However, our understanding toward their fundamental nature is still far from complete. Among the basic questions yet to be answered are why their melting points are so low despite their ionic characters and why they are not readily crystallized upon cooling.

Detailed studies on the melting and crystallizing processes of ionic liquids will give us an answer to the questions. Using thermoelectric modules, we constructed a super-sensitive differential scanning calorimeter (DSC) of a heat-flux type [1]. The baseline stability is ±3 nW. The rate of cooling or heating is controllable in the range from 0.01 to 10 mK/s. By using this apparatus, we have recently studied the details of thermal properties of some imidazolium-based ionic liquids and proved that the unique thermal behaviors such as premelting, long-ranged supercooling, and complex thermal histories, are largely attributable to the cooperative conformational changes of component ions [2].

We chose 1-butyl-3-methylimidazolium bromide ($[C_4mim]Br$) as the present sample, because $[C_4mim]^+$ is a representative cation of ionic liquids. Furthermore, we have the information on the crystal structure from the X-ray diffraction study and characterization of isomers of the cation is possible by Raman spectroscopy. Summing up the results of previous studies, the crystal of $[C_4mim]Br$ consists of the *gauche-trans* (*GT*) conformation of the butyl group in the $[C_4mim]^+$ ion [3], while two conformations of *GT* and

trans–trans (*TT*) coexist in the liquid and supercooled liquid states [4], as shown in the inset of Fig. 1. As a result, it can be expected that the melting and crystallizing occur linking the co-operative conformational change of the butyl groups.

2. Experimental

As for most ionic liquids, it is well known that a little impurity, especially adventitious water, excessively affects their physical and chemical properties and sometimes prevents the liquids from crystallizing. To make the sample as purified as possible, we tried to get single crystals of $[C_4mim]Br$ by recrystallization from the acetonitrile solution. For the present DSC experiments, a single crystal was used as the sample. Because it is very hygroscopic, it was dried under vacuum for 6 h and then sealed hermitically into an Al pan in dry N_2 atmosphere. The amount of the sample was 2.09 mg. The measurements were carried out by use of the above-mentioned DSC. The reference was an empty Al pan.

There are some reports on the influence of water on crystallization of $[C_4mim]Br$. Fredlake et al. [5] reported that they observed neither melting nor crystallizing peak in their DSC trace of $[C_4mim]Br$ after in situ drying and concluded that a presence of water prompted the crystallization referring to two previous reports [6,7]. However, the later studies [2,8] as well as the present one have confirmed that the presence of water inversely prevents the sample from crystallizing. For avoiding the contamination of adventitious water, it is important to use a single crystal as the sample.

To outline the feature of the phase transitions of $[C_4mim]Br$, the overall DSC traces are shown in Fig. 1. In the experiment, a single crystal of $[C_4mim]Br$ was heated up to 360 K at the heating rate of 1 mK/s. At this temperature, the sample melts completely. The

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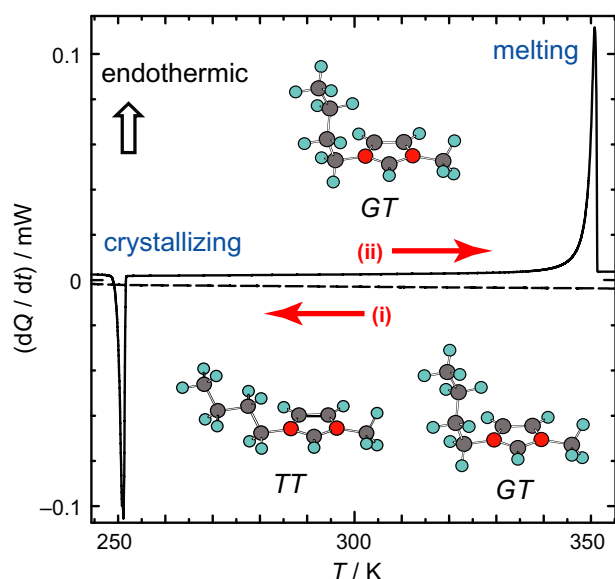 *E-mail address:* k.nishikawa@faculty.chiba-u.jp (K. Nishikawa).

Fig. 1. DSC traces of [C_4mim]Br. Process (i) of cooling from 360 K to 223 K (broken line) and Process (ii) of heating from 223 K to 360 K (solid curve). The cooling and heating rates are 1 mK/s. *Trans–trans* (*TT*) and *gauche-trans* (*GT*) isomers of [C_4mim]$^+$ ion coexist in the liquid and supercooled liquid states, while *GT* isomer exists in the crystalline state.

sample was then cooled at the rate of 1 mK/s from 360 to 223 K whose trace is shown by the broken line (Process (i)), and again heated at the same rate from 223 to 360 K as shown by the solid curve (Process (ii)). There was no thermal activity in the cooling process. In the heating process, however, two peaks were found; one is the exothermic peak for crystallizing of the super-cooled liquid at about 250 K and the other is the endothermic peak for melting at about 350 K. The pre-melting phenomenon ranges over about 10 K.

Next, we carried out detailed measurements, focusing on the melting process of [C_4mim]Br. The single crystal was melt perfectly, cooled down to room temperature, and in turn heated at the rate of 0.02 mK/s from room temperature to 355 K. This heating rate corresponds to 13.9 h to raise the temperature of the sample by 1 K.

We repeated the measurements to get the overall DSC traces and detailed measurements of extremely slow heating rate and confirmed the reproducibility of the observation. Paulechka et al. reported that [C_4mim]Br starts to decompose after long (30 h) exposition in vacuum of ca. 0.1 Pa at 330 K [8]. In the present experimental condition in dry N_2 atmosphere of 0.1 MPa, the decomposition was not observed though we heated the sample up to 360 K and kept it in high temperature state for long time.

3. Results and discussion

The melting trace is shown in Fig. 2a. In this figure, the data of every 40 s are plotted as dots. As shown in Fig. 2a, the DSC curve is very notched. Selecting five representative regions in the curve, we numbered the divisions around 344.5, 345.9, 349.6, 351.2 and 353.2 K as (1), (2), (3), (4) and (5), respectively. The divisions (1) and (2) correspond to the regions near and just on the starting point of premelting, respectively. The division (3) corresponds to the middle point of the premelting curve, and the trace is the most notched at the region. The division (4) is the point where the crystal just melts. The division (5) corresponds to the region where the sample is stabilized as the liquid state. Fig. 2b and c are expanded figures of the divisions of (3) and (5). Each dot in the expanded

figures refers to the measuring point, which is carried out every 4 s. Therefore, the lateral axes correspond to time axes as well as temperature axes.

We made frequency analysis for 5000 points in each division, by drawing the base line and measuring the deviation of each peak-top from the base line. The frequency distributions are shown in Fig. 3. As for the divisions (1) and (5), the distribution curves are regarded almost perfectly as the Gauss functions. And the half widths at 1/e of the peak-tops are about 3–4 nW. Namely, the notches of the divisions (1) and (5) are statistical thermal/electronic noises of the apparatus. The noises just refer to the sensitivity or resolution of the apparatus [1]. On the other hand, other curves slightly differ from the Gaussian distributions, and the widths are wider than the width due to intrinsic noises. Therefore, we can conclude that the states of (2), (3) and (4) are not thermodynamically equilibrium and these notches have some physical meanings.

To understand the present results, the following two reported facts should be reminded. First, the premelting with over 10 K accompanies the conformational change of the butyl group from *GT* and *TT*, as well as the loosing of the crystalline lattice [2,9]. Second, ab initio calculations showed that the energy difference between *GT* and *TT* conformations is within ±1 kJ/mol [10]. Such a small energy-difference implies that the conformational change for a free ion occurs easily. Therefore, the divisions (2) and (3) will denote that, by the local temperature rising due to the fluctuation of the heating, a part of the [C_4mim]$^+$ ions change their conformation from *GT* to *TT* in a domain and the domain melts. As a small thermal energy supplies because of the extremely slow heating rate, the thermal energy is absorbed by the melting domain itself and the neighboring one which is just going to melt. The crystallization of the domain then occurs. In turn, the thermal energy is released by the crystallization. Using this energy and the supplied energy from the thermoelectric modules, a part of crystalline domain melts. These processes can be repeated rhythmically. The rhythmic melting and freezing appear as the notches in the DSC trace as shown in Fig. 2a and b. Just after the melting, namely in the division (4), the aggregation domains where most of the ions are in the *GT* conformation are going to crystallize again, or a great number of ions are going to change their conformations between *TT* and *GT*. In other words, the notched trace of (4) indicates that the state is non-equilibrium. Ions in the domains are going to rhythmically crystallize or melt even at higher temperature than the melting one. We should note that the DSC pattern (frequency or heat flow magnitude) of the change at the just melting (the division (4)) is almost the same as the pattern at the starting point of the premelting shown in the division (2).

The number of [C_4mim]Br unit in the domains can be estimated from the frequency distribution curves. The total enthalpy of the melting is reported to be 23.0–23.6 kJ/mol [2,8]. If we assume that each notched peak or valley in the expanded figures refers to the melting or crystallizing of a domain and regard the half width of the distribution curve at 1/e is the averaged value of the heat flow, the numbers of [C_4mim]Br unit in a domain are 2.0×10^{12} for the divisions (2) and (4), and 1.8×10^{13} for the division (3). The numbers of the [C_4mim]Br unit correspond to 4.9×10^3 nm for (2) and (4) and 1.0×10^4 nm for (3) in radius, if the domains are assumed to be spheres. Possibilities of the existence of local structure in ionic liquids were reported [11,12], though the magnitude of the local structure is not clear. The domain size relating to the melting or crystallizing is firstly proved by the present study.

From the expanded curves, the time scale of melting/crystallization of the domain can be obtained, because the interval of measured points in the expanded figures corresponds to 4 s and 0.08 mK. For the divisions (1) and (5), the widths of the notched peaks are randomly distributed in the range of 4–60 s. On the other
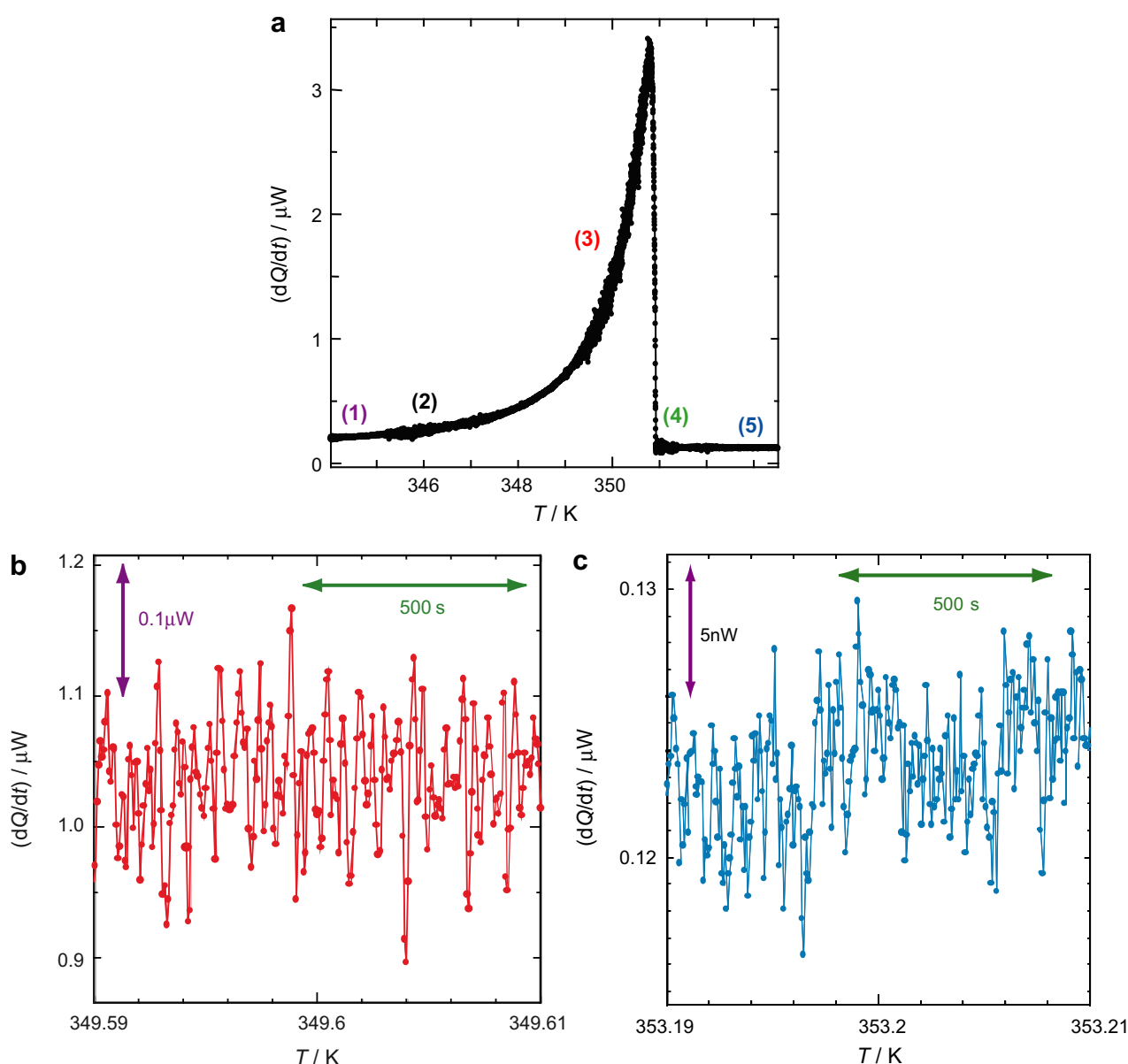
Fig. 2. (a) DSC trace of [C$_4$mim]Br near the melting point. The heating rate is 0.02 mK/s. Five divisions are selected and numbered as (1)–(5). (b) Expanded figure of the division (3). (c) Expanded figure of the division (5). Dots in (b) and (c) refer to the measuring points of every 4 s.

hand, the widths of the notched peaks of (2), (3), and (4) are similar; the half values of the notched peaks in (2), (3), and (4) are 12–16 s, 12–20 s and 8–12 s, respectively. These values correspond to the time scales of the rhythmic transition of the domains. It is reported that several minutes are necessary to achieve equilibrium for the portions of the two conformers of *GT* and *TT* in [C$_4$mim]Cl by the instant melting [11]. The long relaxation time of the present phase transition could be due to accompanying the cooperative conformational change of a large number of ions in the order of 10^{12}–10^{13}. As shown here, a super-sensitive thermodynamic measurement is a very effective method to detect such a slow dynamic behavior involving heat flow. The present heating rate matches to the slow dynamics.

Frenkel proposed a general theory of the heterophase fluctuation in relation to the pre-transition phenomena including the premelting of crystals [13,14]. The concept of the theory is that liquid droplets are generated in small regions of space and time in the vicinity of the melting point and cause some anomalous phenom-

ena. A simulation study of molecular dynamics has been recently performed on simple ionic crystals such as NaCl and AgBr [15]. The present results may be an experimental observation of the Frenkel theory. The direct observation may become possible due to the above-mentioned slow dynamics.

The phenomenon found in this study is so-called rhythmic phase transition. A rhythmic change of volume phase transition in polymer gel is well-known [16]. Because the structures of the ionic liquid constituents are relatively simple compared with polymers, the observed phase transition in the ionic liquid is very unique. We think that the main origin of the rhythmic phase transition of the ionic liquid is a coupling of the melting/crystallizing and cooperative conformational change of the ions.

Acknowledgments
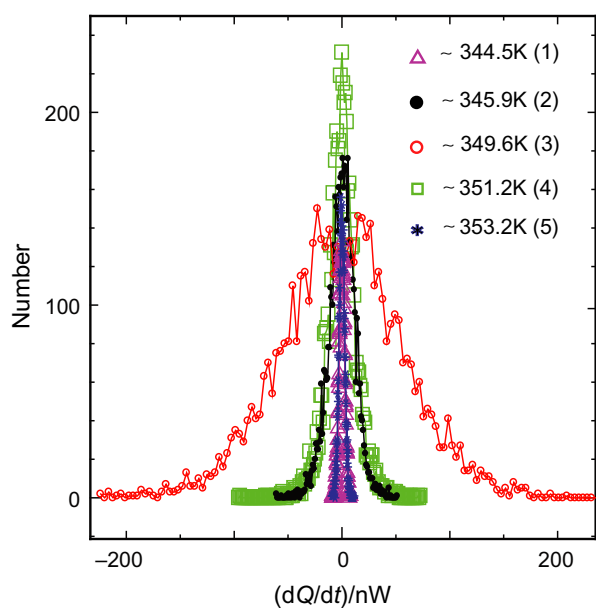
Fig. 3. Frequency distribution curves of the deviations from the base line for the divisions (1)–(5).

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