doi:10.1246/cl.2011.1308

Unusually Long *trans*/*gauche* Conformational Equilibration Time during the Melting Process of BmimCl, a Prototype Ionic Liquid

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The melting process of 1-butyl-3-methylimidazolium chloride (bmimCl), a prototype room-temperature ionic liquid, has been studied with fast low frequency Raman spectroscopy. Simultaneous tracing of the lattice vibrations and *trans*/*gauche* conformational marker bands reveals that the conformational change in the butyl group occurs a few seconds after the loss of lattice vibrations. This finding indicates that the alkyl chain interaction in bmimCl is so strong that the butyl conformation hardly changes in the very early stage of melting.

Room-temperature ionic liquids (RTILs) are a class of salts that are liquid even at room temperature. Since ILs are solely composed of ions, the long-range Coulombic interaction plays a role in forming the liquid structure, which may well be distinct from that of molecular liquids. Exotic liquid structure of ILs is also expected from the many distinct physical properties including viscosity, low vapor pressure, thermal stability, and amphiphilicity. Based on several pieces of Raman spectroscopic evidence, we have suggested that imidazolium-based ILs form local structures, in which the cations and the anions are ordered in a nanometer scale.[1–3] The observation of the melting process may help us to understand the liquid structure of ILs, because the likely structure is "intermediate" of the solid and liquid states. The melting and crystallization processes of imidazolium-based ILs have been studied by calorimetry,[4] ^{1}H NMR,[5] and Raman spectroscopy.[2,6]

1-Butyl-3-methylimidazolium chloride (bmimCl) is a prototype imidazolium-based IL. It shows crystal polymorphism related to the rotational isomerism with regard to the C7–C8 axis of the butyl chain in the bmim$^+$ cation.[2,7,8] One polymorph (crystal(1)) consists solely of the *trans*-isomers, while the other (crystal(2)) consists solely of the *gauche*-isomers. Another type of *gauche*-isomer was recently found in a crystalline bmim[PF$_6$].[6] The *trans*- and *gauche*-isomers coexist in the liquid phase. The structural changes accompanying rotational isomerization is detectable by tracing the *trans* and *gauche* Raman marker bands.[2,6,8]

Tracing the isomer bands of bmimCl after its rapid melting, we found that the conformational change needed unusually long equilibration time,[2] the conformational change from *trans* to *gauche* extended for a few minutes after the melting of bmimCl crystal. Although this finding was of great interest suggesting a strong interaction between butyl chains of cations in the liquid phase, the possibility was not ruled out of invisibly small microcrystals remaining in the liquid causing such apparent long equilibration time. At that time, it was not possible to precisely determine when the melting occurred from the observed Raman spectrum.

Recently, we constructed a fast low frequency Raman spectrometer.[9] It can record the low frequency (>±5 cm^{-1}) region, where optical active lattice vibrations of crystals appear. This spectrometer can record not only low frequency but also higher frequency region simultaneously in a subsecond measurement time. In the present study, we investigate the melting process of bmimCl by using this low frequency Raman spectrometer. Thanks to the simultaneous detection of low and high frequency regions, it is possible to observe simultaneously the disappearance of lattice vibrations and the cation conformational change during the melting.

The low frequency Raman spectrometer is almost the same as described in ref. 9. An iodine vapor filter is used as an ultranarrow (<0.1 cm^{-1}) "notch" filter for eliminating Rayleigh scattering. The light source is a frequency-doubled Nd:YVO$_4$ laser (Verdi, Coherent). Its end mirror is tuned so that the operating wavelength coincides with one of the absorption wavelengths of iodine vapor. Laser power at the sample point is 30 mW. The spectral resolution is 2 cm^{-1}, and the spectral coverage is 1300 cm^{-1}, which is enough for simultaneous recording of the lattice vibration bands below 200 cm^{-1} and the marker bands around 600 cm^{-1}.

Crystalline bmimCl was synthesized as descried in the reference.[8] A small piece (≈1 mm) of a single crystalline bmimCl was put in a 10-mm cuvett under dry nitrogen atmosphere. The cuvett was sealed after the preparation. The crystal structure was identified as crystal(2) from the existence of the *gauche* marker bands in the Raman spectrum. The sample was rapidly heated by using a heating gun from 20 to 90 °C, which is 30 K higher than the melting point of bmimCl. The sample melted in 1 min after the heating started. Raman spectral change during the heating was measured continuously with 0.5-s recording time.

Raman spectral change during the rapid heating of single crystalline bmimCl is shown in Figure 1a. The heating starts at 0 s. Before the heating, a few sharp bands including the one at 111 cm^{-1} exist below 200 cm^{-1}. As the heating proceeds, these bands gradually become weaker and eventually disappear. This disappearance indicates that these bands are due to the lattice vibrations of crystalline bmimCl. After 54 s, when all the sharp low frequency bands totally disappear, a broad and intense spectral feature remains in the low frequency region. The spectral shape looks quite similar to those of bmim-based RTILs in the liquid phase, such as bmim[PF$_6$], or bmim[BF$_4$].[1] This fact indicates that the bmimCl becomes liquid and that interionic interactions in the liquid phase are observed in the low frequency region.

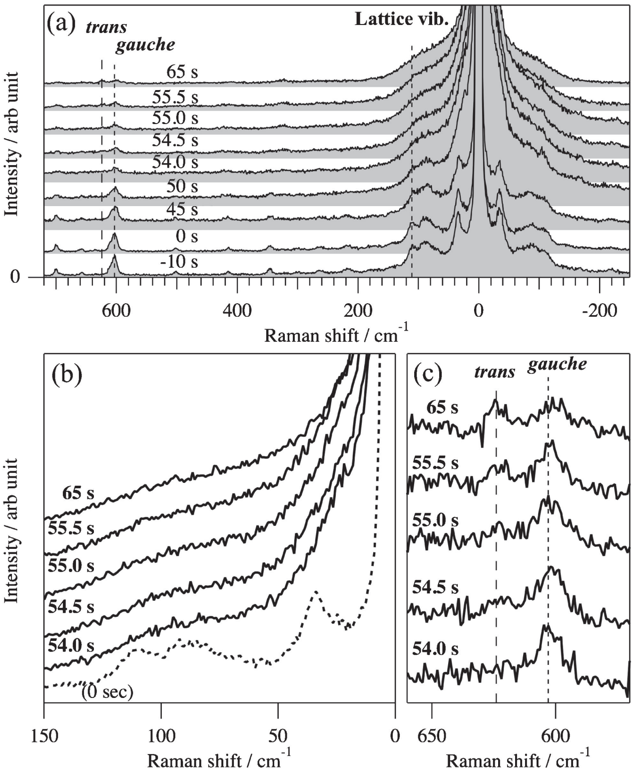

Figure 1. (a) Raman spectral change of a bmimCl crystal during its melting. The heating starts at 0 s. (b) Low frequency spectral change and (c) *trans*/*gauche* marker band change after the disappearance of lattice vibrational bands.

The higher frequency region of the spectral change in Figure 1a shows conformational change of the bmim$^+$ cation. A *trans* marker band is located at 625 cm^{-1} and a *gauche* marker band at 603 cm^{-1}.[2] In the 0-s spectrum, the *gauche* marker band exists, while no *trans* marker band does. After the heating, intensity of the *gauche* marker band decreases and the *trans* marker band gradually appears after 54 s. The intensity ratio of *trans* and *gauche* marker bands is at equilibrium after 65 s. The intensity ratio of these two bands is related to the population ratio of the *trans*/*gauche* isomers.

Interestingly, there seems to be a time lag between the disappearance of lattice vibrations and the appearance of the *trans* marker band. They do not happen simultaneously; in the 54-s spectrum, the sharp lattice vibrational bands are almost missing (Figure 1b), while *trans* marker band is not obviously seen. The *trans* marker band appears a few seconds after the loss of the lattice vibrational bands (Figure 1c).

To make this discussion clear, we compare the loss of the 111-cm^{-1} lattice vibrational band and the change of the marker bands' intensity ratio (625-cm^{-1}/603-cm^{-1}) during the heating (Figure 2). Each band intensity is obtained by a curve fitting with a Gauss function. For fitting the 111-cm^{-1} band, another Gauss-shape slope is used as a base line.

The lattice vibrational band intensity gradually decreases as the heating proceeds. The decreasing rate becomes large after 48 s, which indicates that the crystal structure starts to be lost. After 57 s, the intensity becomes noise level, which is about 20% of the initial intensity before melting.

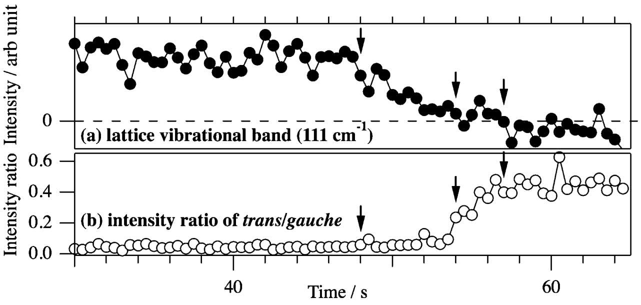

Figure 2. (a) Intensity of lattice vibrational band at 111 cm^{-1}, and (b) intensity ratio of *trans*/*gauche* maker bands (625-cm^{-1}/603-cm^{-1}) during the melting of bmimCl (Arrows indicate 48, 54, and 57 s.)

The *trans*/*gauche* intensity ratio starts to increase at 54 s, when the lattice vibrational band becomes negligibly small. The ratio reaches the equilibrium at 57 s. Thus, the conformational change occurs during 54–57 s. Before 54 s, the *trans*/*gauche* ratio does not change at all. The fluctuation of the intensity ratio before 54 s is less than 10% of the equilibrium intensity ratio after 57 s.

Although the conformation does not change before 54 s, most of the lattice vibration has disappeared, which means that the crystal structure is almost lost by this time. This indicates that the alkyl chains of bmim$^+$ are so strongly interacting with each other that the conformation can hardly change at the beginning of the melting. Such strong interaction may remain after the loss of the crystal structure, which causes long equilibration time (a few seconds) of the butyl conformation. The conformational equilibration time of this study is 100 times smaller than that of the previous study.[2] The crystal type, size, or purity might cause the difference in these equilibration times.

The existence of strong alkyl-chain interaction in liquid phase is consistent with the local structure model suggested by us from other Raman experiments.[1–3] It is also consistent with the tail group aggregation in ILs that is suggested from the MD simulations.[10] It will be possible to gain more insights into the strength of the alkyl-chain interaction inside the liquid by examining the equilibration time more precisely.

This work is supported by Grant-in-Aid for Scientific Research (A) (No. 21245005) from Japan Society for the Promotion of Science (JSPS).

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