



	Experiment title: Influence of pressure on hydrogen bonded polymers; polyamides and biopolymers	Experiment number: Sc1279
Beamline: ID11/ID02	Date of experiment: from: May 12 th -17 th 2004 and Dec 9 th -13 th 2004	Date of report: January 14 th 2005
Shifts: 15/12	Local contact(s): Silvia Capelli/Peter Boesecke	<i>Received at ESRF:</i>

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Report:

In a previous beamtime (sc1279: Sept 2003 and June 2004), we demonstrated that nylon 4,6 could be dissolved in water at elevated pressures by sealing the nylon with water in a glass capillary. Using a new sample stage in which the open glass capillary is sealed by an o-ring, and the temperature can be measured at the sample position, these experiments seek to test the validity of the dissolution process for other nylons. Of particular interest is the role of hydrogen bonding upon the dissolution process in water of nylons and nylon-piperazine copolymers which have an inherently different hydrogen bonding strength due to steric constraints.

Combined SAXS-WAXD and higher resolution WAXD, time-resolved measurements were made on ID02 and ID11 respectively, during the dissolution of nylon 2,14 (PA2,14). PA2,14 was crystallized from the melt and cooled at 10°C/min prior to placing in the glass capillary. Water in the volume ratio 4:1 (water:nylon) was added and the tube sealed. Data were collected upon heating and cooling from ~30°C to 200°C at 10°C/min (fig.1). The WAXS image in (a) shows the PA2,14 going through the Brill transition at ~130°C and dissolving at ~198°C. The SAXS image shows that the single reflection shifts to higher spacings and increases in intensity with temperature, i.e. lamellar thickening and an increase in the degree of crystallinity occurs. On cooling, (c) and (d), the PA2,14 recrystallizes at ~185°C into a single reflection. On cooling, the PA2,14 goes through the Brill transition at ~90°C. The SAXS image shows a single reflection that moves to lower spacings and flattens out considerably with decreasing temperature. The difference between (a) and (c) is significant. In combination with FTIR data we have been able to conclude that during the dissolution process, water molecules are encapsulated in the crystal lattice upon recrystallization. This, plus the increase in crystallinity upon crystallization from solution gives rise to the differences in spectra.

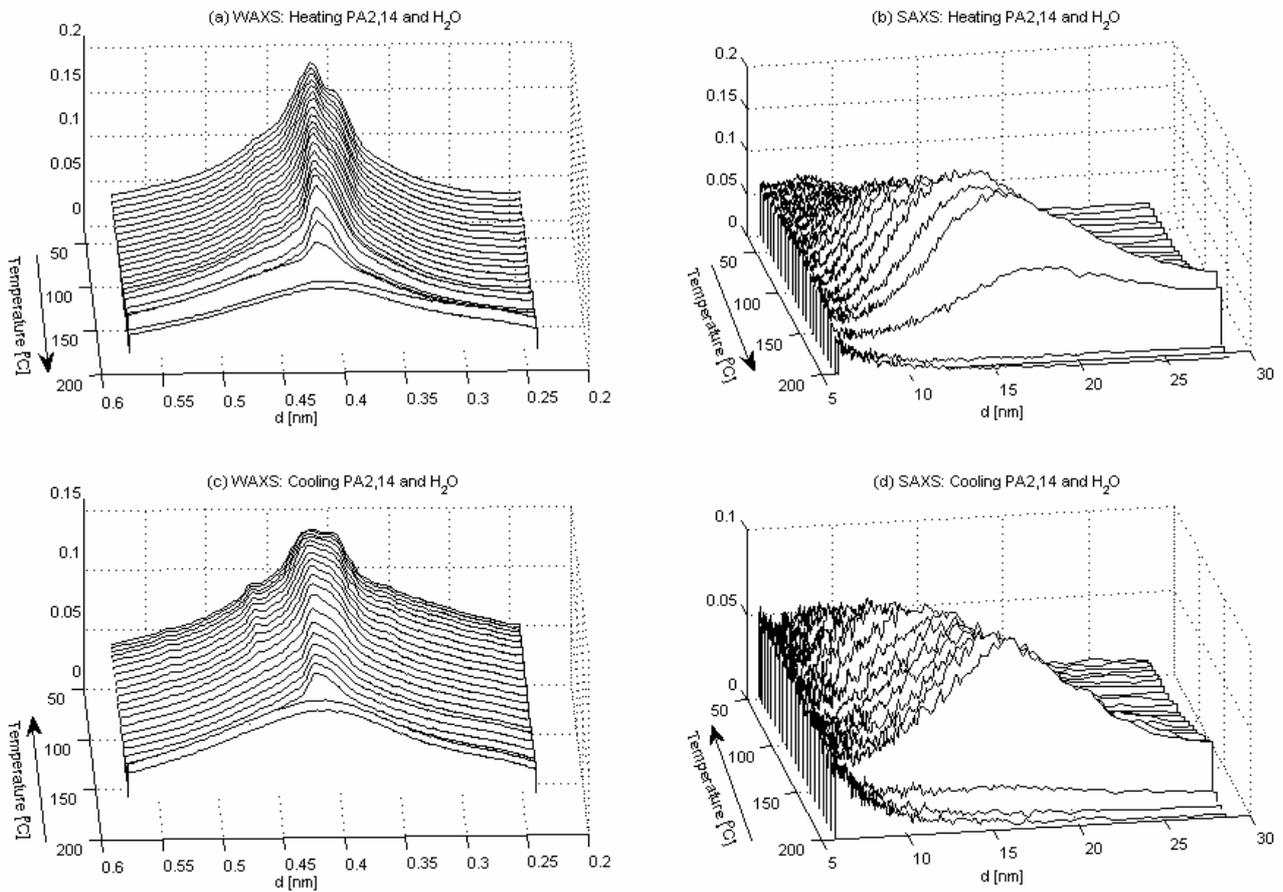


Figure 1: Heating and cooling cycles of PA_{2,14} and H₂O enclosed in a glass capillary. The SAXS/WAXS data were collected simultaneously at ID02. The arrow indicates the temperature direction.

Nylon 2,14, by the above experiments, is seen to dissolve in the same way as nylon 4,6, with almost the same dissolution temperature of $\sim 195^\circ\text{C}$. Nylon 2,14 will exhibit the same strength of hydrogen bonds as nylon 4,6 and thus one might expect the same dissolution temperature. However, the degree of hydrogen bonding can be altered either through packing constraints within the beta-sheets by having mis-matched nylon sequences or by the introduction of other entities within the polymer changes, e.g. in nylon-piperazine copolymers. For this reason, the dissolution of other nylons in water was examined. For nylon 12 where the hydrogen bonding is weakened in comparison to nylon 4,6 or nylon 2,14, the polymer dissolves at lower temperatures ($\sim 162^\circ\text{C}$). Similar behaviour is exhibited in the nylon-piperazine copolymers where increasing copolymer content caused the dissolution temperature to be reduced. Work is on-going to test this further.