MULTISTEP PHASE TRANSITION IN IONIC LIQUID

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Ionic liquids (ILs) consist of cation and anion. 1-Alkyl-3-methylimidazolium ($[C_nmim]^+$) is a representative cation, where *n* reveals the alkyl chain length. ILs have been applied using unique characteristics. For instance, ILs exhibit nanoheterogeneity even in the liquid state. The nanoheterogeneity was estimated by a prepeak on the X-ray diffraction pattern. At low temperature (LT) and high pressure (HP), crystal polymorphs and multiple pathways of phase transitions were observed in the ILs [1-5].

Phase behaviours of $[C_{10}mim][NO_3]$ were investigated at LT [6] and HP [7]. $[C_{10}mim]^+$ possesses a long alkyl chain length (Fig. 1). Judging from the prepeak position of $[C_{10}mim][NO_3]$, correlation length of the nanoheterogeneity was found to be 28.4 Å (Fig. 1). LT crystal polymorph including the liquid crystal (LC) phase was observed using the simultaneous X-ray diffraction and DSC measurements [5]. The LT crystal polymorphs was entirely different from the HP one. The 001 Bragg reflection of the LC phase located at the prepeak in the liquid state. Depending on the cooling rate, the LC phase appeared/disappeared. Below 5 °C/min, simple crystallization occurred. However, multistep phase transition was induced at 5 ~ 8 °C/min (quasiequlibrium). Above 9 °C/min (nonequilibrium), crystallization of $[C_{10}mim][NO_3]$ was suppressed upon cooling, whereas cold crystallization appeared upon heating.

We predict the multistep phase transition of $[C_{10}mim][NO_3]$ as follows (Fig. 1); (i) At the first exothermal peak, small crystal domains were independently formed, and an arrangement of the nanocrystal domains is required for further cooling, (ii) in the second process of the phase transition, the orientational correlation among the nanocrystal domains in the medium-range is indispensable to reach a long-range order, (iii) the third exothermal peak corresponds to the appearance of a homogeneous layered structure in the long range.

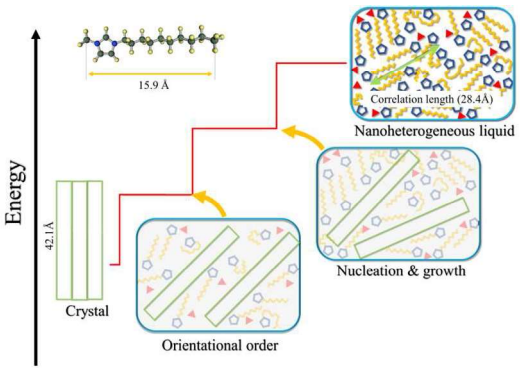

Fig. 1 Multistep phase transition process upon cooling of $[C_{10}mim][[NO_3]$.

At intermediate cooling rates (5.0–8.0 °C/min), a quasiequilibrium state can be realized, and the growth process cannot continuously occur upon cooling. This might be due to the occurrence of a partial pinning effect induced by nanoheterogeneity and weak ionic interaction between cations and anions.

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