



	Experiment title: An eco-friendly route to nano-composites of hydrogen bonded polymers	Experiment number: SC-1955
Beamline: ID02	Date of experiment: from: 17 th May 2006 to: 19 th May 2006	Date of report: 30 th August 2006 <i>Received at ESRF:</i>
Shifts: six	Local contact(s): Peter Boesecke	

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Report: Here we demonstrate that water, in the superheated state, is a solvent for polyamide 4,6 and that water molecules are incorporated in the crystal lattice. In the presence of superheated water, the melting temperature of polyamide 4,6 can be suppressed by nearly 100°C, following the Flory-Huggins principle. The instantaneous dissolution of the polymer hardly influences the molar mass of the polymer. However, if the polymer is retained in solution above the dissolution temperature for more than 10 minutes, hydrolysis occurs. The findings suggest that the dissolution of an aliphatic polymer in superheated water is mainly a physical process as opposed to a chemical process. Time resolved X-ray studies show that the dissolution occurs prior to the Brill transition temperature. Crystallization from the water solution shows that the interchain and intersheet distances are similar to the distances obtained for crystals grown from other known solvents. Crystals grown from the water solution show a lath like morphology and have reminiscence with the single crystals grown from other solvents reported in literature. The single crystal nature of these crystals is further confirmed by electron diffraction which shows that the chains in these single crystals are perpendicular to the ab-plane. SAXS performed on dried sedimented water grown single crystals show a lamella thickness of 6nm, which is also in accordance with other reported studies. These findings further suggest that the single crystals constitute of four repeat units, where the chains are adjacently re-entrant with an amide group incorporated in the tight fold. Solid state NMR studies performed on these single crystals show two different mobilities of the proton associated to the amide groups; a higher mobility linked to the proton in the fold and a suppressed mobility of the hydrogen bonded proton within the crystal. Additionally, the solid state NMR studies on the dried water crystallized single crystals show the existence of water molecule(s) in the vicinity of the amide groups within the crystal which influences the mobility of the protons

from the methylene groups and the associated amide group. This is further confirmed by infrared studies which conclusively demonstrate the appearance of two new bands arising due to the binding of a water molecule in the vicinity of the amide group, i.e. NH^{3+} and CO^{2-} bands. Unlike the water present on the crystal surface, the water within the crystal is retained up to the Brill transition, i.e. 180°C . What follows are our experimental observations on single crystal mats of Polyamide 4,6 crystallized from acid and from water. Dissolution and crystallization aspects in presence of water were followed in-situ.

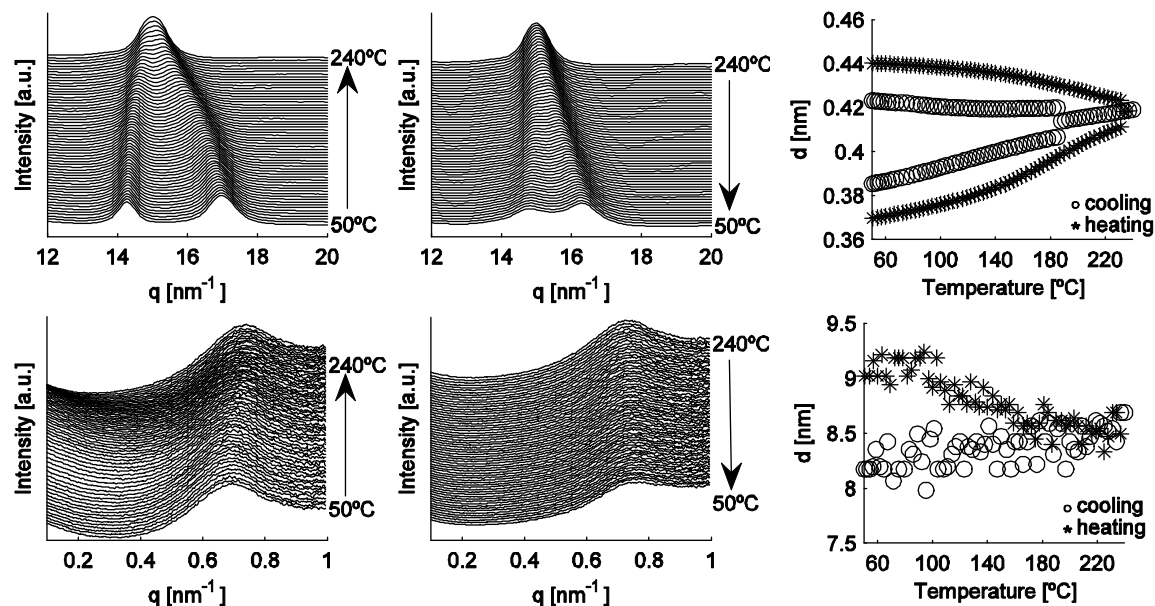


Figure 1: SAXS and WAXD collected on single crystals of PA4,6 crystallized from acid while heating and cooling from 50°C to 240°C both at $10^\circ\text{C}/\text{min}$. The heating run shows expansion of the intersheet while contraction of the interchain distances. The point at which the two reflections merge is known as the Brill transition. Simultaneous SAXS and WAXD studies were performed on ID02.

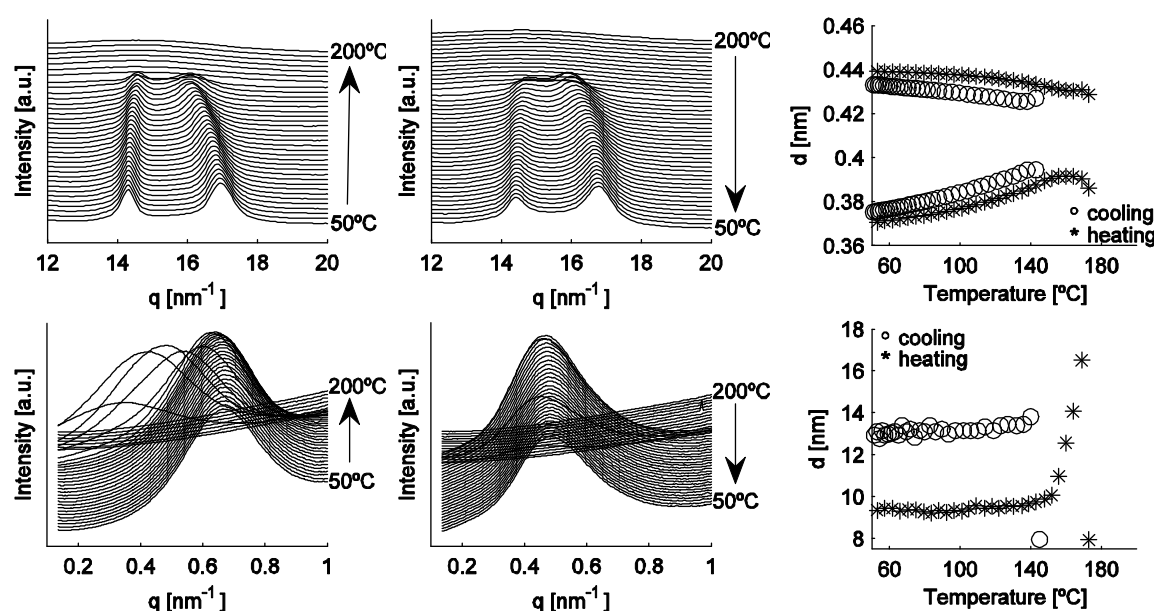


Figure 2: SAXS and WAXD collected on heating 30wt% of PA4,6 in water while heating and cooling from 50°C to 200°C , both at $10^\circ\text{C}/\text{min}$. In the presence of water, which could be retained above the boiling point, the polymer dissolves prior to the intervention of the Brill transition.

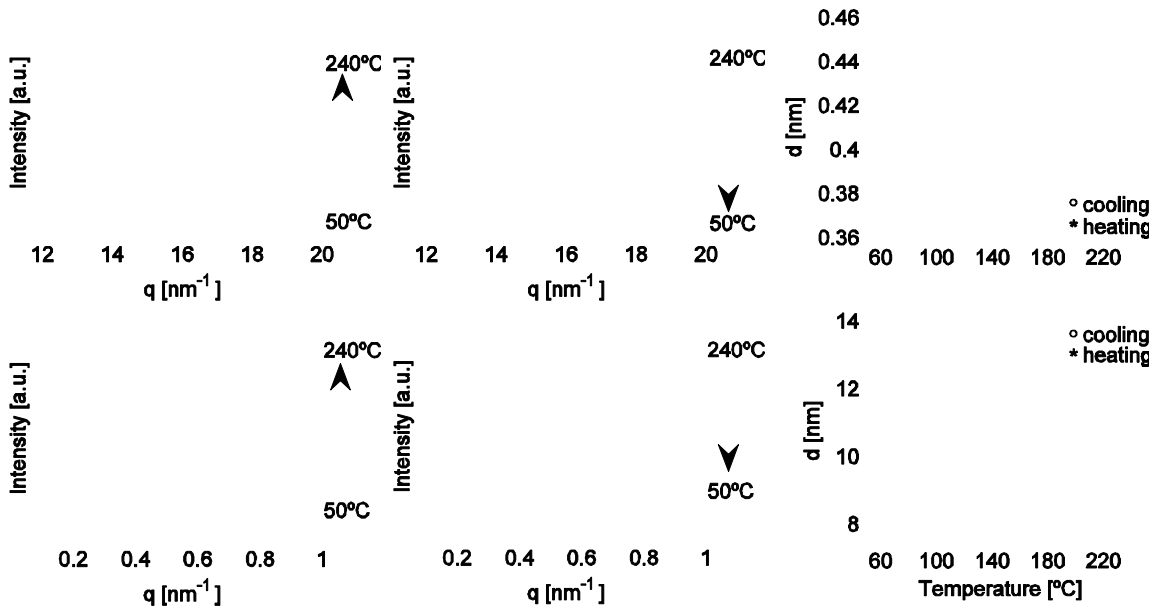


Figure 3: SAXS and WAXD collected on heating PA4,6 crystallized on heating and cooling from 50°C to 240°C, both at 10°C/min. The lid which seals the capillary was removed allowing the evaporation of excess water to evaporate above 100°C.

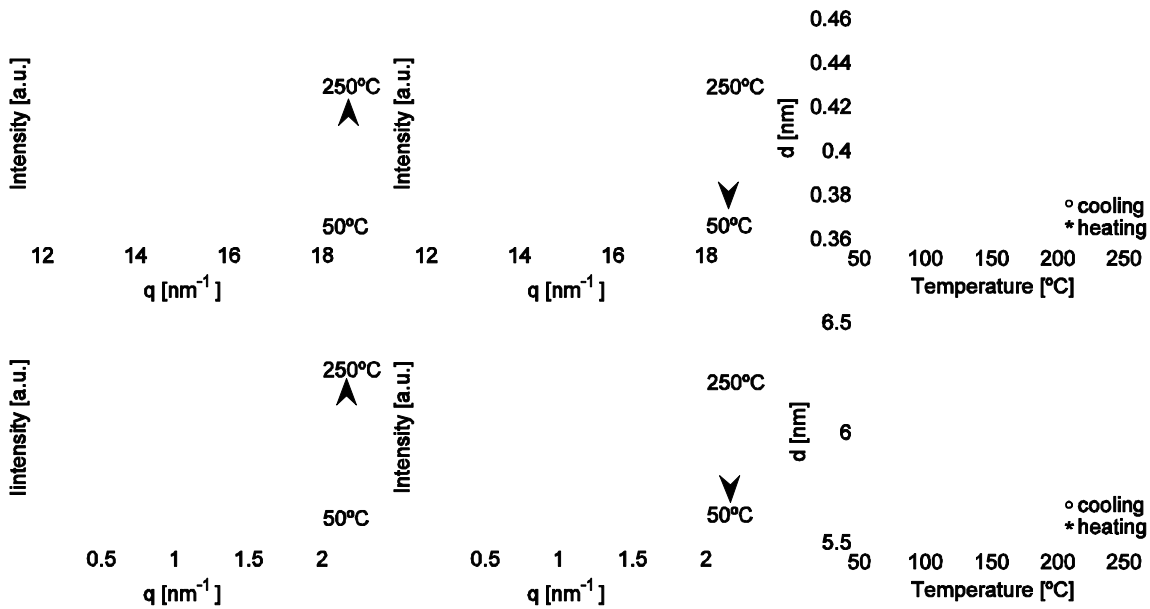


Figure 4: SAXS and WAXD collected on heating PA4,6 mats crystallized from water. X-ray diffraction patterns were recorded while heating and cooling from 50°C to 250°C both at 10°C/min

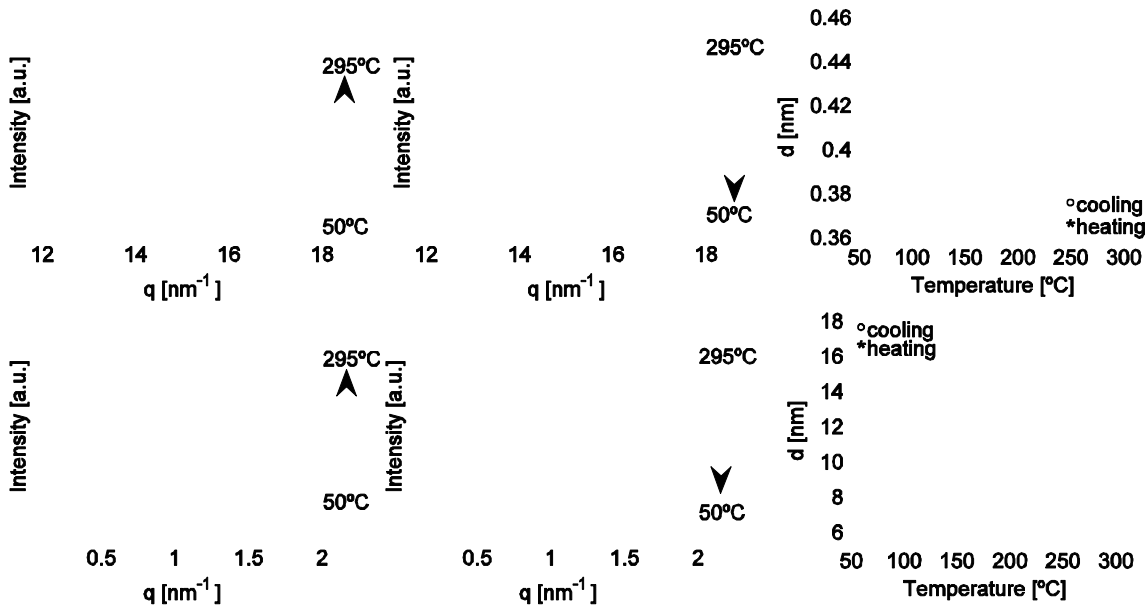


Figure 5: Simultaneous SAXS/WAXD collected on heating and cooling PA4,6 mat (crystallized from water) from 50 $^{\circ}\text{C}$ to 300 $^{\circ}\text{C}$ both at 10 $^{\circ}\text{C}/\text{min}$

For location of water molecules the results obtained are complemented with other characterization techniques for example solid state NMR, FTIR microscopy.