	Experiment title: Structural studies of the phase behaviour of the iodine-doped ionic liquid 1-propyl-3-methyl-imidazolium iodide (PMII)	**Experiment number**: 01-01-775
Beamline: BM01B	**Date of experiment**: from: 24/11/2008 to: 29/11/2008	**Date of report**: 3 March 2009
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Report:

Crystal structures and properties of 1-methyl-3-propylimidazolium polyiodides (PMII) were investigated as a function of a) iodine concentration and b) temperature. Preliminary DSC and viscosity measurements had already shown that, like for many ionic liquids, a direct crystallization by slow freezing of the liquid was not possible. Upon cooling from room temperature, PMII solidified to a glassy solid, a subsequent glass-crystal transition occurred upon subsequent slow warming of the amorphous material (cold crystallization).

In order to determine the crystal structures and properties of PMIIs with various iodine concentrations, XRD measurements were performed at different temperatures by slow warming of nitrogen-cooled samples to the melting point (Figure 1). Independent of the iodine content, the cold crystallisation occurred at 230 K and the crystalline phase remained in all cases stable until 270 K. At 275 K, the samples were completely molten. Although the intensity ratios of several peaks in the diffractograms varied as a function of temperature, no drastic changes of the powder patterns, indicating a phase transition, could be observed.

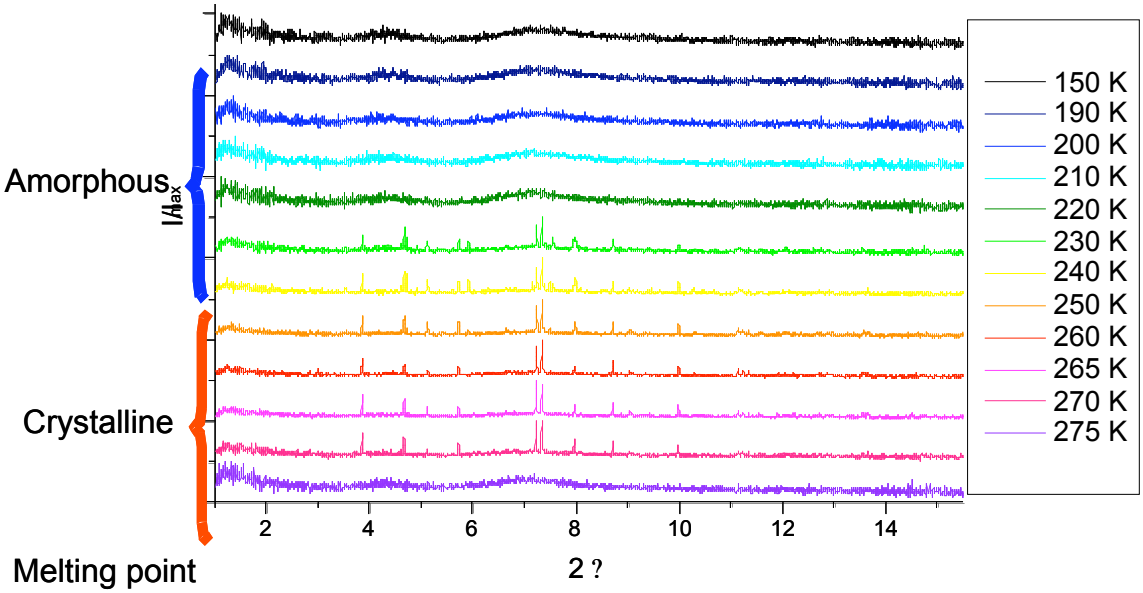

Figure 1: Cold crystallization of PMII • I_2 (5M), as monitored by XRD.

The crystal structure of PMII • I_2(5M), which was solved using Rietveld methods, consists of parallel arrays of linear I_3^- units and disordered PMI cations (Figure 2). Only 2/3 of the iodine positions are occupied, the resulting stoichiometry PMII • I_2 corresponds to a 1:1 adduct. All peaks of the powder diffractogram could be indexed by using the structural model obtained from the Rietveld refinement. The result confirmed the absence of contaminant phases in the material and indicated a strong preferred orientation for the crystallites.

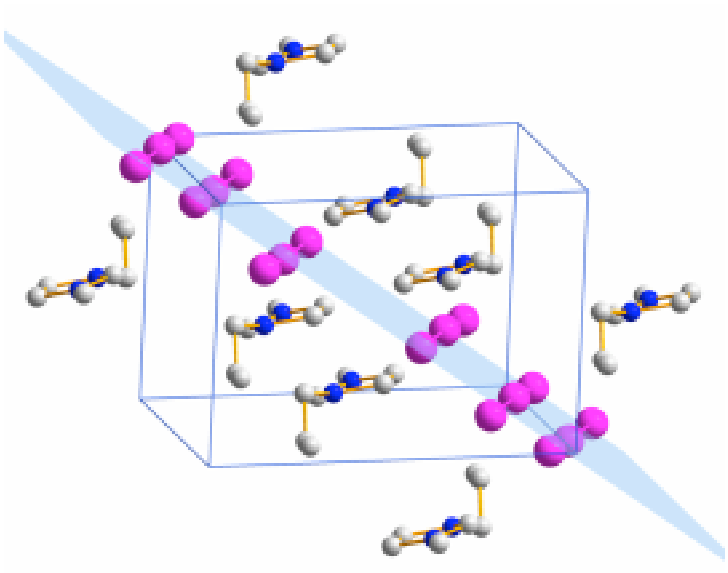

Figure 2: Crystal structure of PMII • I_2(5M), as determined from powder diffraction data. For clarity, only one of the three positions for the disordered PMI molecules is displayed.

For compounds with a higher iodine loading, the formation of higher polyiodide units (e.g. I_5^- or I_7^-), $I_3^{-}\cdots I_2$ adducts or neutral $(I_2)_n$ wires within the crystal structure is to be expected. However, due to the limited ability of the PMI to accommodate extra iodine, beyond a certain concentration, the generation of elementary I_2

crystals in the capillary during the cold crystallization of the PMII is very likely. In fact, the powder diffractogram of PMII • I_2(8.5M), which crystallizes in a different structure, displays also signals arising from the presence of elementary iodine, whereas PMII • I_2(7M), the sample with the intermediate iodine concentration consists of a mixture of PMII • I_2(5M) and PMII • I_2(8.5M) (Figure 3).

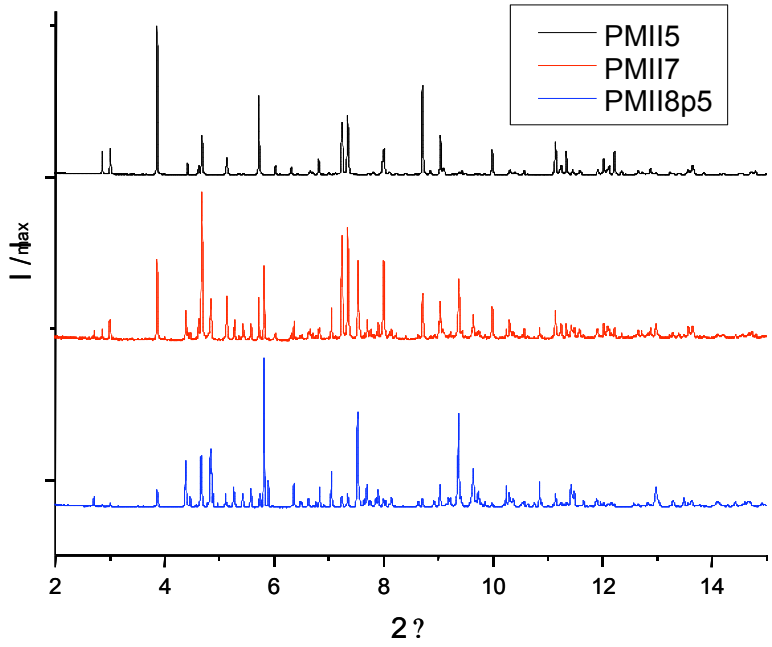

Figure 3: Comparison of powder diffractograms for samples with different iodine concentrations.

Preliminary XRD measurements on PMII • I_2(8.5M), which were performed at ESRF using a MAR345 image plate detector, showed the existence of a crystal-to-crystal phase transition for this compound near 275 K. Our attempts to trap this second crystalline phase using our experimental approach were not successful; this may have been caused by an inadequate temperature profile leading to temperature gradients and local overheating within the capillary containing the sample. Additional measurements in the temperature range between 260 and 275 K using a modified experimental setup with much slower heating rates will be necessary in order to determine the existence range of the second crystalline phase. Besides this, the acquisition of high-resolution XRD data will be essential to determine the crystal structure of this phase. In addition to the collection of powder data, attempts will be made to obtain single crystal data from PMII crystallized in situ from small droplets.